UNIT – VI

NANOMATERIALS AND THEIR FABRICATION

Origin of Nanotechnology, Nano Scale, Surface to Volume Ratio, Quantum Confinement, Bottom-up Fabrication, Sol-gel method, Chemical vapor Deposition technique (CVD); Top-down Fabrication; Ball Milling, Characterization of Nano materials (XRD & TEM), carbon nano tubes (CNTs), Applications of Nano Materials.

Introduction:

Richard Feynman was the first person to suggest that nanotechnology was a possibility. First, Prof.Norio Taniguchi of Japan in 1974 used the word nano technology to describe the extension of traditional silicon machining down into region smaller than one micron.

- The word “nano” is a Greek word and meaning is dwarf (small).
- The prefix nano means “one billionth” or 10^{-9} meter.
- Size limitation of nano material is the 1-100 nm range.

Materials when reduced down to 100nm show drastic changes in respect of Physical, Chemical, Optical, Magnetic, Mechanical and Electrical properties.

All these leads to exciting applications in Bioscience, Medical, Environmental science, Electronics, Security and Cosmetics etc.

Materials reduced to the nano-scale can show different properties compared to what they exhibit on the macro-scale

- They are very hard
- They are exceptionally strong
- They are ductile at high temperatures
- They are chemically very active
- They are wear and erosion resistant
- Opaque substances may become transparent (copper)
- Stable materials turn combustible (aluminum);
- Insulators become conductors (silicon); and
- Solids turn to liquids at room temperature (gold)……

Nanoscience is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale.

Nanotechnology is the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nanometer scale.

The properties of materials can be different at the nanoscale for two main reasons:

1. Increased surface area to volume ratio
2. Quantum Confinement effect

Surface area to Volume ratio:

Nano-materials have a relatively larger surface area when compared to the larger form of the material of same volume.

For a sphere of radius *r, the surface area* and its volume can be given as

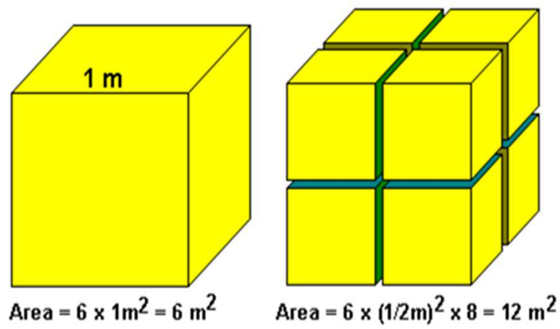
$$\text{Surface area} = 4\pi r^2$$

and its volume can be given as

$$\text{Volume} = \frac{4}{3}\pi r^3$$

Now, the surface to volume ratio $= \frac{3}{r}$

Thus, we find that when the given volume is divided into smaller parts, surface area increases.



Single Box Ratio

$$\frac{6\ m^2}{1\ m^3} = 6\ m^2/m^3$$

Smaller Boxes Ratio

$$\frac{12\ m^2}{1\ m^3} = 12\ m^2/m^3$$

Neglecting spaces between the smaller boxes, the volumes of the box on the left and the boxes on the right are the same but the surface area of the smaller boxes added together is much greater than the single box.

