powder method.

Nanomaterials

Introduction, nanoparticles, metal nanoclusters, semiconductor nanoparticles, carbon clusters, carbon nanotubes, quantum nanostructures - nanodot, nanowire and quantum well. Fabrication of quantum nanostructures.

Bonding in Crystals

Types of

NANOMATERIALS
(Particles of Very Minute Size)

13.1 INTRODUCTION TO NANOSCIENCE AND NANOTECHNOLOGY

The word "*nano*" has a Greek origin meaning dwarf (small). Technically, the prefix nano means "one billionth" or 10^{-9}. Therefore, one nanometer is 10^{-9} metre, one nanosecond is 10^{-9} sec and so on. A nanometer is used to measure things that are very small such as atoms and molecules. For example, hydrogen atom is 0.1 nm, red blood cell is 500 nm in size, visible colour wavelength is 400 to 700 nm, etc. When 'nano' prefix is used with science and technology, it becomes a new field of Physics.

Nanoscience and Nanotechnology

Nano-science in its simplest form is the study of fundamental principles of molecules and structure with the size ~ 1 nm to 100 nm. These structures are called nano-structures. First of all Prof. Norio Taniguchi of Japan in 1974 used the word nanotechnology to describe the extension of traditional silicon machining down into region smaller than one micron. Richard Feynman, in his famous speech, discussed the possibility of manipulating and controlling things on molecular scale in order to achieve electronic and mechanical systems with atomic sized components. An American engineer Eric Drexler has speculated extensively about the laboratory synthesis of machines at the molecular level via manipulation techniques and producing components much smaller than any microprocessor which has been called molecular nanotechnology. We differentiate between nanoscience and nanotechnology as follows :

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

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

In short, nanoscience is the *study* and nanotechnology is the engineering which deals with the design and manufacture of extremely small components and systems. *In other words,* ***the technology of design, synthesis, characterization and application of materials on nanoscale is called nanotechnology.***

The National Nanotechnology Initiative (U.S.A.) defines nanotechnology as consisting of all of the following :

- Research and technology development at the 1 to 100 nm range.
- Creating and using structures that have novel properties because of their small size.
- Ability to control or manipulate at the atomic scale.

13.2 NANOPARTICLES AND NANOMATERIALS

The prefix 'nano' means one billionth. A nanometer is one billionth of a metre (10^{-9} m). This is roughly ten times the size of an individual atom. The diameter of a human hair meausres 50,000 nanometers (nm).

Materials when reduced down to 100 nm show drastic changes in respect of *physical, Chemical, Optical, magnetic, mechanical* and *electrical* properties. All these lead to exciting applications in *Bioscience, Medical, Environmental sciences, Electronics, security* and cosmetics. These applications open new field of research to understand this small world of science and engineering. Nanomaterials are very light, mechanically strong, transparent and totally different from bulk materials. They also become very active and aggressive in chemical reactions.

The important parameter in the study of nano physics is the ratio of surface area to the volume of the particles. In nanoparticles, the atoms on the surface begin to dominate over those in the bulk. As a result, the material properties are modified. For example, metals which are good electrical conductors in the bulk, begin to show insulator like behaviour. It is also observed that some of the metals at nanosize exhibit fluorescence. Further, the magnetic nanoparticles show some peculiar behaviour with the transition from a ferromagnetic to what is known as superparamagnetic behaviour.

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

(1) Nanomaterials have a relatively larger surface area as compared to the same mass of material produced in a larger form, *i.e.*, ***Nanoparticles have large surface to volume ratio than their bulk counterpart.*** This can make materials more chemically reactive and affect their strength or electrical properties. In some cases the materials that are inert in their larger form are reactive when produced in their nanoscale form.

(2) Quantum effects can begin to dominate the behaviour of matter at the nanoscale affecting the optical, electrical and magnetic behaviour of materials. So, ***Nanomaterials have unusual electrical, optical and magnetic properties than their bulk counterpart.***

So, what kind of changes in the properties do we expect? Here are some interesting examples :

(i) Opaque substances can become transparent, *e.g.*, copper.
(ii) Inert materials can become catalyst, *e.g.*, platinum.
(iii) Stable materials can turn combustible, *e.g.*, aluminium.
(iv) Solids can turn into liquids at room temperature, *e.g.*, gold.
(v) Insulators can become conductors, *e.g.*, silicon.

The most far reaching consequence of nanoparticle is the change in their *electronic properties.* When particles are small enough, they become electronic comparable to atoms and molecules following *quantum mechanical properties.* When nanoparticles become small enough, they electronically comparable to atoms and molecules. Now they follow quantum mechanical rules instead of classical physics rules. Due to this fact, they are called as quantum dots or sometimes as artificial atoms. This is due to disappearance of band structures and the formation of discrete energy.

The most striking property of nanoparticles made of **semiconductor elements** is change in their *optical properties* compared to those of bulk material. In chemistry, the size dependent optical properties of colloidal semiconductor particles have been observed. The minimum energy required to create an electron-hole pair in a semiconductor quantum dot is defined by the band gap E_g. If the energy of light is less than band gap energy, it will not be absorbed by quantum dot. The band gap depends on the size of the quantum dot. Therefore, absorption is also size dependent. It is observed that absorption spectrum of smaller quantum dots is shifted to shorter wavelength.

Recent applications of nanoparticles :

(i) Nanoparticles are used in displays that are cheaper, larger, brighter and more efficient.

(ii) They are used in renewable energy ultrahigh performance solar cells.

(iii) Nanoparticles have been found to impart some extra properties to various day to day products. For example, nanozinc oxide particles have found to have a superior ultraviolet blocking properties compare to its bulk state.

(iv) Nanoparticles are used antibacterial silver coating on wound dressing.

(v) Magnetic nanoparticles exhibits unique nanoscale properties of superparamagnetism and are utilized as excellent probes for magnetic resonance imaging (MRI).

(vi) Nanoparticles improve efficiency of coolant in transformers.

(vii) These particles are frequently used in anti-reflection coating and to make light based sensors for cancer diagonosis.

(viii) The microchip and its revolutionary applications in computing, communications, consumer electronics and medicine.

13.3 SYNTHESIS OF NANOPARTICLES

Nanoparticles with size ranging from 1 nm to 100 nm can be synthesized by means of various techniques. Physical, chemical, biological and self assembly techniques are few common of them.

There are six widely known methods used to produce nanoparticles. They are :

1. Mechanical alloying or high energy ball milling.
2. Sputtering or Laser evaporation.
3. Plasma synthesis.
4. Inert gas condensation.
5. Electrodeposition.
6. Sol-gel synthesis.

Here some of which are discussed below :

(1) Ball milling method

Ball milling method is a mechanical method. This is a special type of grinder. Ball mill is a cylindrical device used in grinding materials like ores, chemicals, ceramic raw material, etc. The mill rotates around a horizontal axis and is partially filled with material to be grounded plus the grinding medium as shown in fig. (1). Different materials are used as media. Industrial ball mills can operate continuously fed at one end and discharged at the other end. The grinding works on the principle of critical speed. The critical speed is that speed after which the grinding medium (say steel balls which are responsible for the grinding of particles) start rotating along the direction of the cylindrical device. There will be no further grinding.

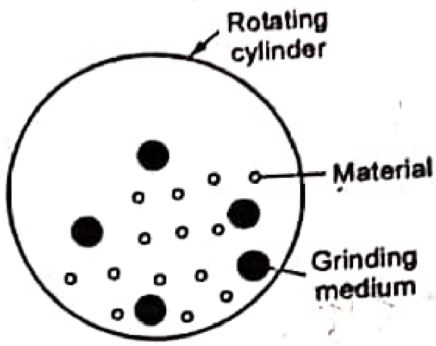


Fig. (1) Ball mill.

