UNIT - V

Nanotechnology

Nano science and technology is the study of the behaviour of objects at a very small scale, roughly 1 to 100 nanometers (nm). one nano meter is one billionth of a meter or the length of 10 hydrogen atoms lined up. Macroscopic scales ~~deal with~~ which mainly deals with the classical physics whereas mesoscopic and microscopic deal with quantum physics. The Nanoscopic scale is that which deal with the nano science and technology.

Name of the scale	Range of the scale:
Macroscopic	1m → 10 mm.
mesoscopic	10 mm to 10 μm.
Microscopic	100 μm to 100 nm.
Nanoscopic	100nm to 100 pm.

Nanoscale science deals with the study of phenomena at a very small scale of the range 10^{-7} m to 10^{-9} m where properties of matter differ significantly from those at ~~a~~ larger scales.

Nanoscale:- Nano science is the study and development of materials and structures in the range of 1nm to 100 nm.

and the unique properties that arise at that scale. at nano scale, we are manipulating objects. ~~that are more than~~

→ A typical atom is any where from 0.1 to 0.5 nm in diameter.

→ DNA molecules are about 2.5nm wide.

→ A bacterium is about 1000 nm.

→ Human cells, such as red blood cells, are about 10,000 nm across.

→ Human hair wide is about 80,000nm.

→ What are Nano materials :-

Nanomaterials could be defined as those materials which structured components with size less than 100 nm at least in one dimension.

→ materials that are nanoscale in one dimension are layers, such as thin films or surface coatings.

→ Materials that are nanoscale in two dimensions include nanowires and nanotubes.

→ Materials that are ~~nanoscale~~ nanoscale in three dimensions are particles, ~~too~~

Ex:- precipitates, colloids and quantum dots

Factors Influencing the properties of Nano Materials:-

In the materials at nano size the properties appear different from bulk. To understand this, we have to focus on four main factors mentioned below that are influencing the properties nano scale objects.

(1) ~~first~~, due to the small mass of the particles, gravitional forces are negligible. In its place electromagnetic forces are dominant in determining the behavior of atoms and molecules.
(Quantum confinement effect).

(3) (2) At nano scale sizes, we need to use quantum mechanical discriptions of particles motion and energy transfer in the place of the classical mechanical descriptions.

(2) (3) Nano sizeed particles have a very large surface to volume ratio i.e $\frac{S}{V}$ is high.

(4) At this nano size, the influences of random molecular motion play a much more greater role than they do at the macro scale.

I). ~~Domo~~ Dominance of Electromagnetic forces :-

There are four basic forces are in the Nature.

(1) Gravitational force.
(2) Electromagnetic "
(3) Strong nuclear "
(4) weak nuclear "

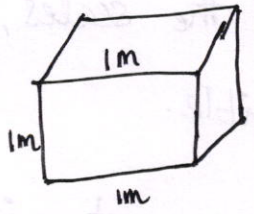
The Gravitational force $= G\frac{m_1 M_2}{s^2}$, is the attraction force between the two objects. The mass of Nano scale objects is so ~~mass~~ small, the force of gravity has very little effect on the attraction between objects of this size.

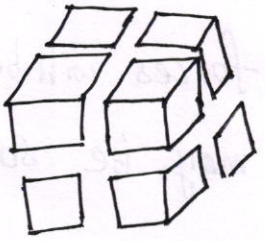
Electromagnetic forces $F = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{s^2}$ are forces of attraction and repulsion between objects based on their charge and magnetic properties. ~~Since~~ Since the electromagnetic forces are not affected by mass, they can be very strong even with nano sized particles.

$$\therefore \frac{S}{V} = \frac{3}{r}$$

Thus when the radius of the sphere decreases, its surface area to volume ratio increases.

