

---

## UNIT-IV NANOTECHNOLOGY

---

**Syllabus:** Introduction, Physical & Chemical properties of nanomaterials, Fabrication: AFM, SEM, TEM, STM. Production of nanoparticles: Plasma Arcing, Sol-gel, Chemical vapor deposition. Carbon nanotubes: SWNT, MWNT. Formation of CNT's: Arc discharge, Laser ablation. Properties of Carbon nanotubes, Application of CNT's & Nanotechnology.

---

### Introduction:

The word 'nano' means 'one-billionth' of a meter, i.e.,  $10^{-9}$  m. **Nanotechnology deals with the design, characterization, production and application of structures, devices and systems by controlling shape and size at the nanometer scale.** In nanotechnology, the fundamental properties of materials depend on their size. For example, a nanoscale wire or circuit component does not obey Ohm's law. In 1959, Feynman, a Nobel Laureate in Physics, brought this nanotechnology into daylight by delivering a lecture in "There is plenty of the room at the bottom."

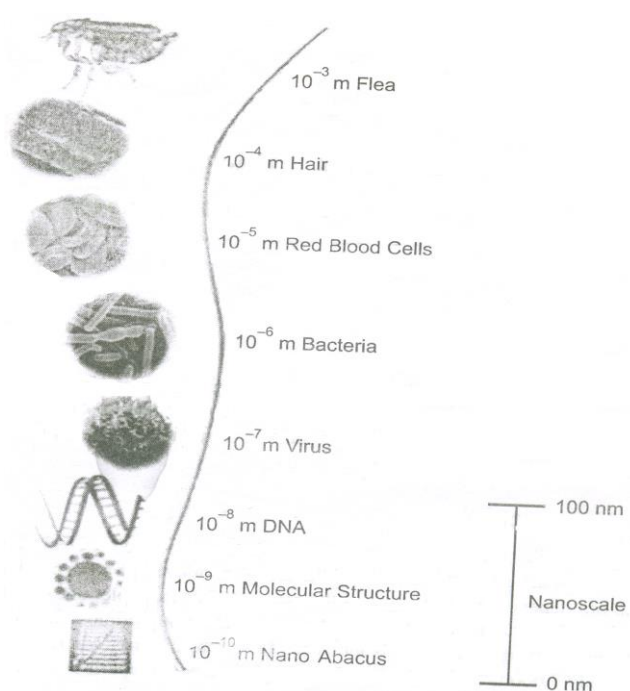
**Nanoscience is the study of the fundamental principles of molecules and structures having sizes in between 1 – 100nm.**

**Nanomaterials are defined as those materials which have structured components with a size less than 100nm at least in one dimension.**

- Materials that are nanoscale in one dimension are layers, such as thin films or surface coatings.
- Materials that are nanoscale in two dimensions include nanowires and nanotubes.
- Nanoscale materials in three dimensions are nanoparticles, for example, precipitates, colloids and quantum dots.

### Origin of Nanotechnology:

While the word nanotechnology is relatively new, the existence of nanostructures and nanodevices is not new. Such structures have existed on earth as long as life itself. Though it is not known when humans began to use nanosized materials, the first known use date back to the fourth century A.D. Roman glassmakers were fabricating glasses containing nanosized metals. Lycurgus cup exhibited in the British Museum in London belongs to this period. This cup was made from soda-lime glass containing silver and gold nanoparticles inside it. In the reflected light, the mug appears green. When a light source is placed inside, it appears deep red in transmitted light. The glass is found to contain 70 nm particles when seen in the



transmission electron microscope. The beautiful colours of the windows of medieval cathedrals are due to the presence of metal nanoparticles in the glass materials.

## Nanoparticles

Nanoparticles sized between 1 and 100 nm are available in different forms such as clusters, metal nanoparticles, colloids, nanocrystals, quantum dots, etc.

- Nanoclusters have a dimension between 1 and 100 nm and narrow size distribution.
- Nanopowders are agglomerates of nanoparticles or nanoclusters.
- Nanometer-sized single crystals or single-domain ultrafine particles are called nanocrystals.
- When nanoparticles are in suspended form in liquid phase, it is called nanocolloids.
- **Quantum dots are tiny particles of semiconductor materials.**

Because of their small size, nanoparticles have a high surface area/volume ratio resulting in an increased reactivity. They exhibit quantum confinement effects also.

### Why the Properties of Nanomaterial are different:

The properties of materials at the nanoscale are very much different from those at a larger scale. Two principal factors that cause nanomaterials' properties to differ significantly from other materials: 1) increase in relative surface area and 2) quantum confinement effect.

#### 1. Increase in surface area to volume ratio:

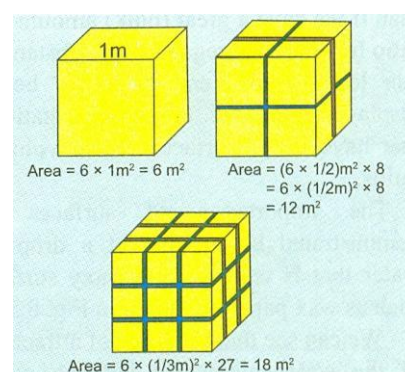
Nanomaterials have a relatively larger surface area when compared to the same volume (or mass) of the material produced in a larger form. Let us consider a sphere of radius "r,"

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

$$\text{Its volume} = (4/3)\pi r^3$$

$$\text{Surface area to its volume ratio} = (3/r)$$

Thus when the radius of the sphere decreases, its surface area to volume ratio increases. Let us consider another example. For one cubic volume shown in fig., the surface area is  $6\text{m}^2$ . When it is divided into eight pieces, its surface area becomes  $12\text{m}^2$ . When the same volume is divided into 27 parts, its surface area becomes  $18\text{m}^2$ . Thus we find that when the given volume is divided into smaller pieces, the surface area increases. Hence as particle size decreases a greater proportion of atoms are found at the surface compared to those inside. For example, a particle of size 30nm has 5% of its atoms on its surface, at 10nm 20% of its atoms, and at 3nm 50% of its atoms. Thus nanoparticles have a much greater surface area per given volume compared with larger particles. It makes materials more chemically reactive. As growth and catalytic chemical reactions occur at surfaces, this means that a given mass of material in nanoparticulate form will be much more reactive than the same mass of material made up of larger particles. In



*Fig. : Total surface area increases as you cut the block into smaller pieces, but the total volume stays constant*

some cases materials that are inert in their larger form are reactive when produced in their nanoscale form. This effects their strength or electrical properties.