Quantum Confinement Effect

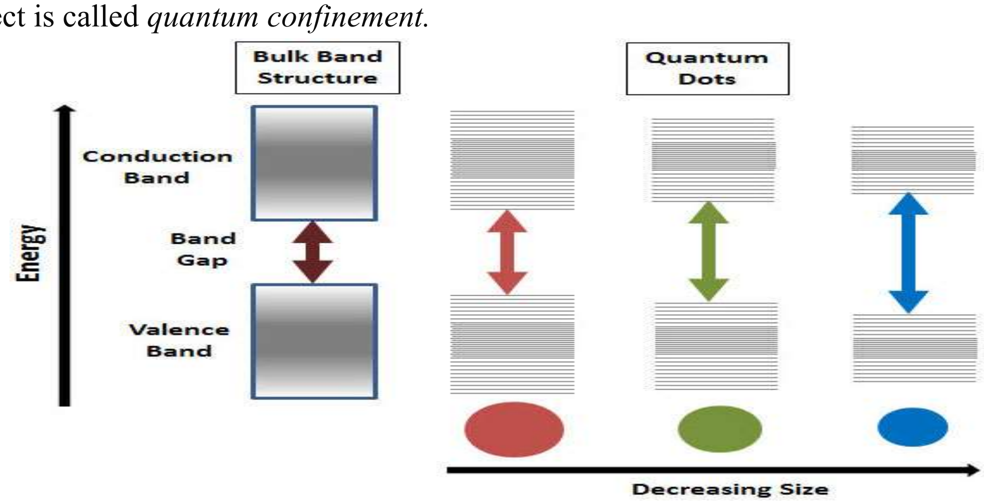
At reduced dimensions, they are said to be either a quantum well, a quantum dot, or a quantum wire.

The physics at these dimensions is entirely different. Actually, when the size of the grains is reduced to nano-level, then overlapping of wave function and quantum confinements occurs.

If *d is the diameter of the grain size, then the energy* goes up by factor $1/d^2$

When the dimensions of a potential well or a box concerned with a particle are reduced to the order of de Broglie wavelength of electron (within few tens of nanometers), then energy levels of electrons change.

This effect is called *quantum confinement.*



The Quantum effects can begin to dominate the behaviour of matter at the nanoscale - particularly affecting the following properties

1.**Optical:** Spectral shift of optical absorption and fluorescence, increase in efficiency of semiconductor crystal.

2.**Electrical:** Increase in conductivity in ceramics and magnetic nanocomposites.

3.**Magnetic behaviour of materials:** Increase in magnetic coercivity

4. **Mechanical properties** – increased hardness

5. **Chemical properties** – increases reactivity

6. **Catalytic:** Better catalytic efficiency due to high surface area.

<u>DIFFERENT TYPES OF NANOSTRUCTURES:</u> (CONFINEMENT DIMENSIONS 0-D, 1-D, 2-D, AND 3-D)

A bulk conductor has all its three dimensions more than 100 nm.

If one dimension is reduced to the nanorange while the other two dimensions remain large, then we get a structure known as quantum well.

If two dimensions are reduced and one remains large, the resulting structure is referred to as the quantum wire.

The extreme case of this process of size reduction in which all three dimensions reach at the nanorange is called *quantum dot.*

- **0-D (Delocalisation dimensions)**

All dimensions (*x, y,z) at nanometric scale; the other* dimension is large.

Example: Nanoparticles

- **1-D (Delocalisation dimensions)**

Two dimensions (*x, y) at nanometric scale; the other* dimension is large. *Example: Nanorods, nanotubes*

- **2-D(Delocalisation dimensions)**

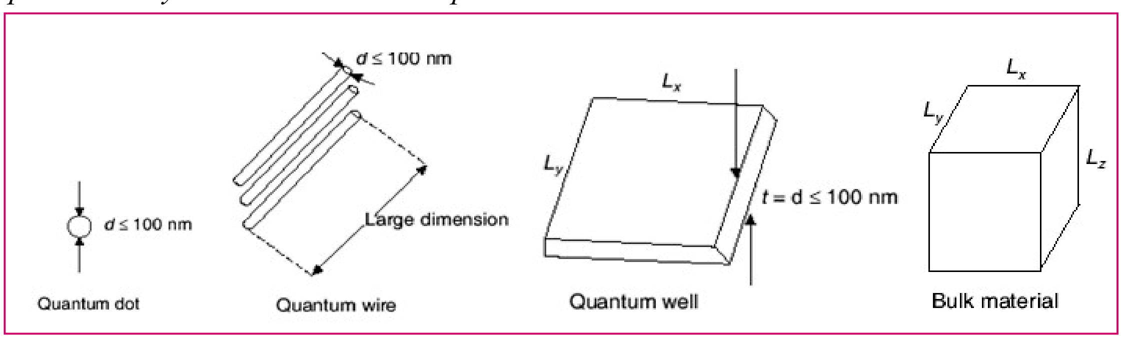
One dimension (*t measured along z-axis) at nanometric scale;*two other dimensions (*Lx, Ly) are large.*

Example: Thin nanofilms

- **3-D (Delocalisation dimensions)**

All of the three dimensions (*Lx, Ly, Lz) are not at nanometric scale.*

Example: Nanocrystalline and nanocomposite materials.



