

15.8 Engineering Physics

called *gel*. Thus *sol-gels* are suspensions of colloids in liquids that keep their shape. Sol-gel formation occurs in different stages.

The sol-gel process can be characterized by a series of distinct steps.

Step 1: Formation of different stable solutions of the alkoxide or solvated metal precursor (the sol).

Step 2: Gelation resulting from the formation of an oxide- or alcohol- bridged network (the gel) by a polycondensation or polyesterification reaction. This results in a dramatic increase in the viscosity of the solution.

Step 3: Aging of the gel (Syneresis), during which the polycondensation reactions continue until the gel transforms into a solid mass. This is accompanied by contraction of the gel network and expulsion of solvent from gel pores.

Step 4: Drying of the gel, when water and other volatile liquids are removed from the gel network. If isolated by thermal evaporation, the resulting monolith is termed a xerogel. If the solvent (such as water) is extracted under supercritical or near super critical conditions, the product is an aerogel.

Step 5: Dehydration, during which surface- bound M-OH groups are removed. This is normally achieved by calcining the monolith at temperatures up to 800°C.

Step 6: Densification and decomposition of the gels at high temperatures ($T > 800^\circ\text{C}$). The pores of the gel network are collapsed, and remaining organic species are volatilized.

The typical steps that are involved in sol-gel processing are shown in Fig.7. By different process one can get either nano film coating or nano powder or dense ceramic with nanograins.

This method has the following advantages:

- i) The possibility of synthesizing nonmetallic inorganic materials like glasses, glass ceramics or ceramic materials at very low temperatures.
- ii) One can get monosized nanoparticles.

The disadvantages of this method are:

- i) Controlling the growth of the particles is difficult.
- ii) Stopping the newly formed particles from agglomeration is also difficult.

Nanoparticles prepared by sol-gel method are $\text{Si}(\text{OR})_3$ where R is alkyl groups of various types.

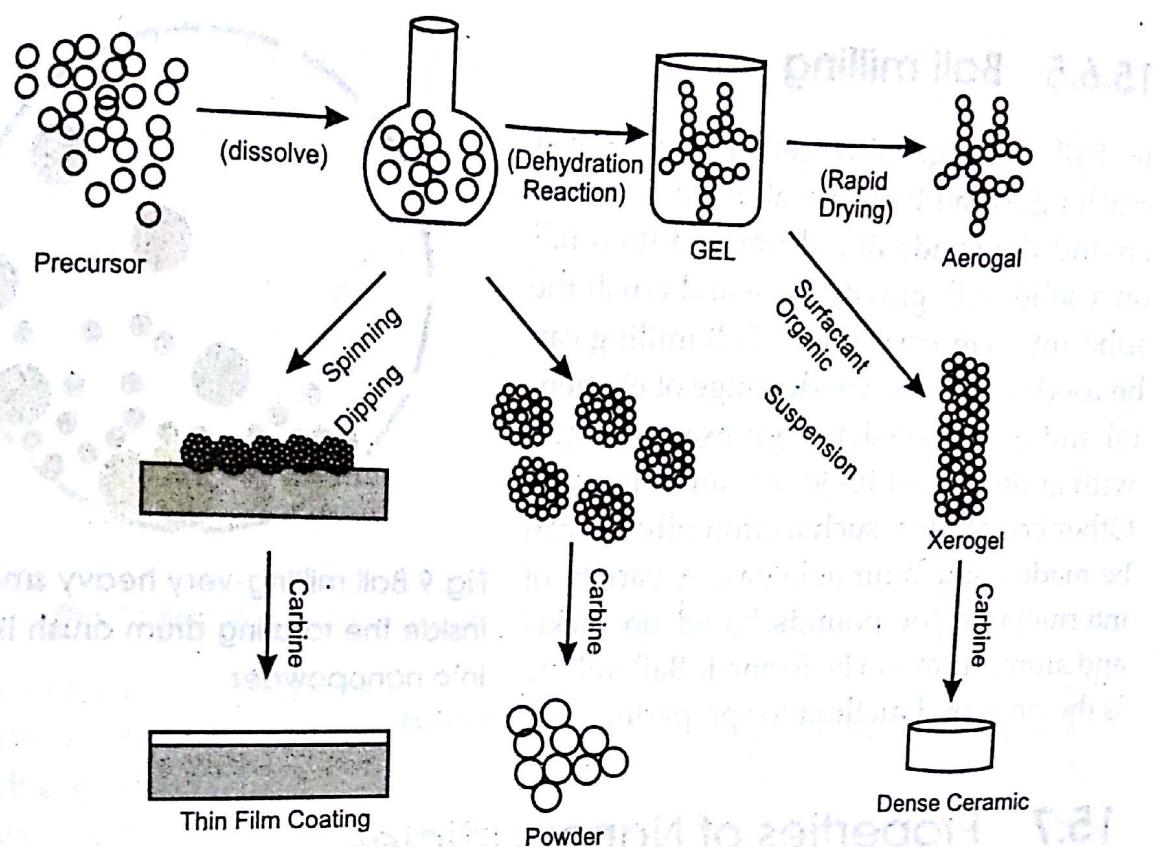
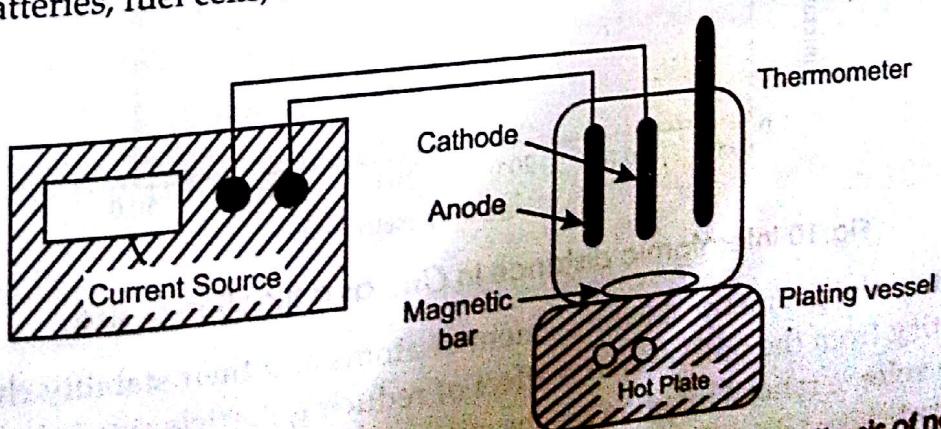