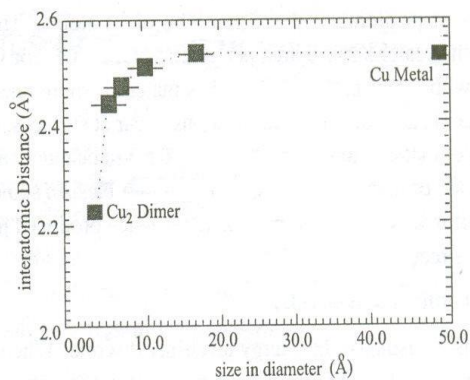
## 2. Quantum confinement effects:

When atoms are isolated the energy levels are discrete. When very large number of atoms are closely packed, to form a solid, the energy levels split and form bands. Nanomaterials represent intermediate stage.

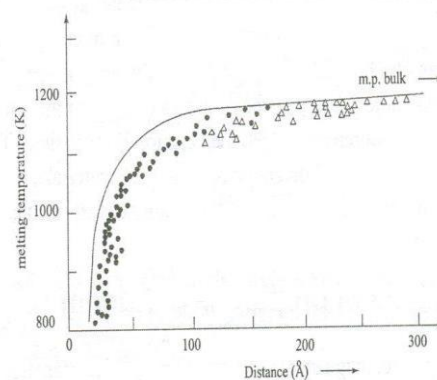
We have studied the problem of particles in a potential well as well as in a potential box. When the dimensions of such wells or boxes are of the order of de-Broglie wavelength of electron or mean free path of electrons, energy levels of electron changes. This effect is called **Quantum confinement**. When the material is in sufficient small size typically 10nm or less, organization of energy levels in to which electron can climb or fall change. Specifically, the phenomenon results from electron and hole being squeezed into a dimensions that approaches a critical quantum measurement, called the “exciton Bhorr radius.” These can affect the optical, electrical and magnetic behavior of materials, particularly as the structure or particle size approaches the smaller end of the nanoscale.

## Physical Properties:

How does the geometrical arrangement of atoms and their stability change with size? Starting from the bulk, first effect of reducing particle size is to create more surface sites i.e. surface to volume ratio increases. This changes the surface pressure and results in a change in the interparticle spacing. This effect is shown in below figure, for the case of  $Cu_n$  particle. The interatomic spacing decreases with size. This is due to competition between the long range electrostatic force and the short range core-core repulsion.



Interatomic distance in  $Cu_n$  as a function of size



Melting point of small  $Au_n$  particles as a function of size

The change in interparticle spacing and the large surface-to-volume ratio in particles have a combined effect on material properties. Variations in the surface free energy change the chemical potential. This effect, for example the thermodynamic properties of which the simplest example is the melting point. The below figure shows the melting point of  $Au_n$  particles as a function of size. The melting point decreases with size and at very small sizes the decrease is faster.

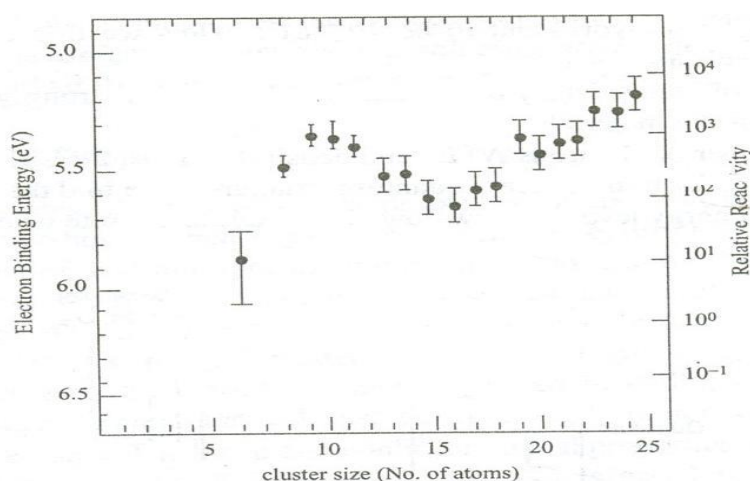
1. Nanomaterials may have a significantly lower melting point or phase transition temperature and appreciably reduced lattice constants, due to a huge fraction of surface atoms in the total amount of atoms.

2. Mechanical properties of nanomaterials may reach the theoretical strength, which are one or two orders of magnitude higher than that of single crystals in the bulk form. The enhancement in mechanical strength is simply due to the reduced probability of defects.
3. Optical properties of nanomaterials can be significantly different from bulk crystals. For example, the optical absorption peak of a semiconductor nanoparticle shifts to a short wavelength, due to an increased band gap. The color of metallic nanoparticles may change with their sizes due to surface plasmon resonance.
4. Electrical conductivity decreases with a reduced dimension due to increased surface scattering. However, electrical conductivity of nanomaterials could also be enhanced appreciably, due to the better ordering in microstructure, e.g. in polymeric fibrils.
5. Magnetic properties of the nanomaterials are due to the large surface area to volume ratio results in a substantial proportion of atoms having different magnetic coupling with neighbouring atoms, leading to different magnetic properties.

### **Chemical Properties:**

The large surface-to-volume ratio, the variation in geometry and the electronic structure have a strong effect on catalytic properties. As an example, the reactivity of small clusters has been found to vary by orders of magnitude when the cluster size is changed by a few atoms. Below figure shows this for the case of  $Fe_n$  clusters reacting with hydrogen.

Another important possible application is hydrogen storage in metals. It is well known that most metal do not absorb hydrogen, and even among those that do, hydrogen is typically on surfaces with a hydrogen-to-metal atom ratio of 1. This limit is significantly enhanced in small sizes. It has been shown that small positively charged clusters of Ni, Pd, and Pt and containing between 2 and 60 atoms can absorb up to eight hydrogen per metal atom. The number of absorbed atoms decreases with increasing cluster size. This shows that small particles may be very useful in hydrogen storage devices in metals.