Ex:-





Surface Area $= 6 \times 1\,m^2 = 6\,m^2$

Volume $= 1 \times 1 \times 1 = 1$

Surface area $6 \times \left(\frac{1}{2}\right)^2 \times 8 = 12\,m^2$

Volume $= \left(\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}\right) 8 = 1\,m^3$.

fig ①: (cubic volume element) ~~fig 2~~

For one cubic volume shown in fig ①; the surface area is $6\,m^2$. when it is divided into eight pieces its surface area becomes $12\,m^2$. When the same volume devided into 27 pieces its surface area becomes $18\,m^2$. Thus we find that when the given volume is divided into smaller pieces, the surface area increases. Hence as particle size ~~dere~~ decreases, a greater portion of atoms are found ~~to~~ at the surface ~~the surface~~ compared to those inside.

The magnetic and electrostatic forces are very important forces that determine the behaviour of substances chemically and physically at the nanoparticle level.

The other two forces, the strong and weak forces are negligible in the nano-scale range. It should be noted that those four forces will be present in all the scales, but their magnitude may be some times negligible.

Since electromagnetic force is most influential at nano scale, nano particles donot behave like macro sized objects.

(2) Increase in surface area to volume ratio:-

Nanomaterials have a relatively larges surface area when compared to the larges form of the material of same volume.

Let us Consider a sphere of radius 'r'

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

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

$$\frac{\text{Surface area}}{\text{Volume}} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3}$$

We have studied the problems of particles in a potential well as well as in a potential box. When the dimensions of such wells or boxes are of the orders of de Broglie wavelength of electrons or mean free path of electrons, the energy levels of electrons change. This effect is called Quantum Confinement.

When the material is in sufficiently small size typically 10 nm. or less, ~~origin~~ organization of energy levels into which electrons can climb or fall change. specially, ~~The approaches critical~~ the phenomenon result ~~quantum measurement, called the exciton Bohr~~ from electrons and holes being squeezed into a dimension that approaches a critical quantum measurement, called the "exciton Bohr radius". These can effect the optical, electrical and magnetic behaviour of material, particularly as the structure or particle size approaches the smaller end of the nanoscale.

(4) Random Molecular Motion :- Random molecular motion is the ~~movent~~ movement that all molecules in a substance exhibit due to ~~their~~ their kinetic energy. This motion increases at higher temperatures. This motion can involve molecules moving around in space, rotating around their bonds and vibrating along their bonds. While Random kinetic motion is always present, at the macro

For example, a particle of size 30 nm has 5% of its atoms on its surface, at 10 nm 20% of its atoms, and at 3 nm 50% of its atoms. Thus nanoparticles have a much greater surface area per given volume compared with larger particles. It makes materials more chemically reactive. As growth and ~~chemical~~ catalytic chemical reactions occur at surfaces, this means that a given mass of material in nanoparticle form will be much more reactive than the same mass of material made up of larger particles. In some cases materials that are inert in their larger form are reactive when produced in their nanoscale form.