Fig. 7 Schematic representation of sol-gel process of synthesis of nanomaterials

15.6.4 Electrodeposition

Electrodeposition technique is used to electroplate a material. In many liquids called electrolytes (aqueous solutions of salts, acids etc.), when current is passed through two electrodes immersed inside the electrolyte, certain mass of the substance liberated at one electrode gets deposited on the surface of the other. By controlling the current and other parameters, it is possible to deposit even a single layer of atoms. Nanostructured films of copper, platinum, nickel, gold etc. can be produced by electrodeposition. The films thus obtained are mechanically robust, highly flat and uniform. Since these films have larger surface areas, they exhibit quite different and favorable electrical properties. They have very wide range of applications. These include batteries, fuel cells, solar cells, magnetic read heads, etc.



Schematic diagram of electrodeposition method of synthesis of nanostruc-

15.6.5 Ball milling

In ball milling, also called mechanical crushing, small balls are allowed to rotate around the inside of a drum and then fall on a solid with gravity force and crush the solid into nanocrystallites. Ball milling can be used to prepare a wide range of elemental and oxide powders. For example, iron with grain sizes of 10-30 nm can be formed. Other crystallites, such as iron nitriles, can be made using ammonia gas. A variety of intermetallic compounds based on nickel and aluminium can be formed. Ball milling is the preferred method for preparing metal oxides.

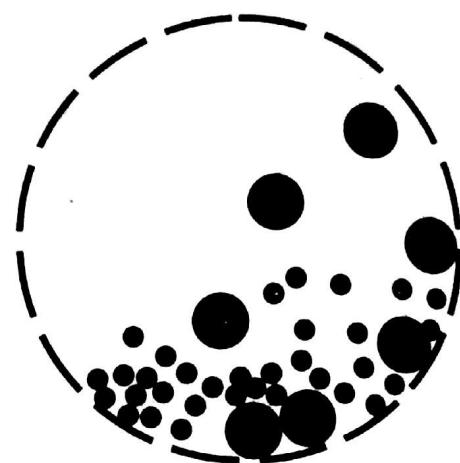


Fig. 9 Ball milling—very heavy small balls inside the rotating drum crush the solid into nanopowder

15.7 Properties of Nanoparticles

The physical, electronic, magnetic, and chemical properties of materials depend sensitively on size. Small particles display behaviours that are different from those of the individual atoms or bulk. Let us see few of them in brief.

15.7.1 Physical properties

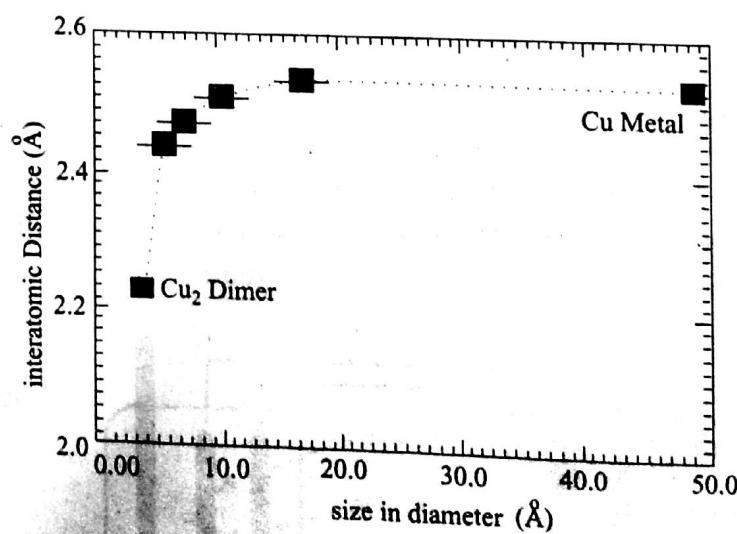


Fig. 10 Interatomic distance in Cu_n as a function of size

How does the geometrical arrangement of atoms and their stability change with size? Starting from the bulk, the first effect of reducing particle size is to increase of surface to volume ratio. This changes the surface pressure and results in a change in the interparticle spacing. This effect is shown in Fig. 10 for the case of Cu_n particles. The interatomic spacing increases with size.

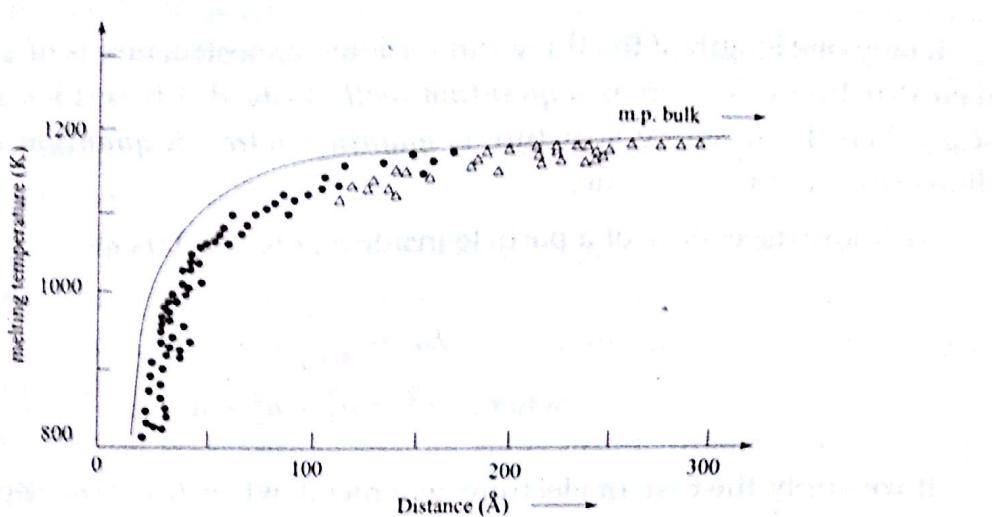


Fig.11 Melting point of small Au_n particles as a function of size

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 affects, for example, the thermodynamic properties of which the simplest example is the melting point. Fig.11 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.