<u>SYNTHESIS OF NANOMATERIALS</u>

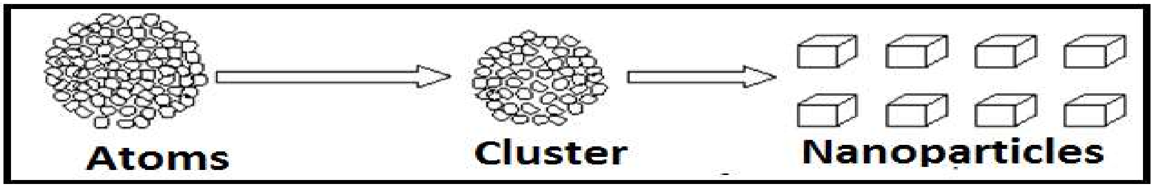
Nanomaterials can be synthesized by '**Bottom up**' and '**Top down**' techniques.

<u>Bottom-Up Process</u>

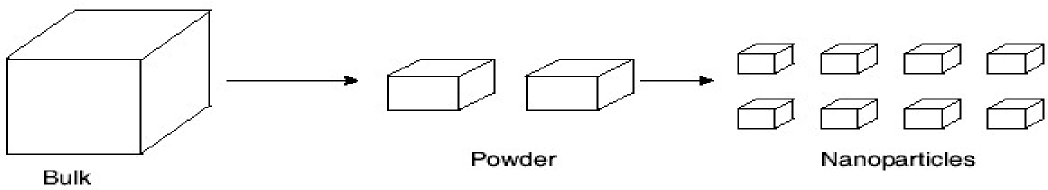
Bottom-up approach refers to the building up of a material from the bottom, i.e., atom by atom, molecule by molecule, or cluster by cluster.

Colloidal dispersion is a good example of bottom-up approach in the synthesis of nanoparticles.

There are different methods used for the synthesis are:
(i) Sol–gel method
(ii) Colloidal method
(iii) Electrodeposition
(iv) Solution phase reductions
The most important feature of this process is that the size and morphology of fabricated nanoparticles are well controlled.



Top-Down Process
Under this process of fabrication, bulk materials are broken into nano-sized particles.
In this approach, there is no control over the size and the morphology of particles.
Some common methods of top-down method are as follows.
(i) Ball milling method
(ii) Plasma arcing
(iii) Laser sputtering
(iv) Vapour deposition method



Sol-Gel Method:

The sol-gel process is very long known since the late 1800s. The versatility of the technique has been rediscovered in the early 1970s when glasses were produced without high temperature melting processes.

Sol-Gel is a chemical process used to make ceramic and glass materials in the form of thin films, fibers or powders.

A sol is a colloidal (the dispersed phase is so small that gravitational forces do not exist; only Vander Waals forces and surface charges are present) or molecular suspension of solid particles of ions in a solvent. The colloids in which molecules of size ranging from 20nm to 100nm.

A gel is a semi-rigid mass that forms when the solvent from the sol begins to vaporate and the particles or ions left behind begin to join together in a continuous network.

- Formation of a metal oxide involves connecting the metal centers with oxo (M-O-M) or hydroxo (M-OH-M) bridges, therefore generating metal-oxo or metal-hydroxo polymers in solution.
- The *drying* process serves to remove the liquid phase from the gel thus forming a porous material, then a thermal treatment (*firing*) may be performed in order to favor further polycondensation and enhance mechanical properties.