**Ionization potential and reactivity of  $Fe_n$  clusters as a function of size**

1. The nanostructure in chemistry is colloids and these are formed in a condensed phase in the range from 1 to 100 nm. Nanoscale catalysts have a high degree of dispersion, and this maximizes the contact area of a catalyst with the reactant.
2. In chemical or electrochemical reactions, the rate of increase in mass transport increases as the particle size decreases.

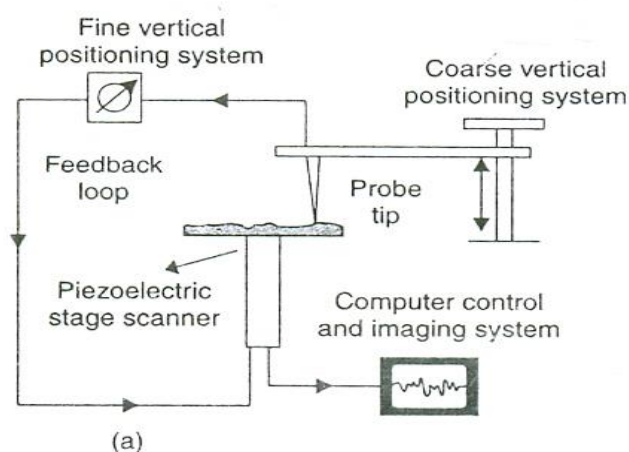
3. The equilibrium vapour pressure, chemical potentials and solubilities of nanoparticles are greater than that for the same bulk material. Exposure to high temperatures or to certain chemicals can increase the size of a nanostructure.
4. Changes in chemical reactivity of nanoscale materials have been expected. Chemical reactions are governed by electrons, electron affinities (or ionization potential) and electron orbital densities. Coupling exists between chemical reactivity and the electronic character of the reactants and any catalyst. It was known that the ionizational potential increases as the cluster size drops below the bulk limit and it has limited applicability.

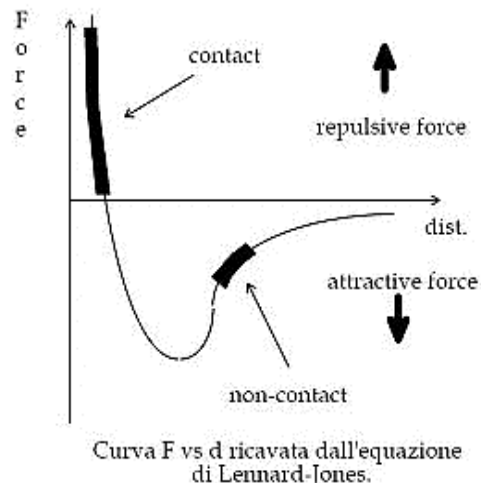
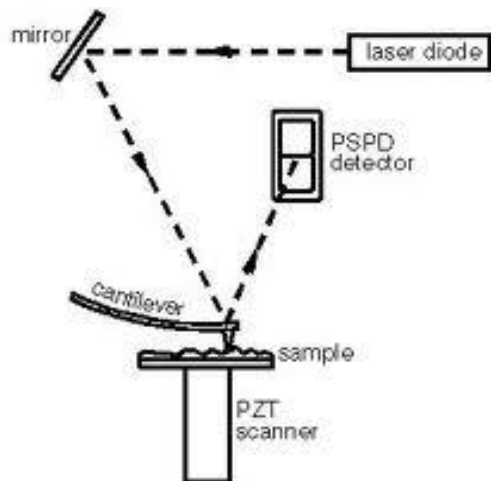
### **Fabrication (Characterizations):**

Fabrication applies to the building of machines, structures or process equipment by cutting, shaping and assembling components made from raw materials. In nanotechnology, the scanning instruments help to a large extent in the development of nanoscience. In these instruments, the tip of the probe slides along a surface. The tip has a nanoscale dimensions, usually of single atom size. During sliding, the instrument measures different properties. To determine these properties, there are different types of scanning probe measurements. They are described in brief below.

### **Atomic Force Microscopy (AFM):**

Unlike STM, it can be used to probe the surface of any materials, insulating or otherwise. This also use as a sharp tip about  $2\mu\text{m}$  long and down to a minimum of  $20\text{nm}$  in diameter. The tip is scanned closely over the specimen surface. In AFM the magnitudes of atomic force rather than tunneling currents are monitored as a function of the probe position on the sample surface. The AFM tip is located at the free end of cantilever that is  $100\text{--}200\mu\text{m}$  long and force between the tip and the sample surface cause the cantilever to bend or deflect. A detector is used to measure the cantilever deflection as the tip is scanned over the sample or alternatively as the sample is scanned under the tip. The measured cantilever deflections allow a computer to generate a map of the surface topography. The position of the cantilever is most commonly detected optically using focused laser beam reflected from the back of the cantilever onto a position sensitive photo detector. Any bending of the cantilever results in a shift in the position of the focused laser spot on the detector and the PSD can measure such displacements to an accuracy of  $<1\text{nm}$ .