15.7.2 Chemical properties

The large surface-to-volume ratio, the variations 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 only a few atoms.

Another important possible application is hydrogen storage in metals. Most metals do not absorb hydrogen, only few met also absorb on their 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 atoms 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*.

15.7.3 Electrical properties

In nanoscale, the electrical properties depend on the size. For example, the resistance of a material is due to the scattering of conduction electrons with vibrating atoms and impurities. The mean distance travelled between two successive collisions is called *mean free path* or *scattering length*. When the dimension of the solid becomes comparable to this quantity the scattering probability decreases and hence electrical properties change. When its size is in the order of mean free path or de-Broglie wavelength of electrons or holes which carry current, electronic structure of the system changes completely.

If only one length of the three-dimensional nanostructure is of a nanodimension, then structure is known as a *quantum well*. Instead if two sides are of nanometer scale, then the resulting structure is *quantum wire*. A *quantum dot* has all three dimensions in the nanoscale.

We know the energy of a particle inside a potential box as

$$E_n = \frac{n^2 h^2}{8mL^2}$$

$$\text{where } n^2 = n_1^2 + n_2^2 + n_3^2$$

If we apply the case of electrons in a metal, when $L = 1\text{cm}$, separation between consecutive energy levels can be shown to be of the order 10^{-14}eV . This we can

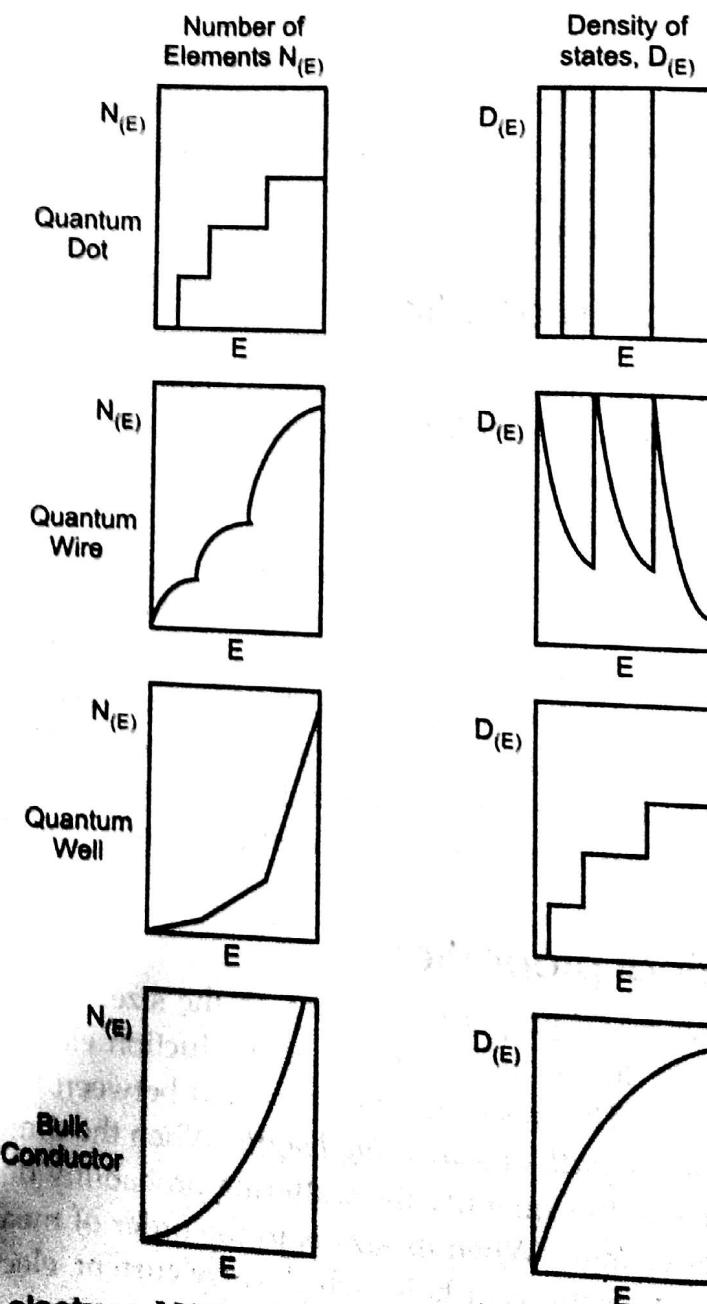


Fig. 12 Number of electrons $N(E)$ (left side) and density of states $D(E)$ (right side) plotted against the energy for four quantum structures

consider to be continuous or quasi-continuous. But when $L = 100\text{nm}$, separation between energy levels works out to be 10^{-4}eV . Thus we find that in nanoscale range, energy levels are discrete.

The density of states $D(E)$ of conduction electrons is strongly affected by the dimensionality of the material.

In Fig.12 number of electrons $N(E)$ and density of states $D(E)$ have been plotted against the energy for four different quantum structures. We find that due to quantum confinement the energy levels narrow down and become discrete when we move from bulk to dot.

The change in electrical properties cannot be generalized. In nanoceramics and magnetic nanocomposites the electrical conductivity increases with reduction in particle size whereas in metals electrical conductivity decreases.

15.7.4 Optical properties

Nanocrystalline systems have novel optical properties. Suppose we have a suspension of nanoparticles in a host. Depending on the particle's size, different colors are seen. Gold nanospheres of 100 nm appear orange in colour while 50 nm nanospheres appear green in colour. If semiconductor particles are made small enough, quantum effects come into play, which limit the energies at which electrons and holes can exist in the particles. As energy is related to wavelength (or colour), this means that the optical properties of the particle can be finely tuned depending on its size. Thus, particles can be made to emit or absorb specific wavelengths (colours) of light, merely by controlling their size. The linear and nonlinear optical properties of such materials can be finely tailored by controlling the crystal dimensions, and the chemistry of their surfaces.

15.7.5 Magnetic properties

The strength of a magnet is measured in terms of coercivity and saturation magnetization values. These values increase with a decrease in the grain size and an increase in the specific surface area (surface area per unit volume) of the grains. Therefore nano-materials present good properties in this field also.