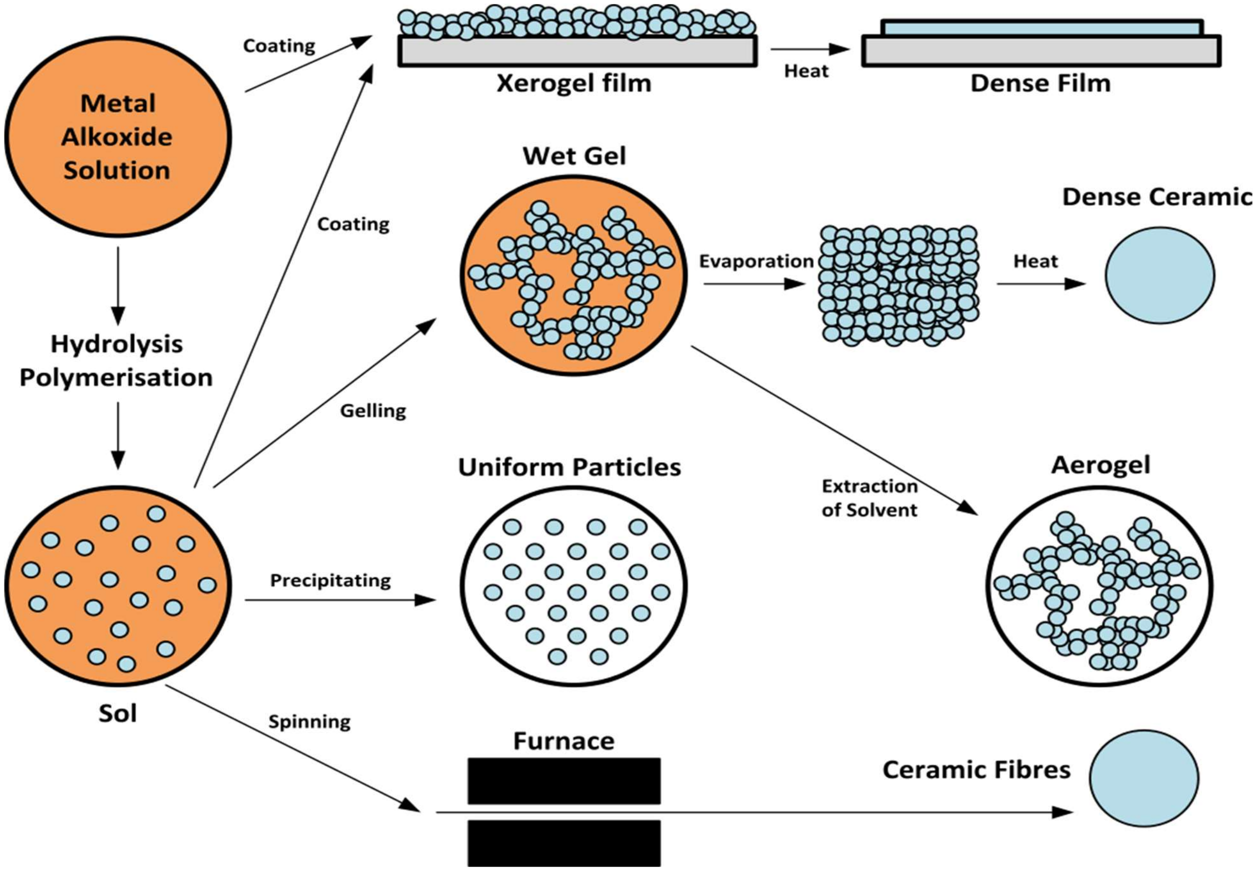
The sol-gel process usually consists of 4 steps:

(1) The desired colloidal particles once dispersed in a liquid to form a sol.
(2) The deposition of sol solution produces the coatings on the substrates by spraying, dipping or spinning.

(3) The particles in sol are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network.

(4) The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating.

The sol-gel approach is easy and cheap low-temperature technique that allows for the fine control on the product's chemical composition like organic dyes and rare earth metals, can be introduced in the sol and end up in the final product finely dispersed.