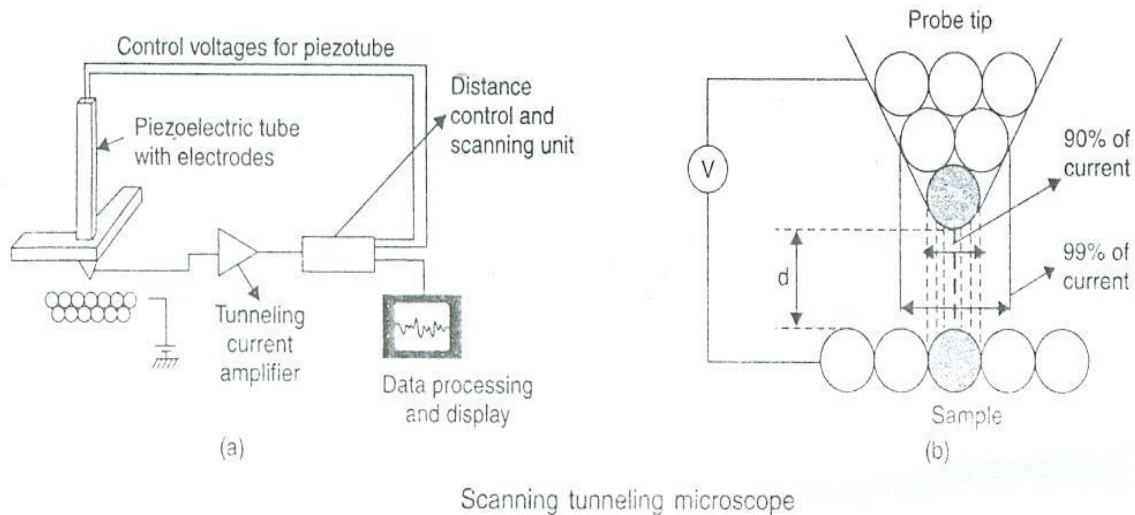


AFM is also designed to operate in either constant force mode or constant height mode. In constant height mode the scanner height is fixed during the scan and the spatial variation of the cantilever deflection is recorded. This forms the data set from which surface topography is constructed. In constant force mode, the deflection of the cantilever is used as an input to a feed back circuit that moves the scanner up and down in the  $z$ -direction. Constant force mode data sets are therefore generated from the scanner's motion in the  $z$ -direction. The dependence of the atomic force on the distance between the tip and the sample is shown in below fig. When the tip is less than a few angstroms from the sample surface, the interatomic force between the cantilever and the sample is predominately repulsive, owing to the overlap of electron clouds associated with atoms in the tip with those at the sample surface. This is known as the contact regime. In non-contact mode regime, the tip is somewhere between ten to a hundred angstroms from the sample surface and here the interatomic force between the tip and the sample is attractive. This is on account of long range attractive force of attraction on account of van der Waals forces.

### Scanning Tunneling Microscopy (STM):

STM is based on quantum mechanical phenomenon of tunneling. It is possible to do real space imaging of surface with atomic dimensions employing no illumination and no lenses. The experimental arrangement consisting of sharp conducting tip (often tungsten) acting as the anode is brought close to the surface of the specimen (the cathode). A bias voltage ranging from 1mV to 1V is applied between the tip and the sample. Above the specimen surface there is an electron cloud due to surface atoms. When the tip is brought within about 1nm of the sample surface, electrons tunnel across the gap. This causes a current to flow in the circuit. The direction of electron tunneling across the gap depends on the sign of the bias voltage. It is this current that is to generate an STM image. The tunneling current falls off exponentially with the distance between the tip and the surface. The tip of the sample is scanned laterally using piezoelectric drivers. The STM image reflects the variation in the sample surface topography. Needless to say that the STM ought to be mounted on a good vibration-isolation table. The tunneling current also depends on the atomic species present on the surface and their local chemical environment.





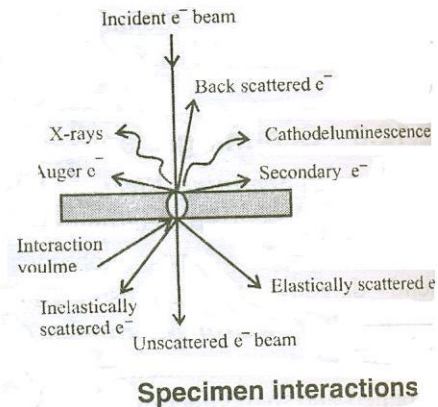
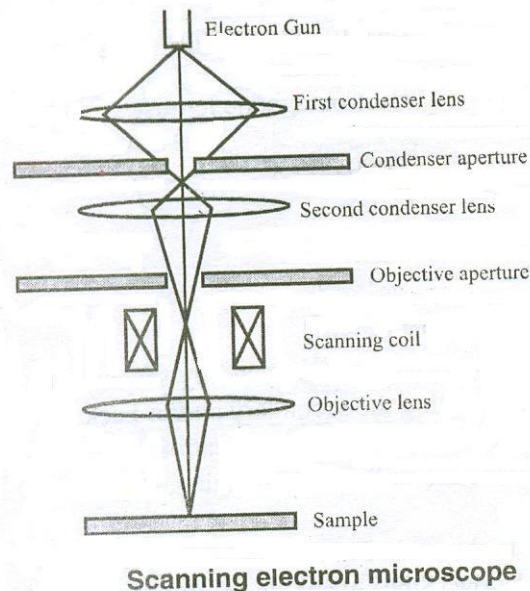
STM is used to operate in constant current mode or constant height mode. In constant height mode the tip travels in horizontal plane above the sample and the tunneling current varies as a function of the surface topography and the local surface electronic states of the sample. Thus tunneling current constitutes the data set from which the surface topography is reconstructed. In constant current mode, the STM uses a feedback system to keep the tunneling current constant by adjusting the height of the scanner at each measurement point. Thus, for example, when there is an increase in the tunneling current, the tip is moved up away from the sample by adjusting the voltage input to the piezoelectric scanner. Thus the motion of the scanner constituting the data from which the topography of the surface is reconstructed. STM cannot image insulating materials and that is its disadvantages.

### **Scanning Electron Microscope (SEM):**

The image in Scanning Electron Microscope (SEM) is produced by scanning the sample with a focused electron beam and detecting the secondary or back scattered electrons. Electron and photon are emitted at each beam location and subsequently detected.

A schematic representation of a SEM is shown in fig. Each component is labeled and their functions are briefly below. Since electrons are used instead of photons, all the lenses are electrostatic or magnetostatic.

1. The electron gun produces a stream of monochromatic electrons.
2. The electron stream is condensed by the first condenser lens. It works in conjunction with the condenser lens to eliminate the high angle electrons from the beam.
3. The secondary condenser lens forms the electrons in to a thin, light coherent beam.
4. Objective aperture further eliminates high angle electrons from the beam.
5. A set of coils acting as electrostatic lens scans and sweeps the beam in a grid fashion (as in television). The beam dwells on points for a period of time determined by the scan speed. Dwells time is usually in millisecond range.
6. The objective lens focuses the scanning beam onto the part of the specimen.
7. When the beam strikes the sample interaction occurs. Before the beam moves to the next dwell point, the various instruments housed to measure various interactions count the number of interactions and displays a pixel on a CRT. The intensity of display is determined by the interaction number. More interactions give brighter pixels.
8. This process is repeated until the grid scan is finished and then repeated. The entire pattern can be scanned 30 times per second.