(2) Sputtering or Laser evaporation

Sputter means to split out or throw out and ***sputtering is a process in which surface atoms are physically ejected from the surface by momentum transfer from an energetic bombarding beam.*** (say laser beam). Fig. (2) shows a laser evaporation sputtering in inert gas atmosphere. A high intensity laser beam is allowed to incident on

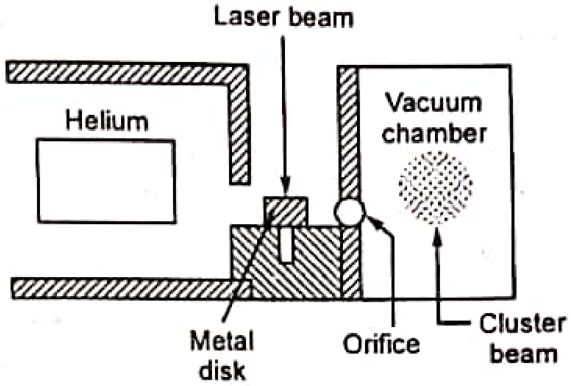


Fig. (2) Laser evaporation method.

target metal disc. This causes the evaporation of atoms from the surface of metal. The atoms are then swept by a burst of helium into vacuum chamber through an orifice. The expansion of gas in vacuum chamber produces a cooling because it has passed through orifice. Now the clusters of metal atoms as nanoparticles are formed in vacuum chamber.

(3) Radio frequency (RF) plasma method

A thermal plasma can also deliver the energy necessary to cause evaporation of small micrometer size particles. Fig. (3) shows a method of nanoparticles synthesis utilizing a plasma generated by radio frequency heating coils. The metal is contained in a pestle in an evacuated chamber. The RF coils are wrapped around the evacuated system in the vicinity of the pestle. The evacuated chamber is provided with an opening to enter helium gas. The evacuated chamber is also provided a cluster collection (collected rod) device of liquid nitrogen filled cold finger scrapper assembly.

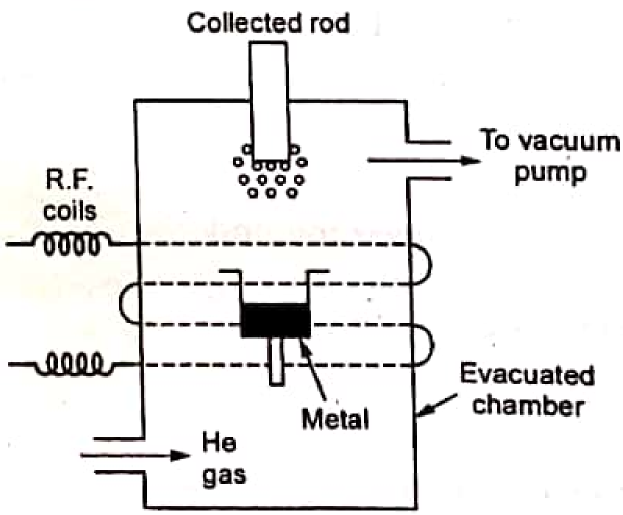


Fig. (3) Showing gas condensation.

The metal is heated above the evaporation points by R.F. coils. Now helium gas is allowed to pass into evacuated chamber which forms a high temperature plasma in the region of coils. The metal vapour nucleates on the helium gas atoms. It is important to mention here that ultra fine particles are formed by collision of evaporated atoms with residual gas molecules. They now diffuse to colder collector rod, where nanoparticles are formed.

(4) Chemical method

The nanoparticles of silver can be prepared by decomposing $(CH_3)_2—C_2H_5NaAlH_3$ in toluene and heating the solution to 105°C for two hours. The titanium isopropoxide is also added to act as catalyst. The size of the particles produced depends on the choice of catalyst. For example, in presence of titanium as catalyst 80 nm nanoparticles are produced.

(5) Sol-Gel method

Sol-Gel is a chemical process used to make ceramic and glass materials in the form of thin films, fibres or powders. A sol is a colloidal (the dispersed phase is so small that gravitational forces do not exist, only van der Waals' forces and surface charges are present) or molecular suspension of solid particles of ions in a solvent. A gel is a semi-rigid mass that forms when the solvent from the sol begins to evaporate and the particles or ions left behind begin to joint together in a continuous network.

Typical precursors are metal alkoxides and metal chlorides. The most widely used are tetramethoxysilane (TMOS) and tetraethoxysilanes (TEOS) which form silica gels. Alkoxides are immiscible in water. Mutual solvent alcohol is used. The metal chlorides undergo hydrolysis* and polycondensation reactions** to form a colloid† dispersed in a solvent. The sol evolves then towards the formation of an inorganic network containing a liquid phase (gel). After this, a drying process is used which serves to remove the liquid phase from the gel thus forming a porous material. Finally, a thermal treatment (firing) is performed in order to favour further polycondensation and enhance mechanical properties.

The sol-gel process usually consists of the following four steps :

(i) The desired colloidal particles once dispersed in a liquid to form a sol.

(ii) The deposition of sol solution produces the coating on the substrate.

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

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

In brief, we can say that sol-gel formation occurs in four stages : (i) Hydrolysis, (ii) Condensatioin, (iii) Growth of particles and (iv) Agglomeration of particles.

(6) Pulsed laser method

This method is used in the synthesis of silver-nanoparticles. Silver nitrate solution and a reducing agent are arranged in a vessel. A solid disc [Fig. (4)] attached with a

... down by

rotating device (motor) is placed inside the solution. So, the disc may rotate inside the solution with the help of motor. The disc is subjected pulses from laser beam. The pulses of laser beam produces hot spots on the surface of the disc. The reaction of silver nitrate and reducing agent at these hot spots results the formation of silver particles. These particles are separated from solution by centrifuge. The size of the particles depend on the energy of incident laser pulses as well as on the rotation speed of disc.

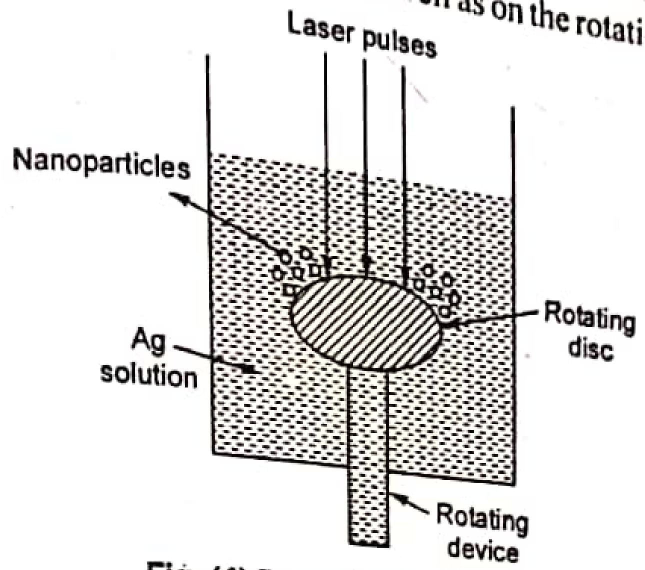


Fig. (4) Pulsed laser method.

13.4 TOOLS TO MAKE NANOSTRUCTURES

A number of tools are used to make nanostructures. Here we shall consider the method of lithography. The word ***"lithography"*** originally belongs to the concept on stone. A lithograph is an image (usually on paper) that is produced by making a pattern on the stone, inking the stone and then pushing inked stone onto the paper. We shall consider the following lithography :

(1) ***Nanoscale lithography***
(2) ***Dip pen nanolithography***
(3) ***E-beam lithography.***

(1) Nanoscale Lithography

A nanoscale lithography cannot use visible light. The reason is that the wavelength of visible light is at least 400 nanometers. Therefore, structures smaller than that are difficult to make directly using it. Indeed, the common methods use *X*-ray lithography. For example, current computer chips normally use this lithography. In this process, a master mask is made using chemical methods and *X*-rays are passed through that mask to produce the actual chip structure.

One of the most straightforward technique doing small scale lithography is micro-imprint lithography. This was developed by George Whitesides and his research group at Harvard University. This method is very simple and works in same way as a rubber stamp. A pattern is made on the rubber surface (actually a rubber-like silicon/oxygen polymer). The rubber surface is then coated with molecular ink. The ink can then be stamped out on a metal, polymer, oxide or any other surface in small-scale stamps just like a stamp rubber on simple paper.