Table 3 gives a brief summary of the observed magnetic behaviour of very small particles of various metals as well as their behaviour in bulk. In small particles a large fraction of the atoms reside at the surface. These atoms have lower coordination

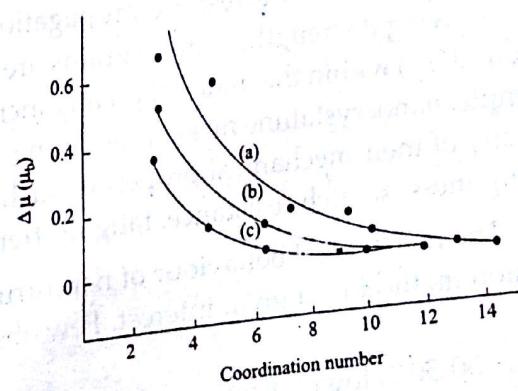


Fig.13 Deviation from the bulk magnetic moment in (a) Fe, (b) Co, and (c) Ni as a function of nearest neighbour coordination (in various structures)

numbers than the interior atoms. Investigation indicate that the local magnetic moment is primarily determined by the local coordination number. Fig.13 shows the calculated dependence of the magnetic moment on the nearest coordination number. It is clear that as the coordination number decreases, the moment increases towards the atomic value. i.e. ***small particles are more magnetic than the bulk material.*** The magnetic moment of Co_n particles of $\sim 2\text{ nm}$ exhibited 20 % higher value than that of the bulk.

Table 1 Magnetism in bulk and in nanoparticles

Metal	Bulk	Cluster
<i>Na, K</i>	Paramagnetic	Ferromagnetic
<i>Fe, Co, Ni</i>	Ferromagnetic	Superparamagnetic
<i>Gd, Tb</i>	Ferromagnetic	Rotors/Superparamagnetic
<i>Cr</i>	Antiferromagnetic	Frustrated paramagnetic
<i>Rh</i>	Paramagnetic	Ferromagnetic

Nanoparticles of ***even nonmagnetic solids are found to be magnetic.*** It has been found theoretically as well as experimentally that the magnetism is special to small sizes and disappears in clusters containing more than 80 atoms. At small sizes, the clusters become spontaneously magnetic.

In addition to free clusters, clusters of nonmagnetic elements supported on metal substrates have also been proposed to be magnetic. Ferromagnetic and antiferromagnetic multilayers have been found to exhibit ***giant magneto-resistance (GMR).***

15.7.6 Mechanical properties

Most metals are made up of small crystalline grains; the boundaries between the grain slow down or arrest the propagation of defects when the material is stressed, thus giving it strength. If these grains are nanoscale in size, the interface area (grain boundary) within the material greatly increases, which enhances its strength. For example, nanocrystalline nickel is as strong as hardened steel. Because of the nanosize, many of their mechanical properties such as hardness and elastic modulus, fracture toughness, scratch resistance, fatigue strength, and hardness are modified.

The mechanical behaviour of nanostructured materials prepared by gas condensation method is of great interest. Few observations are:

- i) 30-50 % lower elastic moduli than for conventional grain size materials.
- ii) 2-7 times higher hardness and strength for nano-crystalline pure metals ($\sim 10\text{ nm}$ grain size) than those of large grained ($> 1\mu\text{m}$) metal.
- iii) Decreasing hardness with decreasing grain size in the nanoscale grain size regime (i.e, when grain size is less than 10 nm).

In Table 2 the properties of nanomaterials are listed.

Table 2 Properties of nanomaterials

Properties	Examples
Catalytic	Better catalytic efficiency through higher surface-to-volume ratio
Electrical	Increased electrical conductivity in ceramics and magnetic nanocomposites, increased electric resistance in metals
Magnetic	Increased magnetic coercivity up to a critical grain size, superparamagnetic behaviour
Mechanical	Improved hardness and toughness of metals and alloys, ductility and superplasticity of ceramic
Optical	Spectral shift of optical absorption and fluorescence properties, increased quantum efficiency of semiconductor crystals
Biological	Increased permeability through biological barriers (membranes, blood-brain barrier, etc.), improved biocompatibility

15.8 Applications of Nanomaterials

Nanoparticles are "the small particles with a big future". Because of their extremely small particle size, they have extremely large specific surface area. Hence they are chemically very active. They are stronger and more ductile. They have electronic states quite different from those of bulk.

In *dispersed state* nanoparticles are used as fillers, paints, magnetic recording media, ferrofluids, drugs, phosphors, rocket propellant, fuel additives etc.

In *consolidate state* nanoparticles are used as catalysts, electrodes of solar cells and fuel cells, sensors, adsorbents, synthetic bone, self-cleaning glass etc.

In *ordered assembly form* nanoparticles are used as quantum electronic devices, photonic crystals, DNA chips, biosensors etc.

In *very dense phase* nanoparticles are used in synthesis of flexible/dense ceramics and insulators, harder metals etc.

In different areas nanoparticles are finding their applications.

i) Materials Technology

- *Cutting tools* made of nanocrystalline materials, such as tungsten carbide, tantalum carbide and titanium carbide, are **more wear and erosion-resistant**, and **last longer** than their conventional (large-grained) counterparts. They are finding applications in the drills used to bore holes in circuit boards.

- **Wear and scratch-resistant hard coatings** are significantly improved by nanoscale intermediate layers (or multilayers) between hard outer layer and the substrate material. The intermediate layers give good bonding and graded matching of elastic and thermal properties, thus improving adhesion.

- It is now possible to synthesis **harder metals** having hardness 5 times higher then normal metals using nanoparticles.
- Ceramics are hard, brittle and difficult to machine. However, with a reduction in grain size to the nanoscale, ceramic ductility can be increased. Zirconia, normally a hard, brittle ceramic, has even been rendered **superplastic** (for example, able to be deformed up to 300% of its original length).
- Nanocrystalline ceramics, such as silicon nitride and silicon carbide, have been used in such **automotive applications as high-strength springs, ball bearings and valve lifters**, because they can be easily formed and machined, as well as exhibiting excellent chemical and high-temperature properties. They are also used as components in high-temperature furnaces.
- A carbon nanoparticles act as fillers in a matrix; for example, they are used as a filler to **reinforce car tyres**.
- Clay particle based composites-containing plastics and nano-sized flakes of clay are also finding applications such as use in **car bumpers**.
- Nanocoating of highly activated titanium dioxide is highly hydrophobic (water repellent) and antibacterial. **Recently developed applications include the self-cleaning windows**. Coatings based on nanoparticulate oxides catalytically **destroy chemical agents**.
- Stronger, lighter, wear resistant, tougher and flame retardant polymers are synthesized with nanoparticles as **fillers**. They are used in replacement of body parts and metals.
- Magnets made of nanocrystalline yttrium-samarium-cobalt grains possess unusual magnetic properties due to their extremely large grain interface area. **High coercivity** can be obtained because magnetization flips cannot easily propagate past the grain boundaries. This could lead to applications in **motors**, analytical instruments like **magnetic resonance imaging (MRI)**.
- Useful as **magnetoresistance spin valves**.
- In general, nanoparticles have a high surface area, and hence provide **higher catalytic activity**.
- **Smart magnetic fluids are used as**

- viscous dampers,
- cooling fluids,
- magnetic separators etc.