### **Bulk specimen interaction used in SEM:**

#### ***Backscattered electrons:***

When an incident electron collides with an atom in the specimen which is nearly normal to the incident path, we get backscattered electron at nearly  $180^\circ$ . The intensity of backscattered electron varies with specimen's atomic number. Hence when backscattered electrons are collected and imaged, higher atomic number elements appear brighter than lower atomic number elements. This interaction is therefore utilized to differentiate parts of the specimen that have different average atomic number.

#### ***Secondary electrons:***

When an incident electrons passes very near an atom in the specimen, it may impart some of its energy to the lower energy electron (usually in the k-shell) resulting in ionization of the electron in the specimen atom. The ionized electron leaves the atom with a very small kinetic energy ( $\sim 5\text{eV}$ ) and is called secondary electrons. Each incident electron can produce several secondary electrons. Since the emitted secondary electrons have low energy, only the secondaries that are very near the surface ( $< 100\text{nm}$ ) can leave the sample. Any change in the topography of the sample changes the yield of the secondary electron gives the topography of the sample.

#### ***Auger electrons:***

During the emission of secondary electron a lower energy electron is released thus leaving a vacancy into inner shell. A higher energy electron from the same atom can fall to the lower energy filling the vacancy. The surplus energy is released by the emission of outer orbit electron. These electrons are called Auger electrons. They have a characteristic energy, unique to each element from which they are emitted. These electrons are collected and stored according to their energies to give compositional information about the sample. **X-rays:**

When the vacancy due to the emission of secondary electron is filled by the fall of an electron from higher orbit to lower orbit, the difference in energy may be released as X-rays. Hence X-rays thus emitted will have a characteristic energy unique to the element from which it originates.

### **Applications:**

1. Topography: The surface features of an object or "how it looks", its textures, detectable features limited to a few nanometers.



2. Morphology: The shape, size and arrangements of particles making up the object those are lying on the surface of the sample or have been expected by grinding or chemical etching, detectable features limited to a few nanometers.
3. Compositions: The elements and compounds the sample is composed of and their relative ratios, in areas  $\sim 1$  micrometer in diameter.
4. Crystallographic information: The arrangement of atoms in the specimen and their degree of order, only useful on single-crystal particles  $> 20$  micrometers.

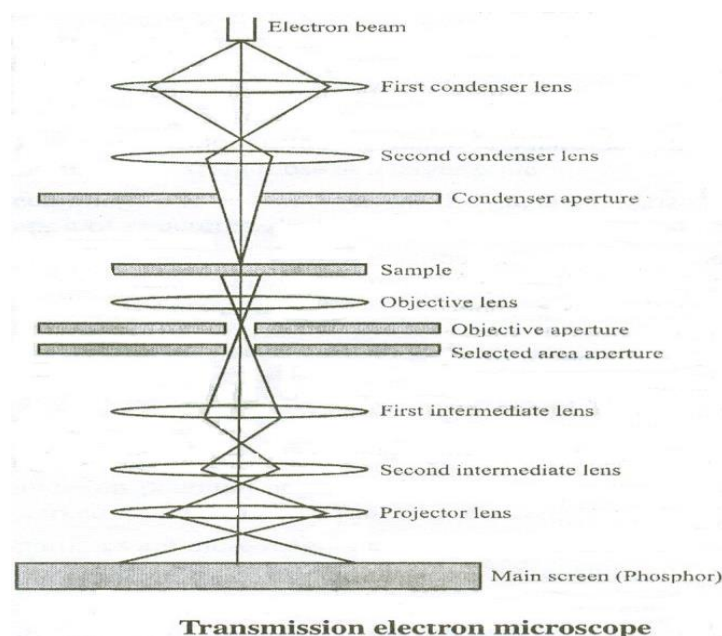
The most common use in the area of semiconductor applications are,

1. to view the surface of the devices
2. for failure analysis
3. cross-sectional analysis to determine the devices dimensions such as MOSFET channel length or junction depth
4. on-line inspection of water processing production
5. Inspection of integrated-circuits etc.

### **Transmission Electron Microscope (TEM):**

A schematic representation of a TEM is as shown in fig. Each component/part is labeled and their functions are briefed below.

1. The electron gun produces a stream of monochromatic electrons.
2. This stream is focused to a small coherent beam by the first and second condenses lenses.
3. The condenser aperture knocks off high angle electrons.
4. The beam strikes the specimen.
5. The transmitted portion is focused by the objective lens into a image.
6. Objective aperture enhances the contrast by blocking out high-angle diffracted electrons.
7. Selected area aperture enables to examine the periodic diffraction of electrons by an ordered arrangement of atoms in the sample.
8. Intermediate and projector lenses enlarge the image.
9. The beam strikes the phosphor screen and image is formed on the screen. The darker areas of the image represent thicker or denser sample areas since these areas transmit lesser electrons. The brighter areas of the image represent thinner or lesser dense sample areas since these areas transmit more electrons.



## Thin specimen interaction used in TEM

### *Unscattered electron:*

These are electrons transmitted through a thin specimen without any interaction occurring inside the specimen. The intensity of transmitted unscattered electrons is inversely proportional to the thickness of the specimen. Hence thicker areas of the specimen appear darker than the thinner areas.

### *Elastically scattered electrons:*

These are electrons that are scattered (deflected from their original path) by atoms in the specimen without loss of energy. These scattered electrons are then transmitted through the remaining portions of the specimen. The scattered electrons follow Bragg's law

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

Hence by collecting the scattered the electrons at different angles, one can get information about the orientation, atomic arrangement and phases presents.

### *Inelastically scattered electrons:*

These are electrons that interact with specimen atoms in an inelastic manner, losing energy. Then they are transmitted through the remaining portion of the specimen. The inelastic loss of energy is characteristic of the elements that have interacted with. These energies are unique to bonding state of each element. Hence this can be used to extract both compositional and bonding information.