(2) Dip pen nanolithography (DPN)

Dip pen nanolithography is a process of writing in the same way as we write lines with a foutain pen. In order to make such lines in nanoscale, it is necessary to have nanopen. Fortunately, an atomic force microscope (AFM) tips are ideal nanopens. Atomic force microscope is a very high resolution type of scanning probe microscope. The scanning probe tip of this microscope is similar to the tip of a fountain pen. This microscope has high resolution of fraction of Å, *i.e.*, more than 100 time better than optical diffraction limit. In DPN, a reservoir of ink (atoms or molecules) is stored on the top of scanning probe tip [fig. (5)]. The tip is manipulated across the surface, leaving lines and patterns behind.

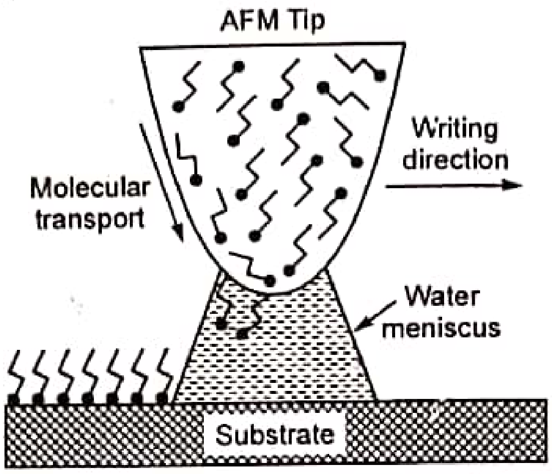


Fig. (5) AFM tip used for dip-pen lithography.

AFM tips are relatively easy to manipulate. This fact makes DPN the techniques of choice for creating new and complex structures in small volumes.

(3) E-beam lithography

The light based industrial lithography is limited to creating features no smaller than the wavelength used. Although we can use smaller wavelengths light but this creates side effects like blowing the feature which we are trying to create. The reason is that smaller wavelength light has higher energy.

An alternate way to solve the problem is to use electrons instead of light. This E-beam lithography may be used to make structures at nanoscale. E-beam lithography also has applications in current microelectronics manufacturing.

13.5 PROPERTIES OF NANOPARTICLES

Following are the properties of nanoparticles.

(1) Mechanical properties

Very small nanoparticles have almost all their atoms on the surface. These atoms have more freedom to go larger from their equilibrium positions. This characteristics can lead to the changes in the structure of these particles. The studies on gold nanoparticles by electron microscope reveals that gold nanoparticles continue to transform between different structural arrangements. This property of nanoparticle material is known as ***fluctuations.*** At very high temperatures, these fluctuations can cause a breakdown in the symmetry of nanoparticle. This results the formation of liquid-like droplet of atoms.

Nanophase metals with their exceptionally small gain size are found to be *exceptionally strong*. The reason is that nanophase materials are mostly free from dislocations. The variation of hardness with diameter of copper nanocrystal is shown in fig. (6).

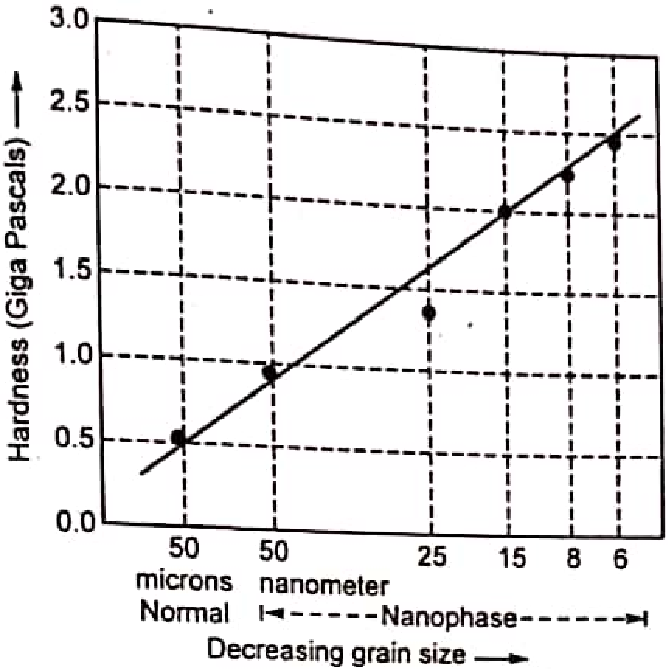


Fig. (6) Strength of nanophase copper as a function of grain size.

Therefore, the material in nanophase has ***very high strength*** and ***super hardness.***

The melting point of the cluster depends on the number of atoms in the crystal. It increases with increase in number of atoms and attains the value of bulk material when the cluster contains 1000 atoms or more. Fig. (7) shows the melting point of gold versus diameter of nanoparticle.

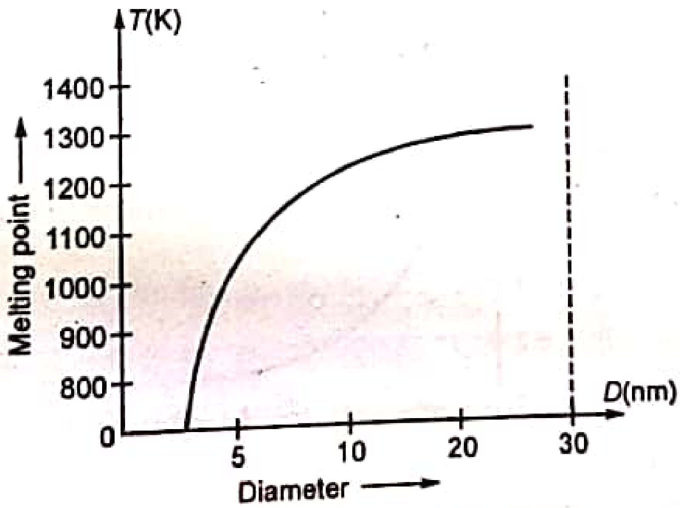


Fig. (7) Melting point of gold as a function of grain size.

It is observed that ***melting point*** reduction is not really significant until the particle size is less than about 10 nm.

(2) Optical properties

The colour of the material is determined by the wavelength of light photon absorbed by it. The absorption of photons occurs because electrons from lower energy state jump to higher energy states. It is observed that clusters of different sizes have different energy level separations. So, their absorption is different for different clusters. Therefore, different clusters have ***different colours.***

In semiconductor nanoparticles, there are pronounced changes in the optical properties as compared to bulk material. For example, let us consider the shift in optical absorption spectra of Cd Se. Fig. (8) shows the optical absorption spectra of Cd Se of two different sizes (2 nm and 4 nm) at 10 K.

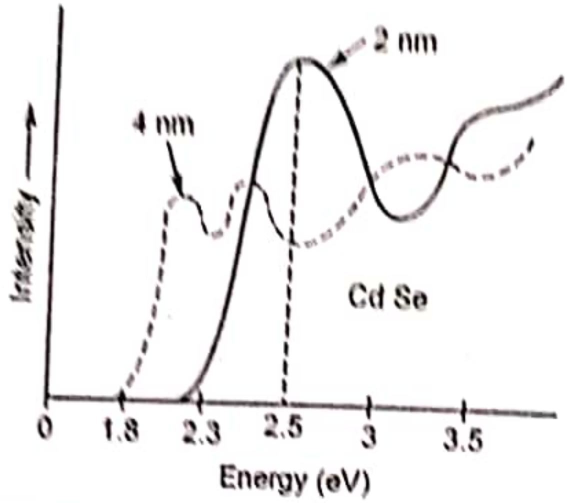


Fig. (8) Optical absorption spectrum of CdSe for nanoparticles of sizes (2 nm) and (4 nm).

It is observed from the figure that lowest energy absorption edge is shifted to higher energy as the size of the particle decreases. Therefore, there is a ***significant shift in optical absorption spectra.***

(3) Magnetic properties

The nanoparticles of a magnetic solid exhibts a new class of magnetic properties. It is important to mention here that small particles differ from bulk particles in the sense that they have lower coordination number. A graph between the change in bulk magnetic moment versus coordination number is shown in fig. (9).