- Nano-engineered membranes could potentially lead to more energy-efficient ***water purification processes***, notably in desalination by reverse osmosis.
- Nanoparticles react with pollutants in soil and groundwater and transform them into ***harmless compounds***. Iron nanoparticles transform chlorinated hydrocarbons (which are carcinogens) into less harmful end products in groundwater.
- Improved control of porosity at the nanoscale has important applications. A range of enhanced textiles, such as ***breathable, waterproof and stain resistant fabrics***, have been enabled by this technique in variety of polymers and inorganics.
- Other novel, and more long-term, applications for nanoparticles lie in paints that ***change colour in response to change in temperature or chemical environment***, or paints that have ***reduced infra-red absorptivity*** and so reduce heat loss.
- Nanosized titanium dioxide and zinc oxide are currently used in ***sunscreens***. They absorb and reflect ultraviolet (UV) rays and yet are transparent to visible light.
- It is possible to produce ***unusual colour paints*** using nanoparticles since nanoparticles exhibit entirely different optical properties.
- Nanosized iron oxide is present in some ***lipsticks*** as a pigment.
- Nanospheres of inorganic materials could be used as ***lubricants***, in essence by acting as nanosized 'ball bearings'.

ii) Information Technology

- Nanoscale-fabricated magnetic materials also have applications in ***data storage***. If the area required to record one piece of information can be shrunk in the nanoscale (and can be written and read reliably), the storage capacity of the disk can be improved dramatically.
- Coatings with thickness controlled at the nano- or atomic scale have been used in ***optoelectronic devices*** or in ***catalytically active*** and chemically functionalized surfaces.
- Nanocrystalline zinc selenide, zinc sulphide, cadmium sulphide and lead telluride synthesized by sol-gel techniques are candidates for the next generation of ***light-emitting phosphors***. They will have huge market for large area, high brightness, flat-panel displays (as used in television screens and computer monitors).

- Nanoparticles are used for *information storage*.
- *Quantum electronic devices* have started replacing bulky conventional devices.
- Nano dimensional *photonic crystals* are used in chemical/optical computers.

iii) Biomedicals

- Nanocrystalline zirconium oxide (zirconia) is hard, wear resistant, bio-corrosion resistant and bio-compatible. It therefore presents an attractive alternative *material for implants*. Other nanoceramics can also be made as strong, light aerogels by sol-gel techniques. Nanocrystalline silicon carbide is a candidate material for *artificial heart valves* primarily because of its low weight, high strength and inertness.
- Biosensitive nanoparticles are used for *tagging of DNA and DNA chips*.
- *Controlled drug delivery* is possible using nanotechnology. Diffusion of medicine through nanoporous polymer reservoir as per the requirement is very useful in controlling the disease.
- Nanostructured ceramics readily interact with bone cells and hence finds application as an *implant material*.

iv) Energy storage

- Addition of nanoparticulate ceria (cerium oxide) to diesel fuel *improves fuel economy* by reducing the degradation of fuel consumption over time.
- In fuel cells, the external surface properties and the pore structure affect performance. The hydrogen used as the immediate fuel in cells is generated from hydrocarbons by *catalytic reforming*. Nano-engineered membranes intensify catalytic processes and enable higher-efficiency, small-scale fuel cells. Nanocrystalline materials synthesized by sol-gel techniques are candidates for separator plates in batteries because of their foam-like (aerogel) structure, which can hold considerably more energy than conventional ones. Nickel-metal hydride batteries made of nanocrystalline nickel and metal hydrides require less frequent recharging and last longer.
- Since the hydrogen absorbing capacity increases with decrease of size of nanoparticles, nanoparticles of Ni, Pd and Pt are useful in *hydrogen storage devices*.
- Useful in *magnetic refrigeration*.
- Metal nanoparticles are very useful in *fabrication of ionic batteries*.

In fact, the ability to control properties by changing size, composition, or dimension shows that nanoscale materials will form the basis of a new class of atomically engineered materials with tailored properties.

15.9 Carbon Nanotubes (CNTs)

Carbon nanotubes were first observed by Sumio Iijima in 1991. So far we know only three forms of carbon, namely diamond, graphite, and amorphous carbon. Now we come to know that there is a whole family of other forms of carbon known as Carbon nanotubes, which are related to graphite. The molecular structure of graphite is one-atom-thick a planar network of interconnected hexagonal rings of carbon atoms. Such a graphite sheet is called *graphene*. When graphite sheets are rolled into a cylinder and their edges joined, they form carbon nanotubes. The way they are rolled is represented by a pair of indices (n, m) called the *chiral vector*. The integers n and m denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If $m = 0$, the nanotubes are called *zigzag*. If $n = m$, they are called *armchair*. Otherwise they are called *chiral*.

15.9.1 Types of CNTs

A nanotube may consist of one tube of graphite, a one-atom thick single-wall nanotubes (Fig.15(a)), or a number of concentric tubes called multiwalled nanotubes (Fig.15(b)). Both of these are typically a few nanometres in diameter. Their length may vary from several micrometres to centimetres.