- **Advantage:** The possibility of synthesizing nonmetallic, inorganic materials like glasses, glass ceramics or ceramic materials at very low temperatures.
- **Disadvantage:** controlling the growth of the particle is difficulty.
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Chemical Vapour Deposition:

- In this method, nanoparticles are deposited from the gas phase. Materials are heated to form a gas and then allowed to deposit on solid surface usually under vacuum condition.
- The deposition may be either physical or chemical. In deposition by chemical reaction new product is formed. Nano powder of oxides and carbides of metals can be formed, if vapours of carbon or oxygen are present with the metal.
- These materials include: silicon, carbon fiber, carbon nanofibers, filaments, carbon nanotubes, SiO_2, silicon-germanium, tungsten, silicon carbide, silicon nitride, silicon oxynitride and titanium nitride.
- CVD process is also used to produce synthetic diamonds.

Working Concept

- A material, often a metal is evaporated from a heated metallic source into a chamber which has been previously evacuated to about 10–7 torrand backfilled with inert gas to a low-pressure.
- The metal vapor cools through collisions with the inert gas atoms, becomes supersaturated and then nucleates homogeneously; the particle size is usually in the range 1–100 nm and can be controlled by varying the inert gas pressure.
- Ultimately, the particles are collected and may be compacted to produce a dense nano material.

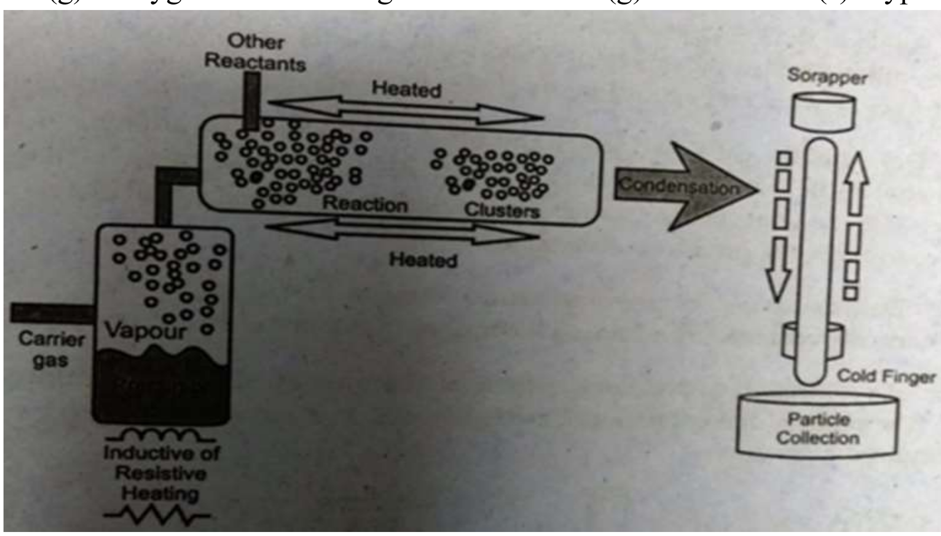
A simplified concept diagram is shown as Fig

Metal deposition

metal halide (g) $\rightarrow$ metal(s) + byproduct (g)

Ceramic deposition

metal halide (g) + oxygen/carbon/nitrogen/boron source (g) $\rightarrow$ ceramic(s)+byproduct(g)



- During the process of chemical vapor deposition, the reactant gases not only react with the substrate material at the wafer surface (or very close to it), but also in gas phase in the reactor's atmosphere.
- Reactions that take place at the substrate surface are known as **heterogeneous reactions**, and are selectively occurring on the heated surface of the wafer where they create good-quality films.

Reactions that take place in the gas phase are known as **homogeneous reactions**.

- In short, heterogeneous reactions are much more desirable than homogeneous reactions during chemical vapor deposition.

Advantages:

- The increased yield of nanoparticles.
- A wider range of ceramics including nitrides and carbides can be synthesized.
- More complex oxides such as $BaTiO_3$ or composites structures can be formed.