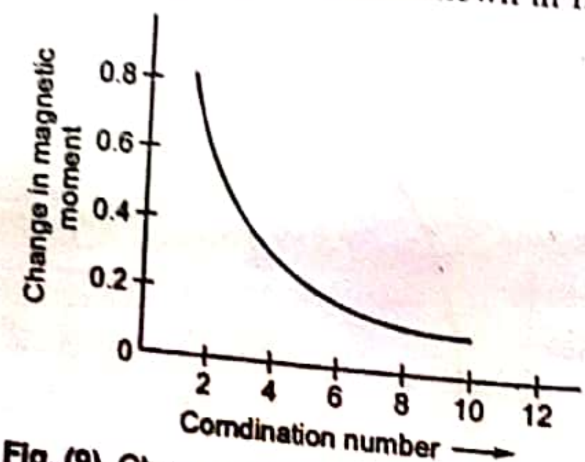


Fig. (9) Change in bulk magnetic moment vescus coordination number.

It is clear that small particles (lower coordination number) are ***more magnetic*** than bulk material.

Table shows the account of magnetic behaviour of very small particles of various metals :

Metal	Bulk	Cluster
Na, K	Paramagnetic	Ferromagnetic
Fe, Co, Ni	Ferromagentic	Super paramagnetic
Gd, Tb	Ferromagnetic	Super paramagnetic
Rh	Paramagnetic	Ferromagnetic

(4) Electronic properties

The electronic structure of nanoparticles can be studied by ultraviolet photo-electron spectroscopy. When ultraviolet photon strikes an electron in the valence band of the atom, the electron is ejected from the atom. The emitted electrons are counted by the device of spectroscope. Now, the number of counts (electrons emitted) versus absorbed energy are noted and plotted. Fig. (10) shows a graph between counts versus energy of copper clusters having 20 to 40 atoms.

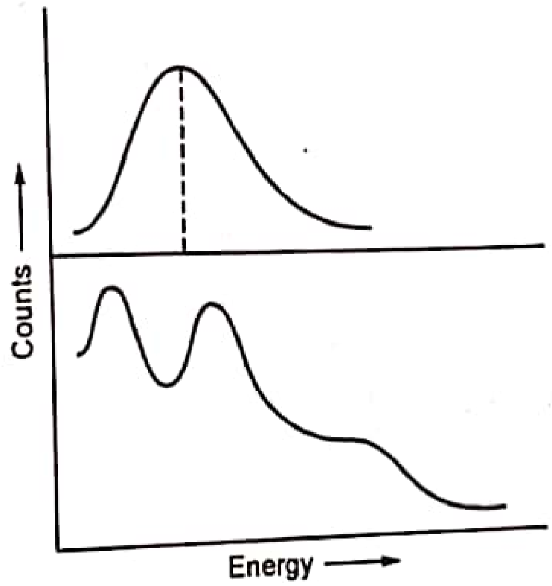


Fig. (10) Ultraviolet photoelectron spectrum in valence band region of copper nanoparticles having 20 and 40 atoms.

The graph shows peaks, thereby indicating that the energy levels of nanoparticles are discrete. Therefore, the ***electronic struture*** in valence region varies with the size of the cluster.

In brief, following are the few properties of nanomaterials :

(i) They are hard.

(ii) They are exceptionally strong.

(iii) They are ductile (drawn out into threads) at high temperatures.

(iv) They are chemically very active.

(v) They are wear resistance.

(vi) They are erosion resistant.

13.6 QUANTUM WELL, QUANTUM WIRE AND QUANTUM DOTS

...ial is continuously reduced from a large or that the properties of the matter remains same in the beginning but small changes occur afterwards. Finally, if the size drops below 100 nm (in nano range), then drastic changes occur in the properties. A progressive generation of diminishing size of rectangular nanostructures takes place in the following way :

1. If one dimension is reduced to the nanorange while other dimensions remain large, then the structure so formed is known as ***quantum well*** as shown in fig. (11b).

2. If the two dimensions are reduced to nanorange while the third remains the same, then the structure so formed is known as ***quantum wire*** as shown in fig. (11c).

3. When all the three dimensions of the material are reduced to nano range, then it is called as ***quantum dot*** as shown in fig. (11d).

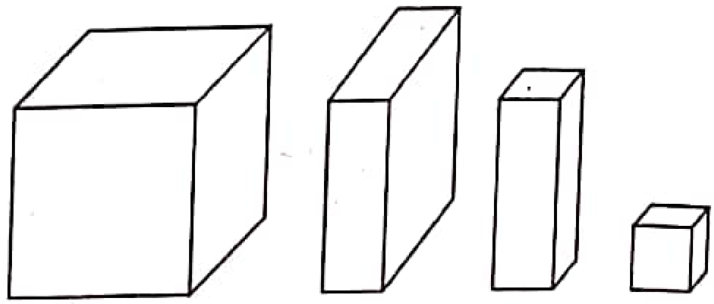


Fig. (11) Progressive generation of rectangular nanostructures.

It is important to mention here that the word quantum is associated with all the three structures. This is because the changes in properties arise from quantum mechanical nature. Fig. (12) represents the corresponding reductions in curvilinear geometry.

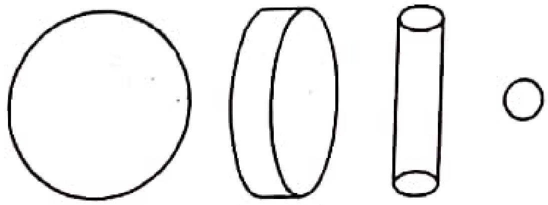


Fig. (12) Progressive generation of curvilinear nanostructure.

Example : Let us consider the case of a macroscopic system (big structure) of copper wire. In this case, free electrons move throughout the entire wire. Here, the wire dimensions are very large as compared to the distance between the atoms. Let us consider the movement of free electrons when the dimensions of copper wire change in one or more directions. When one or more dimensions of copper become so small that it approaches several times the spacing between the atoms in the lattice, then the situation becomes entirely different. Let us consider a copper plate of 5 cm long, 5 cm wide and only 3.6 nm thick. This thickness corresponds to the length of only 10 unit cells. This means that only 20% of the atoms are in unit cells at the surface of copper. Under this situation, the conduction electrons are confined in a narrow dimeniosn. Such a configuration is known as ***quantum well.*** In case of ***quantum wire,*** the coppr wire is long in dimension while a nanometer size in its diameter. So, electrons move freely along the wire but are confined in transverse direction. The ***quantum well*** may have a shape of tiny cube, a short cylinder or a sphere with low nanometer dimensions.

Preparation/synthesis of quantum dots

The following two main techniques are used for the preparation of quantum dots :

(1) *Bottom-up Technique*

(2) *Top-down technique*

(1) ***Bottom up Technique*** : This is a technique in which materials and devices are built up atom by atom, *i.e.*, a technique to collect, consolidate and fashion individual atoms and molecules into the structure. This is carried out by a sequence of chemical reactions controlled by series of catalysts. This process is used widely in biology. For example, catalysts called enzymes assemble amino acids to construct living tissues that forms and supports the organs of the body.

(2) ***Top-down technique*** : This is a technique in which materials and devices are synthesized or constructed by removing existing material from larger entities. Therefore, in this technique, a large scale object or pattern is gradually reduced in dimension or dimensions to nanoscale pattern. This can be accomplished by a technique called lithography. Lithography is an image that is produced by making a pattern on the stone, inking the stone and then pushing the inked stone onto the paper. The lithography used may be a nonoscale lithography or dip-pen lithography or a E-beam lithography. The lithography shines radiation through a tip to the surface coated with radiation-sensitive resist. The resist is then removed and the surface is chemically treated to produce the nanostructure.

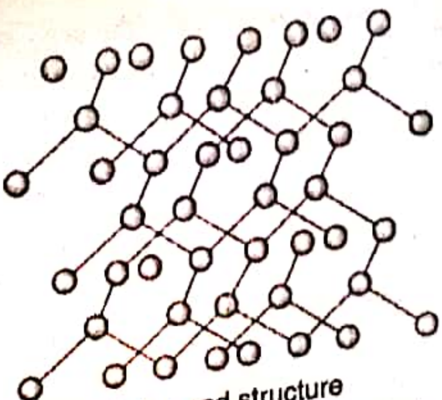
The semiconductors like PbS, GaAs, CdS, etc., can be synthesized in a nanometer level and they are called as semiconductor quantum dots. Their properties like band gap, luminescence, etc., always differ from their bulk counterpart.