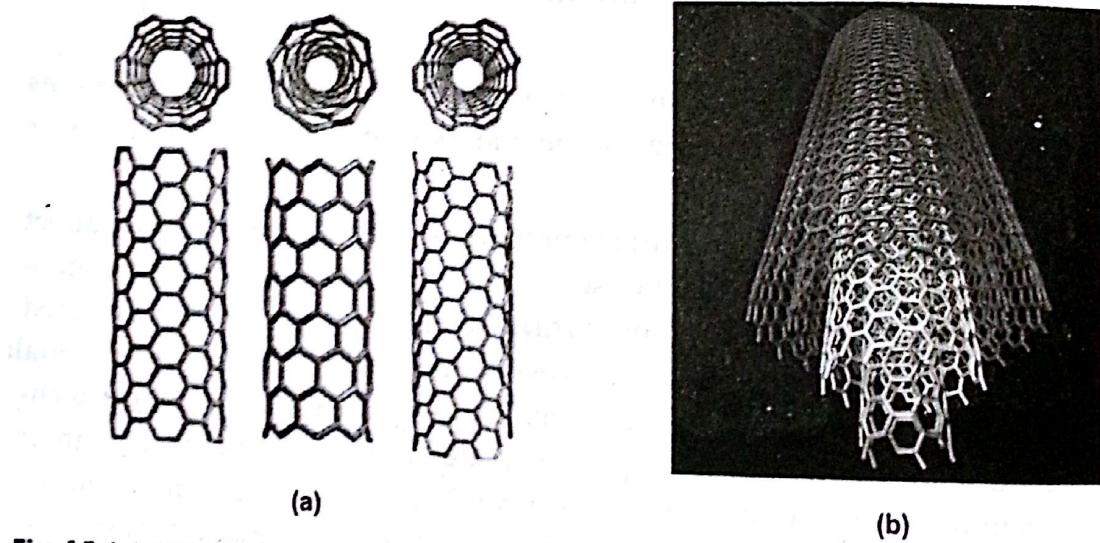


Fig. 15 (a) Different types of single walled nanotubes and (b) Multi walled nanotubes

Multi walled nanotubes can come in an even more complex array of forms. In *Russian Doll* model each concentric single-walled nanotube can have different structures, and hence there are a variety of sequential arrangements. The simplest sequence is when concentric layers are identical but differ in diameter. In *Parchment* model, a single sheet of graphite is rolled in around itself like rolling a newspaper. The structure of the nanotube influences its properties - including electrical and thermal conductivity, density, and lattice structure. Both type and diameter are important. The wider the diameter of the nanotube, the more it behaves like graphite. The narrower the diameter of the nanotube, the more its intrinsic properties depends upon its specific type.

Carbon nanotubes have assumed an important role because of their novel chemical and physical properties. They are

- mechanically very strong (their Young's modulus is over 1 terapascal, making CNTs as stiff as diamond),
- flexible (about their axis), and can conduct electricity extremely well.

The helicity of the graphite sheet determines whether the CNT is a semiconductor or metallic. All of these remarkable properties give CNTs a range of potential applications: for example, in reinforced composites, sensors, nanoelectronics and display devices.

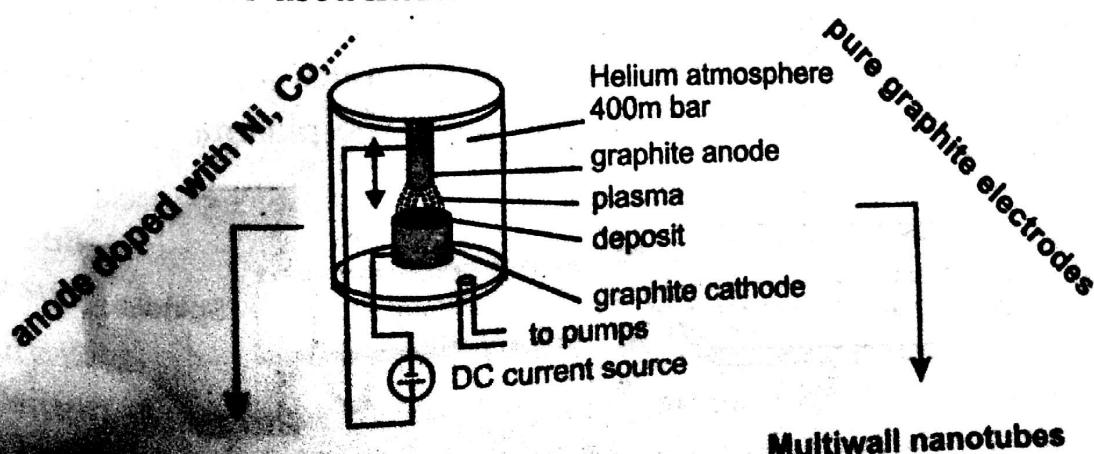
CNTs come in a variety of diameters, lengths, and functional group content. They are available for industrial applications in bulk (metric ton). Several CNT manufacturers have > 100 ton per year production capacity for multi walled nanotubes.

15.10 Fabrication of CNTs

Depending on the exact technique, it is possible to selectively grow SWNTs or MWNTs. Three distinct methods of synthesis with the arc discharge apparatus are presented here.

15.10.1 Arc method in inert gas atmosphere

This method creates nanotubes through arc-vaporisation of two carbon rods placed end to end, separated by approximately 1mm, in an enclosure that is usually filled with inert gas (helium, argon) at low pressure (between 50 and 700 mbar). When the anode is doped with Ni or Co single walled nanotubes are produced. Instead if pure graphite electrodes are used multiwalled nanotubes are obtained.



3. Used for the study of surface engineering.
4. Used in industry to study the structure of paints and characterize them.
5. To study the structure of metals.
6. Very useful in surface engineering of metals.

Limitations

1. Cannot be used for study of living organisms since they decompose in vacuum.
2. Takes more time for each study since very high vacuum has to be achieved.

Comparison between optical microscope and electron microscope

	Optical microscope	Electron microscope
Source	optical light	electron gun
Lenses	optical lenses	electromagnetic lenses
for focusing		
Magnification	1000 X	1,000,000 X
Resolution	100nm	0.1nm
Environment	atmosphere	high vacuum

15.14.3 Scanning Electron Microscope (SEM)

The image in *Scanning Electron Microscopy (SEM)* is produced by scanning the sample with a focussed electron beam and detecting the secondary and / or back scattered electrons. Electrons and photons are emitted at each beam location and subsequently detected. When transmitted electrons are utilized for imaging, it results in *Transmission Electron Microscopy (TEM)*.