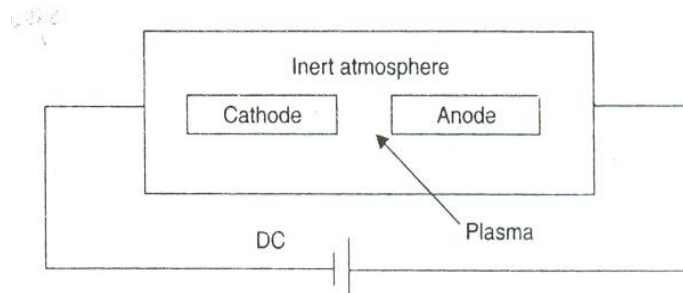
## Applications

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

## Production of Nano Particles:

There are many known methods to produce Nano particles. Let us study briefly few of these methods.

### 1. Plasma Arcing:

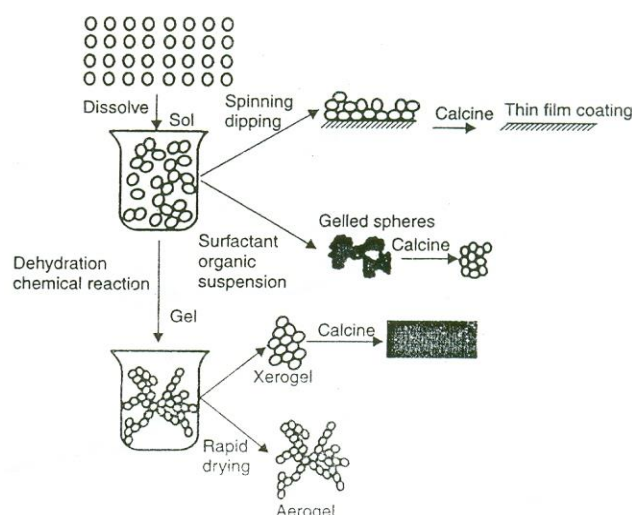


Plasma is an ionized gas. To produce plasma potential difference is applied across two electrodes. The gas yields up its electrons and gets ionized. Ionized gas conducts electricity. A typical plasma arcing device consists of two electrodes. An arc is passed from one electrode to another. From the first electrode (anode) due to potential difference electrons are emitted. Positively charged ions pass to the other electrodes (cathode) picks up the electrons

and are deposited to form nanoparticles. As a surface deposit, the depth of the coating must be only a few atoms. Each particle must be nano sized and independent. The interaction among them must be by hydrogen bonding or Vander Waals forces. Plasma arcing is used to produce CNT's

## 2. Sol-Gel method:

- In solution molecules of different sizes are dispersed and move around randomly and hence the solution are clear.
- In colloids the molecules of sizes ranging from  $20\mu\text{m}$  to  $100\mu\text{m}$  are suspended in a solvent.
- The mixed solution with colloid looks cloudy and even milky. A colloid that is suspended in a liquid is called a sol.
- A gel is a state where both liquid and solid are dispersed in each other which presents solid network containing liquid components. Thus, sol-gels are suspensions of colloids in liquids that keep their shape. Formation of nano particles involves the following four steps



*Hydrolysis:* The desired colloidal particles are dispersed in a liquid to form a sol.

*Condensation:* The deposition of sol on the substrate by spraying, dipping or spinning.

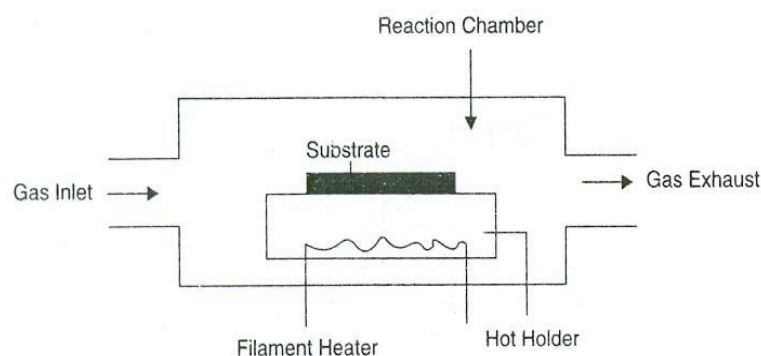
*Polymerization:* The particles in sol are polymerized through the removal of stabilizing components and produce a gel.

*Heat Treatment:* The final heat treatment polymerized the remaining organic or inorganic components and forms an amorphous or crystalline nano particles coating on a substrate.

The rate of hydrolysis and condensation reactions are governed by various factors such as PH nature and concentration of catalyst, temperature and process of drying under proper conditions spherical nano particles are produced.

## 3. Chemical Vapour Deposition:

Chemical methods of synthesis are the most useful due to their potentials. This method involves depositing nano particulate material from the gas –phase. Under high vacuum conditions materials are heated to form gas and are allowed to deposit as a solid on a surface.



Chemical vapour deposition with substrates mounted horizontal

The deposition can be direct or due to chemical reaction which forms a new product which is different from the materials used. This process forms nanopowders of oxides and carbides of metal and vapours of carbon or oxygen are present with the metal. The choice of catalyst determines the size of the particles produced.

Pure metals powder can be produced using microwaves. The microwaves at metal excitation frequencies are used to melt and vapourise the reactants to produce plasma at high temperatures up to  $1500^{\circ}\text{C}$ . Nano sized particles are formed when the plasma enters a reaction column cooled by water. Particles grain size can be altered by flow rate of metal vapour and temperatures. On cooling to  $700^{\circ}\text{C}$  the nanoparticles are filtered from the exhaust gas flow.