13.7 CREATION AND USE OF BUCKYBALLS

Until 1985, there were only two known forms of pure carbon-graphite and diamond. Both these substances consist entirely of carbon atoms. However, they differ greatly in their structure and physical properties. First of all we shall discuss the structure of diamond and graphite.

Diamond.

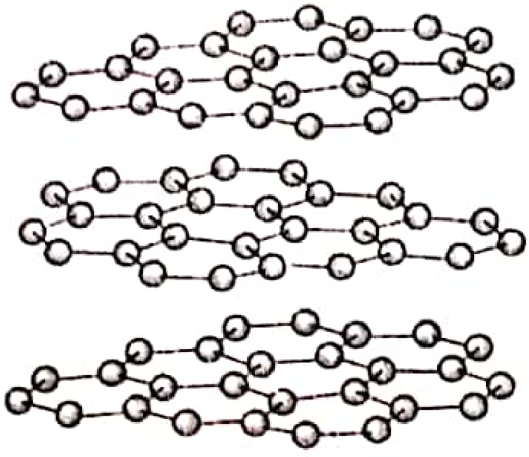
In diamond, all carbon atoms are stacked neatly in a three-dimensional array or lattice. Each carbon atom is bound to four other carbon atoms in a pattern of tetrahedrons. This structure makes diamond extremely hard. Fig. (13a) shows the structure of diamond.



Diamond structure

Structure of diamond

Graphite. In graphite, the carbon atoms form sheets of linked hexagons. Each carbon atom within a sheet forms strong bonds to three other carbon atoms. However, the sheets are held together by weak bonds due to van der Waal's forces. This means that the sheets can slide past each other. Therefore, graphite is soft and greasy. This is the reason that the pencil, which has graphite in its leads, leaves a trail of itself when dragged across the page. Fig. (13b) shows the structure of graphite. Fig. (13c) shows the structure of carbon atoms connected by covalent bonds in a sheet of graphite.



Graphite sheets

Fig. (13b) Structure of Graphite sheets

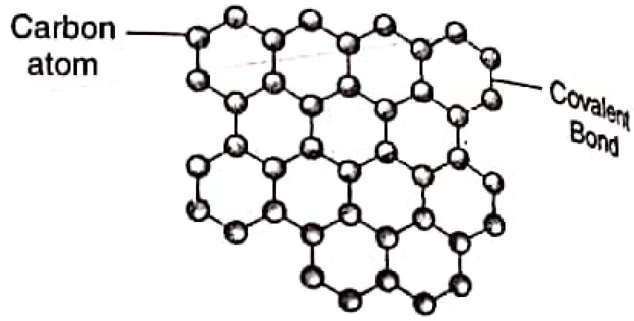


Fig. (13c) Structure of carbon atoms connected by covalent bonds in a sheet of graphite.

Buckyball.

In 1985, a third form of carbon was discovered. It is a hollow cluster of 60 carbon atoms shaped like a football. Just like the case of graphite, in which each carbon atom is bonded to three adjacent carbon atoms and arranged in a sphere about a nanometer in diameter. It was named *Buckminsterfullerene* or in short "*buckyball*" after the famous American architect R. Buckminster Fuller who had already designed domes in this structure. The shape of a buckyball is shown in fig. (14).

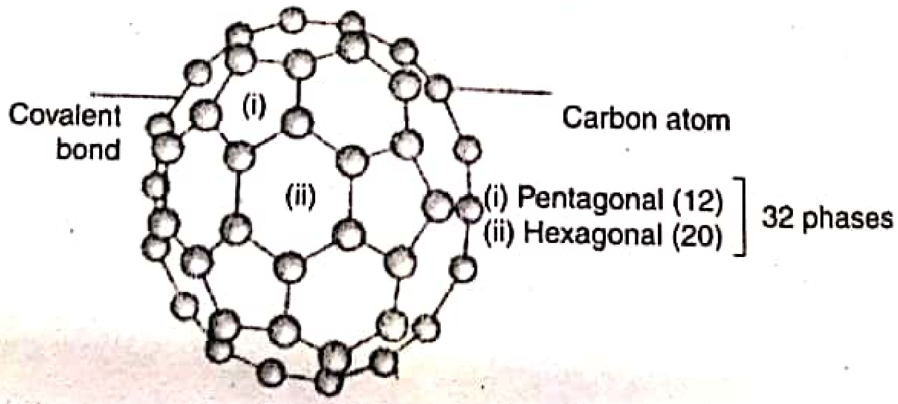


Fig. (14) Sixty carbon atoms in the shape of a sphere with 32 faces–a buckyball.

Buckyball is the roundest and most symmetrical large molecule known in the world. The buckyball has carbon atoms at 60 chemically equivalent vertices that are connected by 32 faces, 12 of which are pentagonal and 20 hexagonal. Today, a whole family of related molecules has been discovered and come under *fullerenes.* The C_{60} buckyballs is the most famous of the fullerene (closed spherical carbon structures) family.

The ball like molecules bind with each other in the solid state to form a crystal lattice having *face centred cubic structure.* In the lattice, each C_{60} molecule is separated from the nearest neighbour by 1 nm. The nucleus to nucleus diameter of a C_{60} molecule is about 0.7 nm. The molecules in the lattice are held together by weak forces called the van der Waals' forces. The C_{60} molecule has two bond lengths. The bond lengths between two hexagons (double bond) are shorter than bond lengths between hexagon and a pentagon.

Larger bulkyballs such as C_{70}, C_{76}, C_{80} and C_{84} have also been found. In addition to it, smaller bulk-balls C_{20}, C_{22} and C_{36} have also been identified.

In face centred cubic structure, 26% of volume of unit cell is empty. The alkali atoms are easily fitted into the empty spaces between molecular ball. When C_{60} crystals and potassium metal are placed in an evacuated tube and heated to 400°C, then potassium vapour diffuses into these empty spaces and a compound K_3C_{60} is formed. It is important to mention that C_{60} crystal is itself an insulator but when doped with alkali atom, it becomes electrically conducting. It is observed that K_3C_{60} shows the superconductivity with transition temperature 18 K. This lead to the discovery of new class of superconducting materials. CS_2 Rb C_{60} also shows superconductivity with transition temperature still high at 33 K.

Creatioin of Buckyballs

Buckyballs can be created by vaporizing carbon placed between two graphite rods which are placed in low pressure helium atmosphere in a reaction chamber. An arc welder supplies the power to arc electrodes. The helium atmosphere is used because helium is an unreactive gas and it is capable of transferring heat rapidly. When an electric arc is generated between the electrodes, a tremendous energy is created which is transferred to carbon. The carbon is evaporated to form root and buckballs. The buckballs are condensed on water cooled walls of chamber. The roots are then separated by using solvents such as benzene. Note that neither helium nor neon can bound with carbon.

Properties of Buckyballs

Various properties of buckyballs are :

(1) Buckyballs can be used in various applications because of their chemistry and unusual hollow, cage-like structure.

(2) Buckyballs are also extremely stable and can withstand very high temperatures and pressures.

(3) The carbon atoms of buckyballs can react with other atoms and molecules, leaving the stable, spherical structure still intact.

(4) New molecules can be created by adding other molecules to the outside of a buckyball and by trapping smaller molecules inside a buckyball.

Uses of Buckyballs

Most of the commercial applications of buckyballs are still under development stages. However, various applications where buckyballs can be used are :

(1) When a buckyball is doped by inserting the right amount of potassium or cesium into empty spaces within the crystal, it becomes a *superconductor*. It is the best organic superconductor known to us.

(2) The C_{60} molecule can absorb one hydrogen atom for each carbon atom. The buckyball structure is also not disrupted. This property suggests that buckyball can be a better storage medium for hydrogen fuel than metal hydrides.