A schematic representation of a SEM is shown in Fig.24. Each component/part is labelled and their functions are briefed below. Since electrons are used instead of photons, all the lenses are electrostatic / 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 aperture to eliminate the high-angle electrons from the beam.

3. The second condenser lens forms the electrons into 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. Dwell time is usually in microsecond 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 display a pixel on a CRT. The intensity of display is determined by the interaction number. More interactions give a brighter pixel.
8. This process is repeated until the grid scan is finished and then repeated. The entire pattern can be scanned 30 times per second.

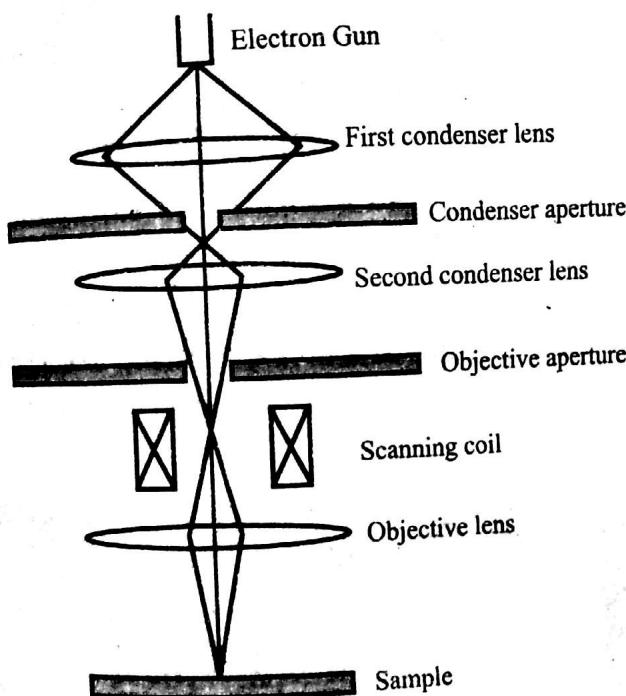


Fig.24 Scanning electron microscope

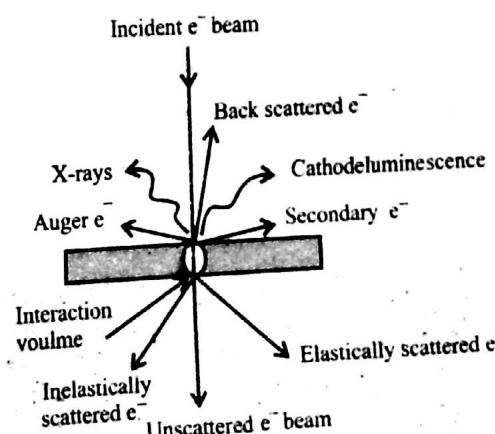


Fig.25 Specimen Interactions

Specimen Interaction

Specimen interaction results in salient features of an electron microscope. When the energetic electrons strike the sample, various interactions occur. The interactions occurring on the top side of the thick or bulk sample result in *Scanning Electron Microscopy (SEM)* while the interactions occurring on the bottom side of the thin sample result in *Transmission Electron Microscope (TEM)*.

Bulk specimen interactions 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° . The intensity of backscattered electrons 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:

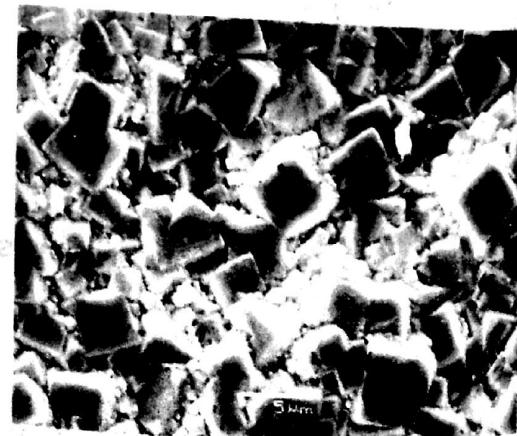
When an incident electron passes very near an atom in the specimen, it may impart some of its energy to the lower energy electron (usually in the K-shell) resulting in ionization of the electron in the specimen atom. This ionized electron leaves the atom with a very small kinetic energy (~ 5 eV) and 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 nm) can leave the sample. Any change in the **topography** of the sample changes the yield of the secondary electrons. Hence image formed collecting secondary electrons gives the topography of the sample.

Augar 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.



(a)



(b)

Fig. 26 Scanning Electron microscopic picture of Chemical Vapour Deposited a) microcrystalline diamond and b) a mixture of microcrystalline diamond and nanocrystalline diamond (magnification 8000x)

These electrons are collected and sorted 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

SEM gives useful information on:

1. Topography:

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

2. Morphology:

The shape, size and arrangement of particles making up the object that are lying on the surface of the sample or have been exposed by grinding or chemical etching, detectable features limited to a few nanometers.

3. Composition:

The elements and compounds the sample is composed of and their relative ratios, in areas ~ 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 semi-conductor applications are

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

15.14.4 Transmission Electron Microscope (TEM)

A schematic representation of a TEM is shown in Fig.27. Each component/part is labelled 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 condense 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 an 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 represents thicker or denser sample areas since these areas transmit lesser electrons. The brighter areas of the image represents thinner or lesser dense sample areas since these areas transmit more electrons.