Chemical vapour deposition is also used to grow surfaces. Objects tube coated is allowed to stand in the presence of the chemical vapour. The first layer of atom or molecules deposited may or may not react with the surface. The structure of these materials is alive on surfaces with unique characteristics

### **Carbon Nano Tubes(CNT's):**

1. Naturally carbon can exist in several forms i.e, graphite, diamond, fullerenes.
2. **Fullerenes are large carbon cage molecule and the most common one is  $\text{C}_{60}$  which is called "Bucky ball".**
3. Bucky ball is the popular name for "Buckminsterfullerenes". This molecule came into prominence in 1985. It is a football like structure made up of carbon atoms which contains 12 pentagon and 20 hexagon rings of carbon joined together to produce  $\text{C}_{60}$ .
4. It is hollow inside and the average bond length is  $1.4\text{\AA}$ . These fullerenes have been found to exist in interstellar dust as well as in geological formations on earth.
5. Depending on weather they are pure or doped with other atoms or molecules. Fullerenes can be insulators, conductors, semiconductors or even superconductors.
6. It is the roundest and most symmetrical large molecule known to man.
7. Fullerenes are related to carbon nano tubes first observed by Japanese scientist Sumino Iijima in 1991.

When the graphite sheet are rolled into a cylinder and their edges are joined forms a carbon nano tubes i.e., **carbon nano tubes are extended tubes of rolled graphite sheets.**

Carbon nano tubes can be classified in to two types those are *Single walled nano tubes* and *Multi walled nano tubes*.

#### **Single walled nano tubes:**

- In 1993 a new class of carbon nano tubes was discovered with just a single layer called as single walled nano tubes with diameters typically in the range 1 to 2 nm and tend to be curved rather than straight.

- Most of single walled nano tubes have a diameter close to 1nm and with a tube length that is 1000's of times longer.
- The structure of single walled nano tubes can be conceptualized by wrapping a one thick layer of graphite called graphene into a seamless cylinder.
- The way the graphene sheet is wrapped is represented by a pair of indices (n, m) called Chiral vectors. The integer's n and m denote the no. of unit vectors along two directions in the honey comb crystal lattice of graphene.
- There are 3 distinct ways in which the graphene sheet can be rolled in to a tube.
  1. Zigzag: If  $m = 0$  the nano tube is called zigzag. Eg (9, 0)
  2. Arm chair: If  $n = m$  the nano tubes is called Arm chair. Eg (9, 9)
  3. Chiral: If otherwise the nano tubes are called Chiral. Eg (5, 10)
- Arm chair and zigzag tubes have high degree of symmetry. The term arm chair and zigzag referred to the arrangement of hexagons around the circumference.
- The third class of tube which is in practice is the most common i.e., chiral. It means that it can exist in two mirrors related forms.
- Single walled nano tubes are most likely used for miniaturizing electronics.

### Multi walled nano tubes:

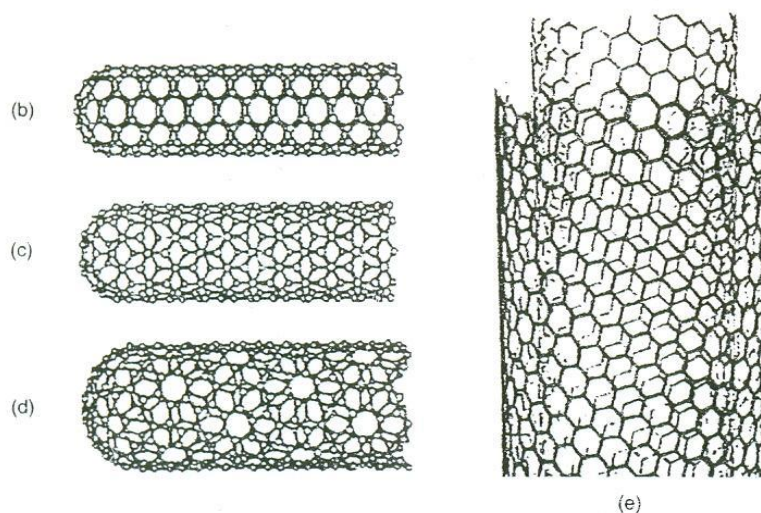
They consist of multiple layers of graphite rolled in on themselves to form a tube shape and have even more complex array of forms. Their length may vary from several  $\mu\text{m}$ 's to cm's.

There are two models which can be used to describe the structures of MWNT's

**1. Russian Doll model:** Sheet of graphite is arranged in concentric cylinders. In this model each concentric SWNT can have different structure and there are a variety of sequential arrangements. The simplest sequence is when concentric layers are identical but differs in diameter. Eg (0, 8) SWNT with in a larger (0, 10) SWNT.

**2. Parchment model:** A single sheet of graphite is rolled in around itself resembling a scroll of parchment or a rolled up newspaper.

The inter layered distance in MWNT is close to the distance between graphene layers in graphite. The structure of nano tubes influences its properties including electrical and thermal conductivity, density and lattice structure. Both type and diameter are important. The wider the diameter of the nano tube the more it behaves likes graphite. The narrower the diameter of nano tube the more its intrinsic properties depend upon its specific type.



(a) Basis vectors of the two dimensional graphene sheet  
(b) armchair (c) zigzag (d) chiral (e) multiwall nanotube



## Properties of Carbon nano tubes:

### 1. Strength and Elasticity:

Carbon atoms of a single sheet of graphite forms a planar honey comb lattice in which each atom is connected via a strong chemical bond to three neighboring atoms. Because of these strong bonds the base plane elastic modules of graphite is one of the largest of any known material. For this reason CNT's are expected to be the ultimate high strength fibers. The stiffness of a material is measured in terms of its Young's modulus.

Eg. 1. The young's modulus of the best nano tube can be as high as 1000 giga Pascal which is approximately 5 times greater than that of steel.

2. The tensile strength or breaking strain of nano tubes are up to 63 giga Pascal which is 50 times greater than steel.

### 2. Thermal Conductivity and Expansion:

All nano tubes are good thermal conductors. The strong in-plane graphite carbon-carbon bonds make them exceptionally strong and stiff against axial strains. The almost zero in -lane thermal expansion but large inter-plane expansion of single walled nano tubes implies strong in-plane coupling and high flexibility against non-axial strains. Preliminary experiments on the thermal properties of CNT's show very high thermal conductivity.

### 3. High Absorbent:

The large surface area and high absorbency of CNT's make them ideal candidates for use in air gas and water filtration.

### 4. Kinetic:

MWNT's exhibit a striking telescopic property where by an inner nano tube core may slide almost without friction with in its outer nano tube shell. Thus creating an automatically perfect linear or rotating bearing. This property is used to create the world's smallest rotational motor.