(3) *Medical applications* : Buckyballs can deliver drugs directly to the infected regions of the body. Another potential use of buckyballs in medicine involves delivering elements for medical imaging. Buckyballs have the ability to act as antioxidants, counteracting free radicals in the human body.
(4) Anti-aging and anti-wrinkle creams are also being developed using buckyballs.
(5) Buckyballs are being used to develop stronger polymers.
(6) A buckyball-based light detector has already been developed by Siemens.
(7) Buckyballs are being used for production of diamonds and carbides as cutting tools or hardening agents.
(8) Option for silicon chip in computers.

13.8 CARBON NANOTUBES

Richard Smalley (1990) was the first to give the concept that if buckyballs get big enough, they can become carbon cylinders. Sumio Iijima discovered these carbon cylinders in 1991 and named them *nanotubes* [fig. (15)]. Their name is derived from

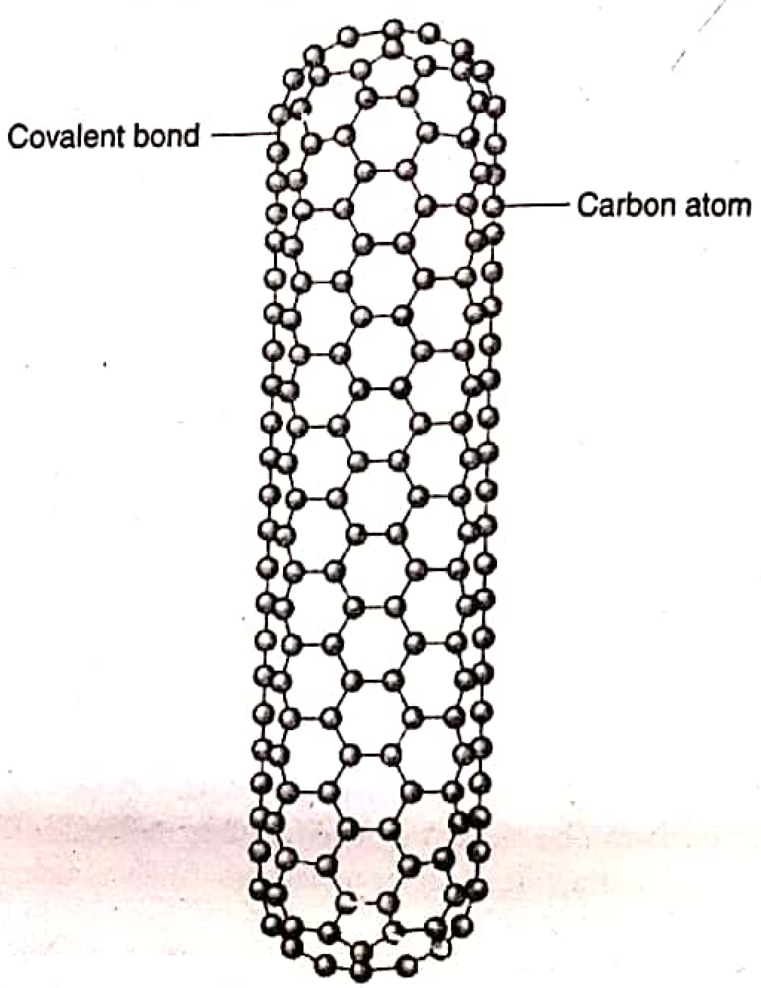


Fig. (15) Carbon nanotube.

their size. The diameter of a nanotube is in the order of few nanometer while they can be up to several millimeter in length. Carbon nanotubes are allotropes of carbon with a nanostructure that can have a length-to-diameter ratio greater than 1,000,000. Nanotubes are formed at the same time when buckyballs are formed. Nanotubes are members of the fullerene structural family which also includes the spherical buckyballs.

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.

Comparison with Buckyballs

Like buckyballs, carbon nanotubes are each a lattice of carbon atoms. Each atoms is covalently bonded to three other carbon atoms. Basically, carbon nanotubes are buckyballs. However, their end never closes into a sphere when they are formed. Instead of forming the shape of a sphere, the lattice forms the shape of a cylinder as shown in fig. (15).

Types of Nanotubes

Nanotubes can be of two types :

(1) Single-Walled Carbon Nanotube (SWNT)

(2) Multi-Walled Carbon Nanotube (MWNT)

(1) ***Single-walled carbon nanotubes***: A SWNT can be thought of a one-atom-thick layer of graphite (called graphene) wrapped into a seamless cylinder. They are an important variety of carbon nanotubes because they exhibit electric properties which are not shared by MWNT. In the near future SWNT will be used for miniaturizing electronics beyond the micro electromechanical scale.

(2) ***Multi-walled carbon nanotubes*** : A MWNT consists of multiple concentric nanotube cylinders, *i.e.*, they consist of multiple layers of graphite rolled in on themselves to form a tube shape.

These are shown in fig. (16)

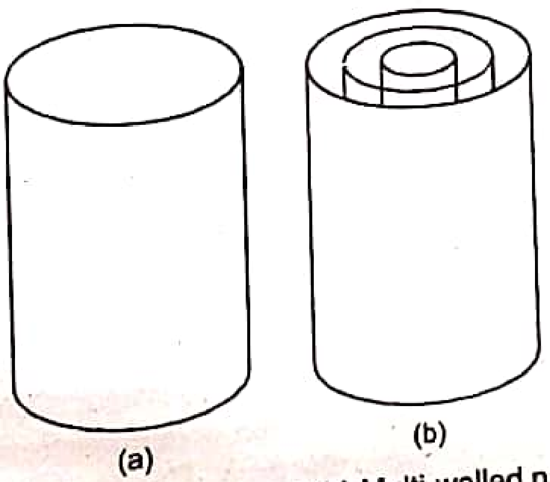


Fig. (16) (a) Single-walled and **(b)** Multi-walled nanotubes.

Production (Synthesis) of Nanotubes

Nanotubes can be produced by adding a few percentage points of vaporized nickel nanoparticles to the vaporized carbon. Carbon atoms dissolve in the metal nanoparticle. When the metal nanoparticle is filled to the brim with carbon atoms, carbon atoms start sweating onto the surface of the particle and bond together. This leads to the growth of a nanotube. Now a question arises as to why it takes the shape of a tube and not a sphere (buckyball). The reason is that when one end of the growing nanotube is anchored to the metal nanoparticle, it can not close into the sphere shape of a buckyball. This is also the reason why nanotubes have more carbon atoms (101) as compared to buckyball (60).

Commercially, nanotubes are being produced with a number of methods. Two of these methods are now discussed.

(1) *High-Pressure Carbon monoxide Deposition* (HiPCO) :

This method involves a heated chamber through which carbon monoxide gas and small clusters of iron atoms flow. When carbon monoxide molecules land on the iron clusters, the iron acts as a catalyst. This helps a carbon monoxide molecule to break up into a carbon atom and an oxygen atom. The carbon atom bonds with other carbon atoms and a nanotube lattice is formed. The oxygen atom combines with another carbon monoxide molecule to form carbon dioxide gas. The gas then floats off into the air.

(2) *Chemical-Vapour Deposition* (CVD)

In this method [Fig. (17)], a substrate is prepared with a layer of metal catalyst particles such as nickel, cobalt or iron. The substrate is heated to approximately 700°C in a chamber. To initiate the growth of nanotubes, two gases are blown into the chamber. One is a *process gas* such as ammonia, nitrogen or hydrogen. The other is a carbon-containing gas such as methane. We know that methane contains one carbon atom and four hydrogen atoms. The high temperature in the chamber breaks the bonds between the carbon atoms and the hydrogen atoms in the methane molecules. This results in carbon atoms with no hydrogen atoms attached. These carbon atoms attach to the catalyst particles where they bond to other carbon atoms. This results in the formation of a nanotube.