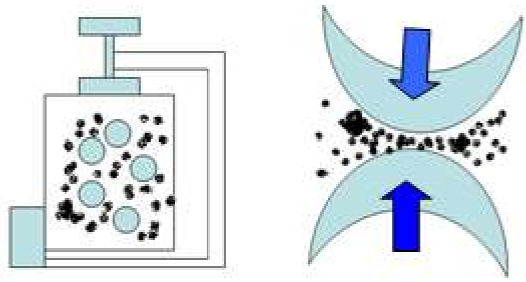
<u>Ball Milling methods:</u>

Attrition Ball Mill

The milling procedure takes place by a stirring action of a agitator which has a vertical rotator central shaft with horizontal arms (impellers). The rotation speed was later increased to 500 rpm. Also, the milling temperature was in greater control.

Vibrating Ball Mill

It is used mainly for production of amorphous alloys. The changes of powder and milling tools are agitated in the perpendicular direction at very high speed (1200 rpm).



Nano – TiAl, PdFe, CuFe

The drawback of the ball milling technique is the lack of uniformity in the size and morphological characteristics of the synthesized nanoparticles.

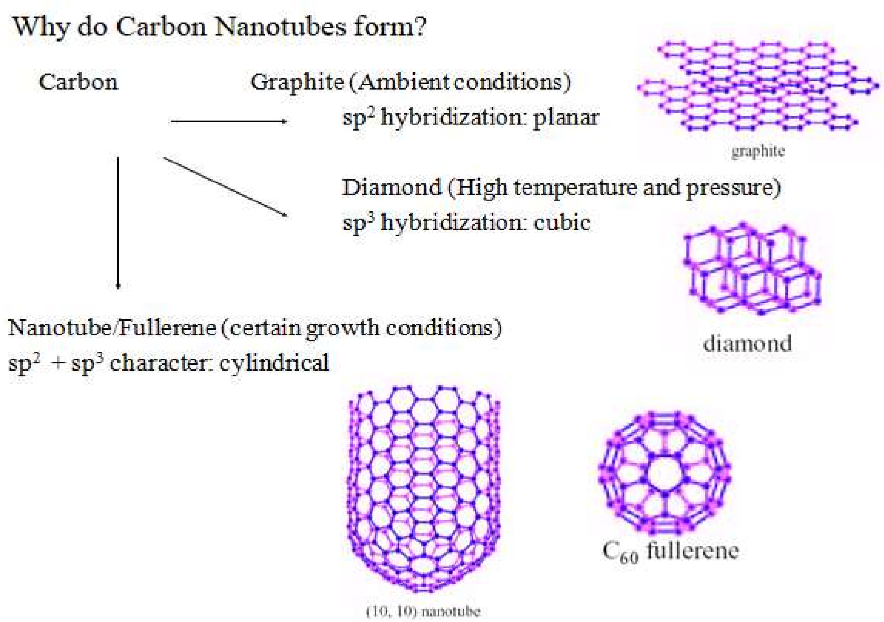
Carbon Nanotubes:

Carbon nanotube is a sheet of graphite rolled into a cylindrical structure in which one carbon atom is covalently bonded to three other carbon atoms.

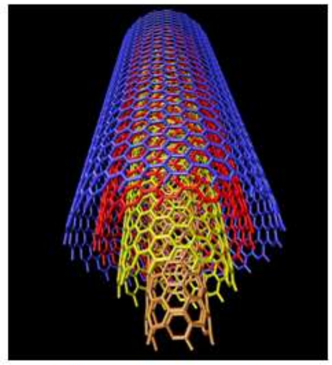
Carbon nanotubes (CNTs) were first observed by **Sumio lijima** in 1991.

There are two types of CNT: single-walled (one tube) or multi-walled (several concentric tubes).

Both of these are typically a few nanometers in diameter and several micrometres to centimeters long. CNTs have assumed an important role in the context of nanomaterials, because of their novel chemical and physical properties. They are mechanically very strong (CNTs as stiff as diamond), flexible (about their axis), and can conduct electricity extremely well. All of these remarkable properties give CNTs a range of potential applications: for example, in reinforced composites, sensors, nanoelectronics and display devices.