### 5. Electrical conductivity:

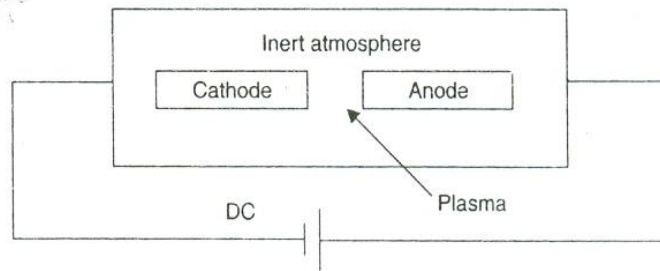
Because of the symmetry and unique electronic structure of graphene structure of nano tubes strong effect its electrical properties. For a given nano tube if (n, m) is a multiple of 3 then the nano tube is metallic otherwise it is a semiconductor. In theory metallic nano tubes can have an electrical current density more than 1000 times greater than silver and copper. The resistivity of SWNT's was of the order  $10^{-7}$  ohm-cm at  $27^{\circ}\text{C}$ . This means that SWNT's are most conducting carbon fibers known. Due to the defects in SWNT's they can behave as rectifying diodes and transistors.

## Preparation of Nano materials:

There are many known methods to prepare Carbon Nano tubes. Let us study briefly few of these methods.

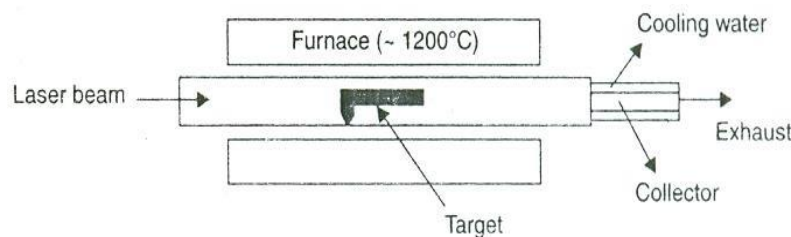
### 1. Carbon Arc Discharge:

A potential of 20-25V is applied across carbon electrodes 5-20 $\mu\text{m}$  diameter and separated by 1mm at 500 torr pressure of flowing helium. Carbon atoms are rejected from the positive electrode and form nano tubes on the negative electrode. As the tube form, the length of the positive electrode decreases, and a carbon deposit is formed on the negative electrode. To produce a single walled nano tube, a small amount of cobalt, nickel, or 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. This method can produce SWNT of diameter 1-5 nm with a length of 1 $\mu\text{m}$ .



## 2. **Laser Ablation:**

The laser beam is used to vaporize a target of a mixture of graphite and metal catalyst such as Co or Ni at temperature of approximately  $1200^{\circ}\text{C}$  in a flow of controlled inert gas and pressure. The argon gas sweeps the carbon atoms from the high temperature zone to the colder copper collector on which they condense into nano tubes. Tubes 10-20 nm in diameter and  $100\mu\text{m}$  long can be made by this method. The mechanism of nano tube growth is not understood since metal catalyst is necessary for the growth of SWNT.



Preparation of CNT by laser ablation

## **Applications of Carbon Nano Tubes:**

1. The CNT's are very light in weight, but they are very strong, hence they are used in aerospace.
2. They are used in constructing nano scale electronic devices.
3. CNT's are used in battery electrodes, fuel cells, reinforcing fibers etc.
4. Nano tubes are used in the development of flat panel displays for computer monitors and televisions.
5. Plastic composite CNT's are used as a light weight shielding materials for protecting electromagnetic radiation.
6. Semiconductor CNT's are used as switching devices.
7. Semicircular CNT's are also used as chemical sensors to detect various gases.
8. Nano tubes can also serves as catalysts for some chemical reactions.
9. Because of the carbon nanotube's superior mechanical properties, many structures have been proposed ranging from everyday items like clothes and sports gear to combat jacket and space elevators.
10. Nanotube reinforcements in polymeric materials may also significantly improve the thermal and thermo mechanical properties of the composites.
11. The nanotubes versatile structure can be used for localized drug delivery in and around the body. This is especially useful in treating cancerous cells.
12. Nanotubes are used to improve ultra capacitors.

### **Applications of Nanotechnology:**

1. Magnets made of nanocrystalline yttrium-samarium-cobalt grains possess unusual magnetic properties.
2. Nanocrystalline ceramics, such as silicon nitride and silicon carbide, have been used in automotive applications as high-strength springs, ball bearing and valve lifters.
3. Nano sized titanium dioxide and zinc oxide are currently used in sun screens.
4. Nano sized iron oxide is present in lipsticks as a pigment.
5. A carbon nanoparticles act as filter to reinforce car tyres.
6. Wear and scratch-resistant hard coating are significantly improved by nano scale intermediate layers.
7. Cutting tools made of nanocrystalline materials, such as tungsten carbide, tantalum carbide and titanium carbide, are more wear and erosion-resistant and last longer.
8. Other novel, and more long-term, applications for nanoparticles lie in paints that change color in response to change in temperature or chemical environment.
9. Nanoparticles react with pollutants in soil and ground water and transform them into harmless compounds.
10. In general, nanoparticles have a high surface area, and hence provide higher catalytic activity.
11. Nano spheres of inorganic materials could be used as lubricants, in essence by acting as nano sized ball bearings.
12. It is possible to produce unusual colour paints using nanoparticles.
13. Nano metallic colloids are used as film precursors.
14. Nanoparticles are used for information storage.
15. Quantum electronic devices have started replacing bulky conventional devices.
16. Nanocrystalline zirconium oxide (zirconia) is hard, wear resistant, bio-corrosion resistant and bio-compatible. It therefore presents an attractive alternative material for implants.
17. Controlled drug delivery is possible using nanotechnology.
18. Using nano particles in the manufacturing of solar cells, reduces the manufacturing and installation cost and it also increases the efficiency of solar cell.
19. Nanotechnology is having an impact on several aspects of food science, from how food is grown to how it is packaged and stored.
20. Nanotechnology is used in manufacturing of reinforced tennis rackets and balls.