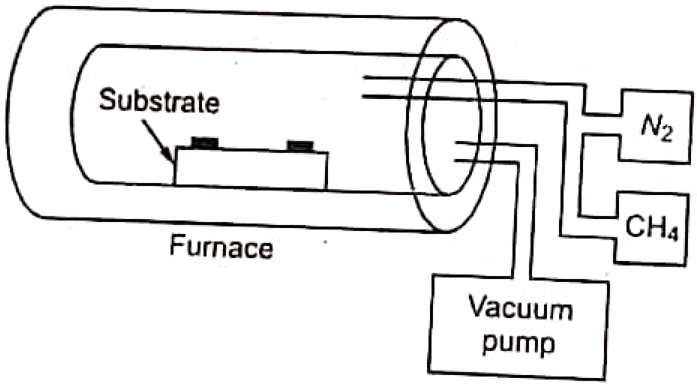


Fig. (17)

(3) *Laser Evaporation method*

The experimental arrangement of laser evaporation method is shown in fig. (18). It consists of a quartz tube containing an inert gas (argon gas). A graphite target is placed inside the tube. The graphite target contains a small amount of cobalt and nickel that act as catalytic nucleation sites for the

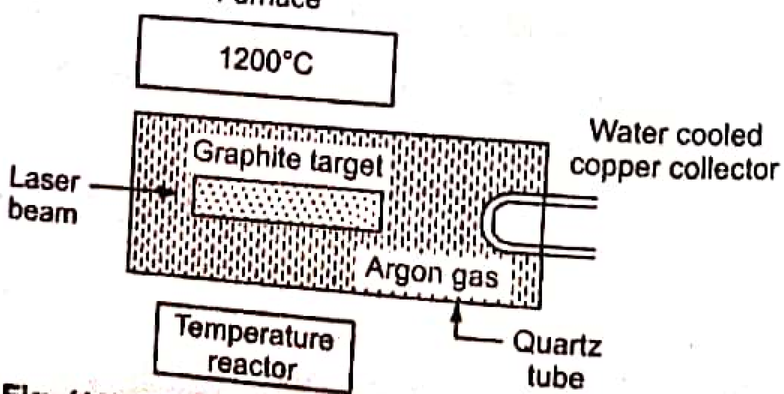


Fig. (18) Showing synthesis of carbon nanotubes by laser evaporation

formation of nano tubes. A part of the quartz tube outside the furnace consists of water cooled copper collector. This graphite is heated to 1200°C with the help of furnace. An intense pulsed laser beam is allowed to incident on the target. The laser beam evaporates the carbon atoms from the graphite. The argon gas sweeps the carbon atoms from high temperature side to colder copper collector. Now nanotubes are developed as the vaporized carbon condenses on the cooler surface of copper collector. This method produces single walled carbon nanotubes. This is an expansive method in comparison to other methods.

(4) ***Carbon arc method***

In this method, nanotubes are produced in the carbon soot of graphite electrodes during an arc discharge [fig. (19)]. A potential difference of 20-25 V is applied across graphite electrodes which are separated by 1 mm and have dimensions 5-20 μm diameter. Carbon atoms are ejected from the positive electrode due to high temperature generated during the discharge and form nanotube on the negative electrode. When a small amount of cobalt, nickel or iron is incorporated as a catalyst in the central region of cathode, a single walled nanotubes are produced. If no catalyst is used, then multiwalled tubes are produced.

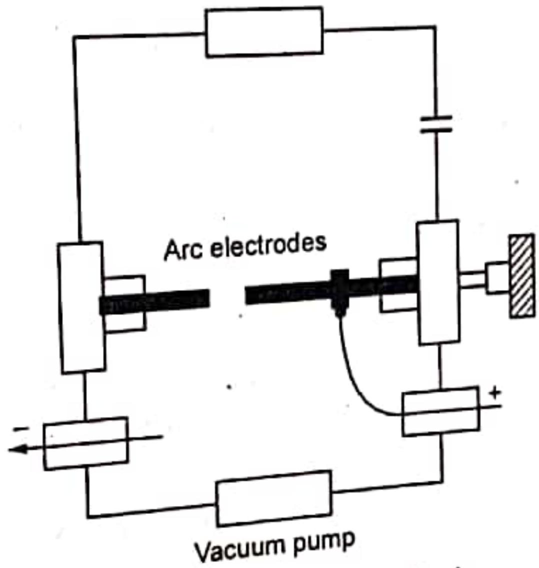


Fig. (19) Carbon arc method.

13.9 PROPERTIES OF NANOTUBES

(1) Carbon nanotubes are ***super-strong***. The tensile strength (amount of force which an object can withstand without tearing) of carbon nanotubes is approximately 100 times greater than that of steel of the same diameter. This is due to the fact that firstly, each carbon nanotube is one large molecule and secondly the strength provided by the interlocking carbon-to-carbon covalent bonds is very large.

(2) Nanotubes are ***very elastic***. We know that Young's modulus is a measure that how much force a material takes to bend it. The Young modulus of a nanotube is 5 times higher than for steel. This is due to the fact that nanotubes have a perfect structure and bond strength between carbon atoms is very strong.

(3) In addition to being strong and elastic, carbon nanotubes are ***light weight*** with a density about one quarter that of steel.

(4) The ***thermal conductivity*** of nanotubes is ***very high***. The thermal conductivity of a nanotube is more than 10 times of silver. The process of thermal conductivity in

nanotubes is different that of conductors. The conduction in conductors takes place due to movement of free electrons. On the other hand, the conduction in nanotubes takes place due to vibration of covalent bonds holding the carbon atoms together. Diamond also uses this method to conduct heat. Therefore, nanotubes are good conductor of heat.

(5) A carbon nanotube happens to be a ***nonpolar molecule*** (a molecule without a positive end and a negative end).

(6) The carbon nanotubes show ***negative magnetoresistance*** (a phenomenon of change in resistance of a material due to variation in d.c. magnetic field).

(7) Carbon nanotubes are metallic or semiconducting depending upon the diameter and how they are rolled. The synthesis of carbon nanotubes generally results in a mixture of tubes, two-thirds are semiconducting and one-third are metallic. The metallic nanotubes can have an electrical current density more than 1000 times greater than metals such as copper and silver.

In brief, the nanotubes have the following unique properties :
- High flexible, can be bent considerably without damage.
- Very elastic ~ 18% elongation to failure.
- Very high tensile strength.
- High thermal conductivity.
- High electrical conductivity.
- Low thermal expansion coefficient.
- High absorbent.
- Good field emission of electrons.

Explanation of Properties.

Now we explain the reasons why carbon nanotubes exhibit these properties in detail :

(1) Due to the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For a given (n, m) indice nanotube, if (n, m) is zero or a multiple of 3, then the nanotube is *metallic*. Otherwise, the nanotube is a *semiconductor*. Hence, all armchair nanotubes for which $n = m$ are metallic. However, only about a third of all zigzag and chiral nanotubes have electrical properties like metals and others (two-third) are like semiconductors. For example, nanotubes (5, 0), (6, 4), (9, 1) etc. are all semiconductors.

Carbon nanotubes conduct electricity better than metals. We know that flow of electrons is known as electric current. When electrons flow in a metal, they bump into metal atoms. Hence some resistance is offered to their movement. In case of carbon nanotubes, the flow of electrons is governed by rules of quantum mechanics. Hence, electrons behave like a wave travelling down a smooth channel with no atoms to bump into. This quantum movement of an electron within nanotubes is called *ballistic transport*.

(2) Carbon nanotubes are super-strong because of the covalent sp^2 bonds formed between the individual carbon atoms. Another reason for being super-strong is that each carbon nanotube is one large molecule.

(3) The reason for carbon nanotubes to be stiffest material on earth is that the bonds in the atomic lattice donot break when we bend or compress a nanotube.

(4) Thermal conductivity in nanotubes takes place just like as in case of diamond. Carbon nanotubes conduct heat by the vibration of the covalent bonds holding the carbon atoms together. The atoms are wiggling around themselves and transmit the heat through the material. The stiffness of the carbon bonds helps in transmitting this vibration throughout the nanotube.

(5) Nonpolar molecules are molecules without a positive end and a negative end. The electron clouds on the surface of each nanotube provide a mild attractive force between the nanotubes and is called van der Waal's force.