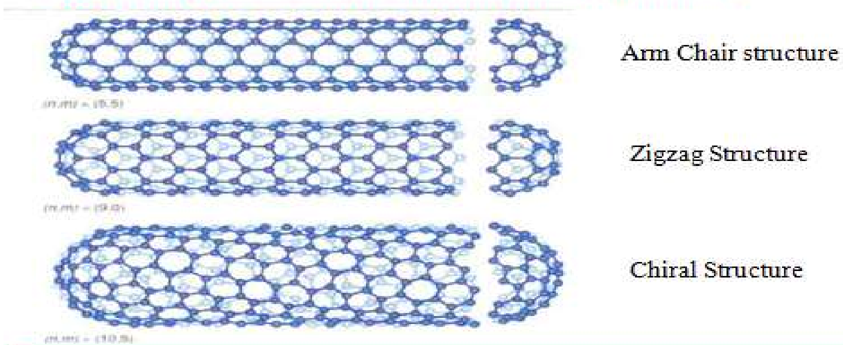


Single Walled Nano Tubes
SWNT



Multi Walled Nano Tubes
MWNT

Different types of single walled carbon nanotubes



Graphene sheet can be rolled into a tube in three ways.
Armchair and Zigzag structure have a high degree of symmetry and arrangement looks like hexagons around the circumference.
Chiral structure, chiral meaning that it can exist in two mirror related forms.

<u>Properties of Nano Tubes:</u>

Physical Properties:-

1. Nano tubes have a high strength. This value is 100 times that steel and twice that of conventional carbon fibers.
2. Highly resistant to chemical attacks. It is difficult to oxidize.
3. High thermal conductivity which increases with decrease in diameter.

Mechanical Properties:

High strength, the ability to withstand extreme strain on tension.

Electrical Properties:-

- Electrical conductivity six orders higher than copper.
- Can be metallic or semiconducting depending on chirality
  - tunable by band gap
- Very high current carrying capacity
- Excellent field emitter: High aspect ratio and small tip radius of curvature are ideal for field emission.

Applications of CNT:-

1. As electrical conductors. 2. Field effect transistors. 3.As connectors 4.As naoprobes
5. As battery electrodes, 6.Electronic devices 7. To make stronger composites
8. A plastic composite of CNT could provide lightweight shielding material for electromagnetic radiation.

CHARACTERIZATION OF NANOMATERIALS

1.X-Ray Diffraction (XRD)
2. Transmission Electron Microscope (TEM)

X-ray diffraction (XRD):

XRD is a very important experimental technique that has long been used to address all issues related to the crystal structure of solids, including lattice constants and geometry, identification of unknown materials, orientation of single crystals, preferred orientation of polycrystals, defects, stresses, etc. in XRD, a collimated beam of X-rays, with a wavelength typically ranging from 0.7 to 2 A^0, is incident on a specimen and is diffracted by the crystalline phases in the specimen according to Bragg's law:

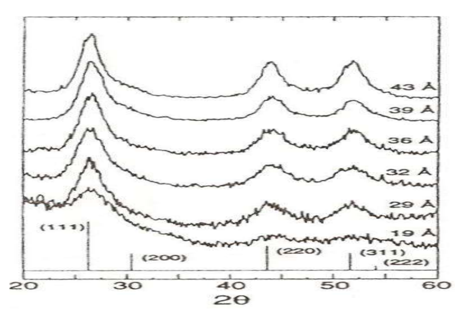
$$\lambda = 2d \sin\theta$$

Where d is the spacing between atomic planes in the crystalline phase and λ is the X-ray wave length. The intensity of the diffracted X-rays is measured as a function of the diffraction angle 2θ and the specimen's orientation. This diffraction pattern is used to identify the specimen's crystalline phases and to measure its structural properties. XRD is nondestructive and does not require elaborate sample preparation, which partly explains the wide usage of XRD method in materials characterization.