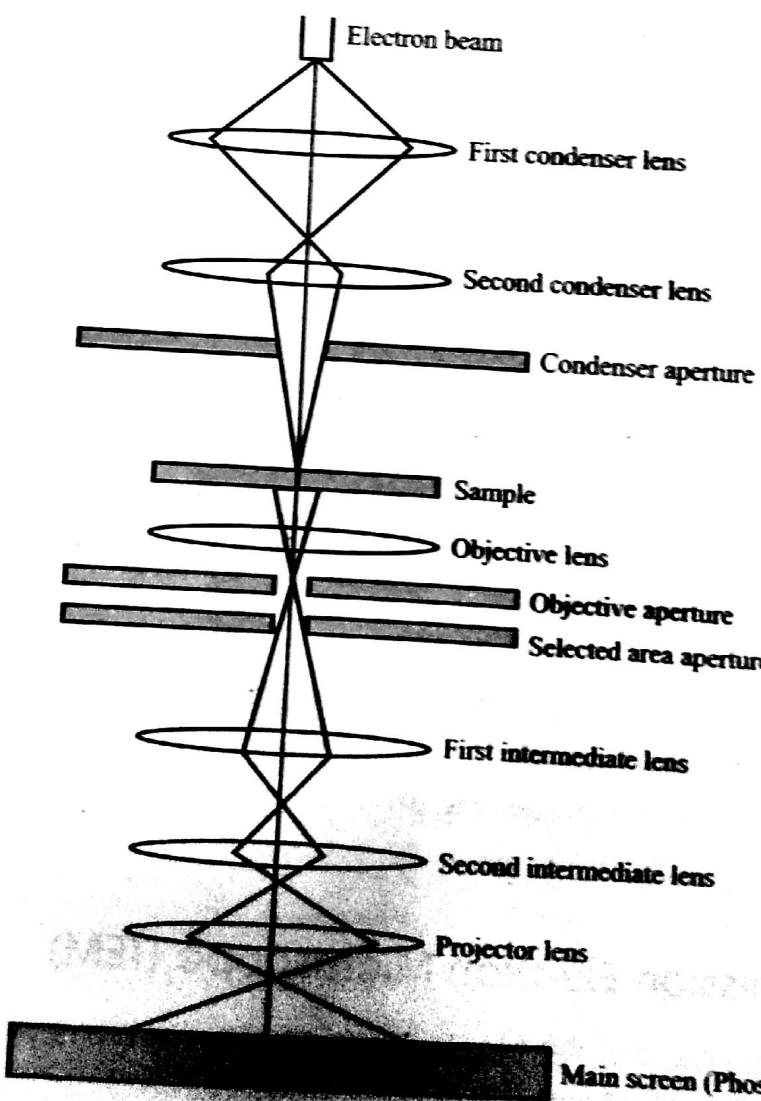


Fig. 27 Transmission electron microscope

Thin specimen interactions 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 electrons at different angles, one can get information about the orientation, atomic arrangement and phases present.

Inelastically scattered electrons:

These are electrons that interact with specimen atoms in an inelastic manner, losing energy. Then they are transmitted through the remaining portions 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.

TEM Analysis

A TEM image of the silver nano particles studied using XRD in section 15.14.1 is shown in the Fig.28. The A_g nano particles are spherical in shape with a smooth surface morphology. The diameter of the nano particles is found to be approximately 15 nm. TEM image also shows that the produced nano particles are more or less uniform in size and shape.

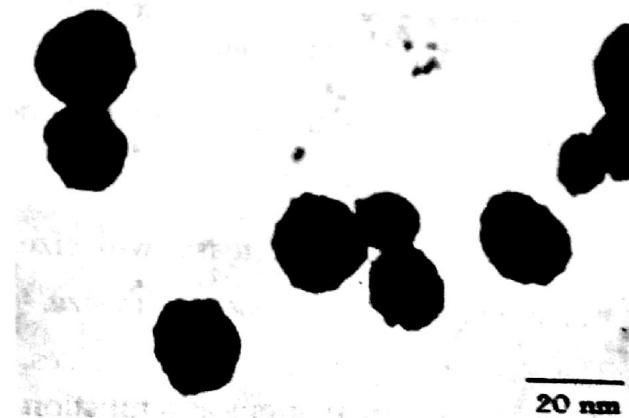


Fig. 28 TEM image of Ag nano particles

Applications

TEM gives the following useful informations:

1. Morphology:

Shape and arrangement of particles as well as their relationship to one another on the scale of atomic diameters.

3.8 Atomic Force Microscope (AFM)

The tunneling microscope has been modified and instead of keeping the needle tip at a distance from the sample, the needle is pushed right against the surface. The force present in the tip is kept constant and the tip is scanned across the surfaces like a phonograph needle running in the groove of a record. A record of the tips vertical motion is made by reflecting a laser beam from a mirror fixed to the top of needle and is using an interferometer to accurately measure the distance traveled by laser beam and hence the position of the tip as shown in figure 3.12.

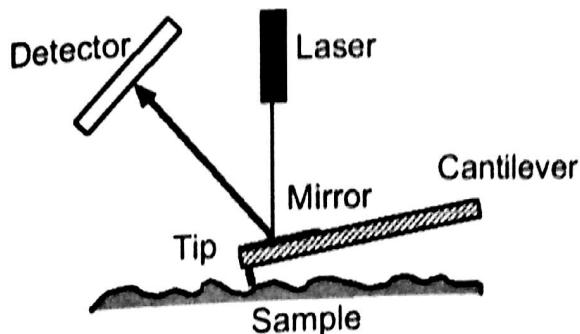


Figure 3.12 Basic components of Atomic Force Microscope.

This record can be converted and displayed as an image of surface. Since the atomic force microscope does not depend on current, it can be used to visualize the surfaces of conductors as well as non conducting materials. However, viewing biological samples such as cells or proteins is still a problem, as the tip tends to distort them. The basic structure of the cantilever tip over the sample i.e. conventional AFM is shown in figure 3.13.

The fundamental difference between STM and the AFM is that the former monitors the electrical tunneling current between the surface and the probe tip while the latter monitors the force exerted between the surface and the probe tip. The AFM can operate in close contact mode in which the core to core repulsive forces with surface dominate or in a greater separation non contact mode in which the relevant force is the gradient of the Vander walls potential. A typical AFM image of Cu nanowire of diameter 8 nm is shown in figure 3.14. As in the STM, a piezoelectric scanner is used. The vertical motions of the tip during the scanning may be monitored by the interference pattern of light beam from an optical fiber by the reflection of the laser beam. The AFM is sensitive to the vertical

component of the surface forces. A related but more versatile device called a friction force microscope simultaneously measures both normal and lateral forces of the surface of tip. Other microscopes have been built which are based roughly on the same principle of a tip scanning the surface. In each different type of microscopes a different force is measured. Thus we have friction force microscopes, magnetic force microscopes, electrostatic force microscopes and scanning thermal microscopes. The last may be described as the world's smallest thermometer. A thermocouple attached to the needle tip measures the temperature at each position. Since heat is essentially motion at infrared wavelengths, it may soon be possible to measure the infrared spectrum of a single molecule.