13.10 USES OF NANOTUBES

Due to the properties discussed in the previous article, nanotubes can be used in many applications as under :

(1) Due to its unusual current conduction mechanism, wires made from nanotubes can conduct huge amount of current with less power wastage. Note that wires made from nanotubes are different from *nanowires.*

(2) With nanotubes and nanowires, we can produce transistors and memory devices about a nanometer wide. This can be used to reduce the size of the devices and wires as the complexity of computer chips increases. Nanotube based transistors can operate at room temperature and are capable of digital switching using a single electron.

(3) Nanotubes can produce materials with toughness unmatched by natural and man-made materials. Due to its great mechanical properties, nanotubes can be used to produce from everyday items likes clothes, sports gear to combat/bulletproof jackets and space-suits.

(4) Nanoscale electric motors have also been developed using nanotubes.

(5) Chemical vapours are also being detected using nanotubes. Sensors using carbon nanotubes have shown to detect chemical vapours with concentrations in the parts per billion (ppb).

(6) Research is being done to store hydrogen in nanotubes. If successful, this would act as a fuel tank for hydrogen fuel cell-powered cars.

(7) In medical applications, the carbon nanotube can be used as a vessel for transporting drugs into the body. It is especially being used for treatment of cancer in destroying cancer cells.

13.11 APPLICATIONS OF NANOTECHNOLOGY

Many people believe that nanotechnology is a far-fetched idea with no near-term applications. However, till April 08, about 600 products have already been developed using nanotechnology. We have already discussed the uses of buckyballs and nanotubes in the previous articles. To make the discussion complete here, we now present the various applications of nanotechnology :

(1) ***Electronics*** : Electronics is currently the workhorse technology for computing and communications as well as a major components of consumer goods. The electronic devices with typical dimensions of nanometers in either of the three directions, display many unique properties. Single electron transistor (SET), spin values and magnetic tunnel junctions (MTJ) are

conceptually new devices which are based on nanotechnology. These devices are faster, compact and relatively cheaper. Spin valve devices are already being used in personal computers to increase the storage capacity of hard discs. The use of spin valves and magnetic tunnel junctions is growing as a new field called spintronic (spin based electronics or magnetoelectronics). Using nanostructures, it is possible to reduce the size of memory bits substantially more and thereby to increase the density of a magnetic memory, increase its efficiency, and lower its cost. Nanolithographic methods are already being used to prepare some strikingly powerful memories. Nanotechnology and nanoscience offer different memory possibilities. Other methods for very high density memories have been proposed in the general area of molecular electronics. A number of spin based devices like spin FET, spin LED, encorders, decorders for modern computers are being prepared. The quantum computers using nanotechnology will be more powerful than existing computers. The flat panel television or computers monitors are the products of nanotechnology.

(2) ***Optics*** **:** Electric light and fluorescent lights are in common use. Nanoscience has entered in the field of light emission by the use of light emitting diode (LED). In LEDs, oppositely charged electrical carriers (electrons and holes) recombines in an excited state. This excited state loses its energy by light emission. Most LEDs are based on semiconductors. The phenomenon of luminescence is also of substantial interest in a number of applications. For example, luminescent bar code structures are available.

Charles Lieber's group at Harvard has recently demonstrated that crossed wires, made of semiconductors with nanoscale dimension, can act light emitting structures. These cross-wire emitters are probably the smallest current light sources. They are intense and their colours can be chosen. Therefore, light emission, like photovoltaics, is one of the most immediately attractive applications of nanostructure.

Almost all communication involves the transfer of messages. Nanotechnolgoy and nanoscience have been active in producing effective fibre-optic structures. Fibre optics permit high speed, efficient, high density, high reliability passage of enormous densities of signal. A single fibre network can carry tens to thousands of data streams and voice conversations at once.

We have studied that in electronic circuits, the resistive heating causes dissipation of energy and wasted power. In addition, high frequency electronic devices such as computer networks and microprocessors face issues of mutual and self inductance. The circuits can act like antennae and signals can jump from wire to wire when frequencies are high and wire spacing is low. Optical computers and optical devices, because they do not move electronic charge, are nearly immune to above both problems. This is one of the signal advantages of optical circuitry.

(3) ***Diagnostics*** **: Nanotechnology is helping in medical diagnostics by providing faster, cheaper and portable diagnostic equipments.**

(4) ***Novel drugs*** **: Nanotechnology aids in delivery of just the right amount of medicine to the exact spots of the body that need it.**

(5) ***Energy*** **: Nanotechnology will provide new methods to effectively utilize our current energy resources. It will also present new alternative fuels. Solar cells will also become cost effective.**

(6) ***Water*** : Nanotechnology will provide efficient water purification techniques. Water from the oceans can also be converted into drinking water.

(7) ***Superior, light weight materials*** : The strength and light weight of nanomaterials make them suitable for use in tear resistant clothes, body armour (bullet-proof clothings), spouts materials, etc.

(8) ***Computers*** : Computers can be made more powerful and smaller using nanotechnology.

(9) ***Sensors*** : Sensors based on nanotechnology are more sensitive and hence more effective.

DEPARTMENT OF PHYSICS

CERTIFICATE COURSE ON NANO SCIENCE

2021-22 for (30 days)

Resource Person: Dr.D.Ravinder(Prof of Physics)

Number of students:25

S.No			NAME OF THE STUDENT	HALL TICKET NO.
1	108519468001	A.SUSHMITHA		
3	**108519468003**	A.BHARGAVI		
4	**108519468004**	A.SWATHI		
5	**108519468005**	A.ANUSHA		
6	**108519468006**	A.SRAVIKA		
7	**108519468007**	B.SOUMYA		
8	**108519468008**	B.UMARANI		
9	**108519468009**	B.RISHITHA		
10	**108519468010**	B.AMRUTHA		
11	**108519468011**	B.NIKHITHA		
12	**108519468012**	B.SANJANA		
13	108519468013	B.RAJANI		
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17	108519468017	C.ESHWARAMMA		
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19	108519468019	CH.SURYASRI		
20	108519468020	CH.KALYANI		

21	108519468021	CH.AKSHITHA		
22	108519468022	CH.KAVERI		
23	108519468023	CH.KALYANI		
24	108519468024	D.AKSHITHA		
25	108519468026	D.PRAVALLIKA		

SYLLABUS:

- Introduction of Nanoscience.
- Definition of Nanoscience.
- Importance of Nanoscience.
- Applications of Nanoscience&nanotechnology.
- Methods of synthesis of Nanomaterials
- Summary.

AIMS FOR THE STUDY OF NANOSCIENCE

- The aims of Nanoscience.
- To incorporate Practice of synthesis methods.
- Interpret the finding into the broader study of Nanoscience.
- Emphasizing on Methods of synthesis techniques
- The aim of the Nanoscience working in this is to focus on better integration of the data and interpretation with the wider professional community and dissemination of their research to the public.
- Similarly many of citizens of our country are involved in locating, exploring for the future.

OBJECTIVES OF NANOSCIENCE

- To explore on synthesis methods.
- To document and research traditional methos and navigational techniques.
- To disseminate the knowledge gained to scholars, researchers and students of similar disciplines, as well as to the general public.
- To understand applications in different fields

OUTCOMES OF NANOSCIENCE.

- Understanding of several of these disciplines and sub-disciplines.
- Acquire an understanding of the concept of Nanoscience
- Display a broad understanding of the historical development of human culture and apply this information with sensitivity and an appreciation for diversity in prehistoric, historic and modern cultures.
- Develop an awareness of intercultural influences and exchanges between different culture groups, and the mechanisms through which these operated in the past.
- Acquire knowledge of the geography of regions of interest and how this has affected the rise and development of human resources in these areas.
- Identify and distinguish the steps involved in carrying out quantitative and qualitative research using available library and internet resources, as well as primary materials, including literary, historical sources.

- Produce and express coherent, persuasive and innovative written studies with attention to academic integrity and respect for diverse, including contrary opinions and ideas.
- Demonstrate an understanding of the historical development of Nanoscience and the progress.
- Gain and understanding of the major theoretical perspectives and debates within Nanoscience how these have affected our view of the past, and how they may be applied to research in this field.
- Demonstrate knowledge of the Nanoscience: how to record, investigate, analyze and interpret in technology for sustainable development.