If there is no inhomogeneous strain, the crystallite size, D, can be estimated from the peak width with the Scherrer's formula:

$$D = \frac{K\lambda}{B \cos \theta_B}$$

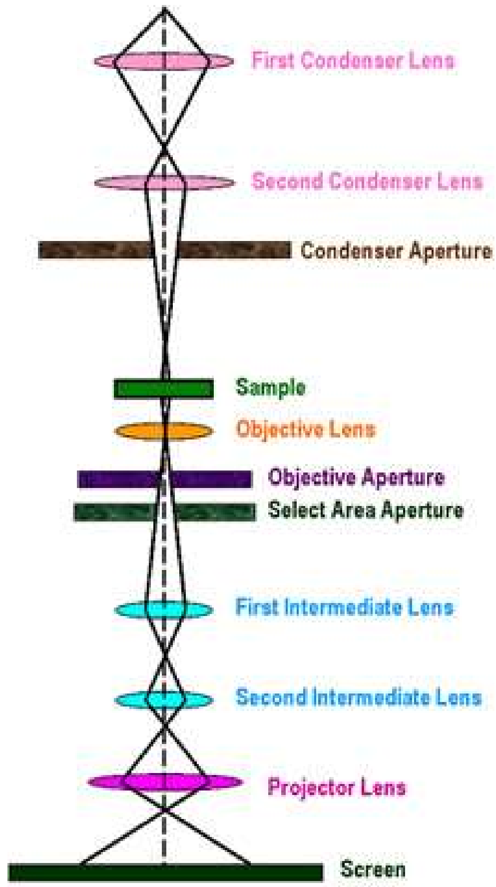
Where λ is the X-ray wave length, B is the full width of height maximum of a diffraction peak, θ_B diffraction angle, and K is the Scherrer's constant of the order of unity for usual crystal.
Similarly, the film thickness of epitaxial and highly textured thin films can also be estimated with XRD.



TEM (Transmission Electron Microscopy):

The transmission electron microscope (TEM) forms an image by accelerating a beam of electrons that pass through the specimen. In TEM, electrons are accelerated to 100 KeV or higher (up to 1MeV), projected onto a thin specimen (less than 200 nm) by means of the condenser lens system, and penetrate the sample thickness either undeflected or deflected.

The greatest advantages that TEM offers are the high magnification ranging from 50 to 10^6 and its ability to provide both image and diffraction information from a single sample.



- The electron gun produces a stream of monochromatic electrons.
- This stream is focused to a small coherent beam by the first and second condense lens.
- The condenser aperture knocks off high angle electrons.
- The beam strikes the specimen.
- The transmitted portion is focused by the objective lens into an image.
- Objective aperture enhances the contrast by blocking out high-angle diffracted electrons.
- Selected area aperture enables to examine the periodic diffraction of electrons by an ordered arrangement of atoms in the sample.
- Intermediate and projector lenses enlarge the image.
- The beam strikes the phosphor screen and image is formed on the screen.

Applications:

- **Morphology:** The size, shape and arrangement of particles as well as their relationship to one another on the scale of atomic diameters.
- **Crystallographic information:** The arrangement of atoms in the specimen and their degree of order, detection of atomic scale defects a few nanometers in diameter.
- **Compositional Information:** The elements and compounds the sample is composed of and their relative ratios.

Applications of Nanotechnology:-

- **Automotive Industry:-**
- Light weight construction, painting as filler or base coat, Catalyst, Tires as fillers, Sensors
- **Chemical Industry:**
- Fillers, adhesives, magnetic fluids, coatings etc.,

- **Engineering:-**
- Lubricant free bearings, Wear protection for tools and machines (scratch resistant coatings)
- **Electronic Industry:-**
- Data memory, Displays (OLED), Laser diodes, Glass fibers, Optical switches, Conductive coatings etc.,
- **Medicine:**
- Drug delivery system, Active agents, Medical rapid test, Antimicrobial agents and coatings, Agents in cancer therapy.
- **Energy storage:**
- Fuel cells, Solar cells, Batteries, capacitors, magnetic refrigeration etc.
- **Cosmetics:**
- Sun protection creams, Lipsticks, Skin creams, Tooth paste etc.

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