(3) Quantum Confinement effect:-

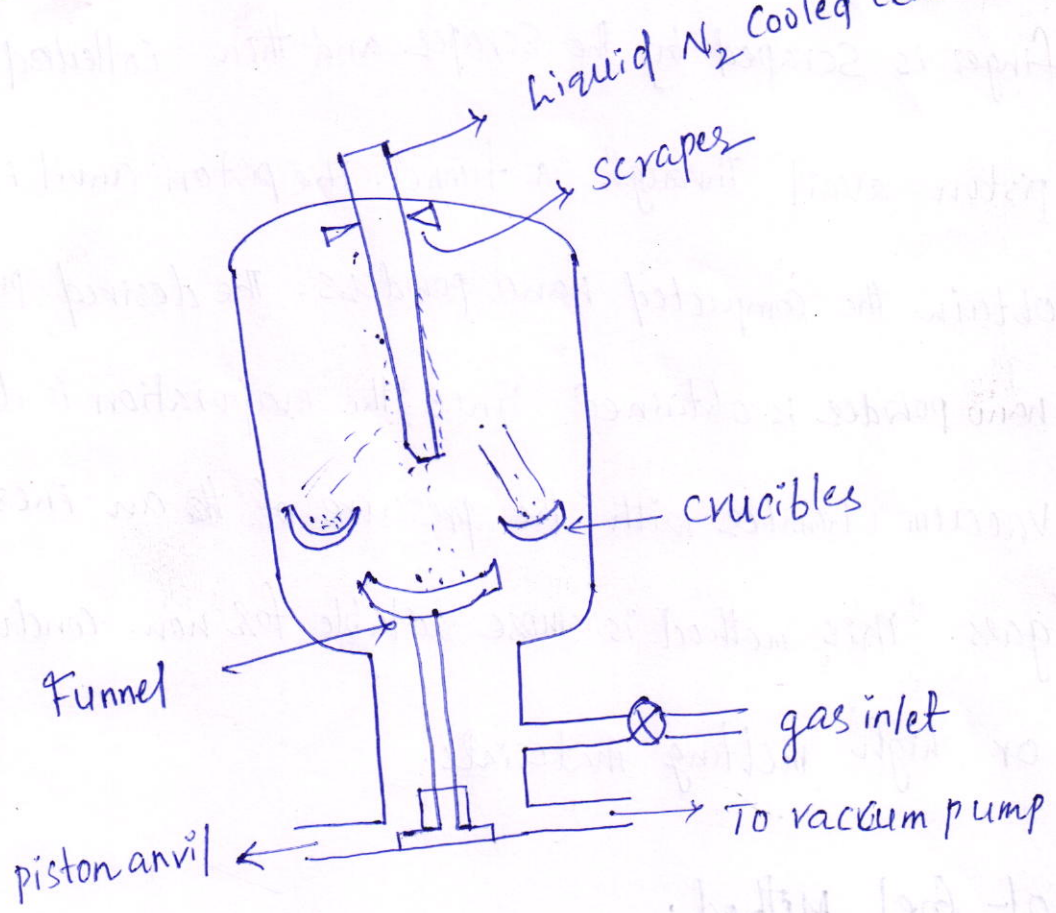
When atoms are isolated the energy levels are discrete. When very large number of atoms are closely packed to form a solid, the energy levels split and form bands. ~~Nano~~ Nanomaterials represent intermediate stage.

scale this motion is very small compared to the sizes of the objects and thus is not very influential in how object behave. At nano scale however, these motions can be on the same scale as the size of the particle and thus have an important influence on how particles behave.

✿ Physical Vapour Deposition:-

The material of Interest are evaporated and hence, the atoms or molecules are in gas phase. The gas phase atoms or molecules are used to obtain the nanostructured material by evaporation method.

Evaporation:-



fig①: physical Vapour deposition - Evaporation.

The schematic representation of the experimental set-up used for the sythesis of nano materials by evaporation is shown in fig①: It consists of a bell jar, in which

an inert gas or reactive gas is filled after vaccum. The material to be evaporated are placed in the crucibles and are heated either by resistance or an electron gun until sufficient vapour develops. The evaporated atoms or molecules are allowed to condense on a cold fingers which is cooled ~~extreme~~ externally by liquid N_2. The nano particles on the cold finger is scraped by the scraper and then collected to the piston avail through a funnel. The piston anvil is used to obtain the compacted nano powders. The desired purity of the nano powder is obtained since the evaporation is done at the vaccum chamber with the pressure of an inert or reactive gass. This method is more suitable for non-conductive materials or high melting materials.

Sol-Gel Method:

The sol-gel process is a wet-chemical technique. i.e chemical solution deposition technique used for the production of high purity and homogeneous nanomaterials, particulary metal oxide nanoparticles.

Characterization of XRD:-

When new materials are synthesized one should know about its elements, composition, crystal structure, crystal symmetry and its grain size etc. one of the most useful characterization technique is X-ray diffraction (XRD) studies,

different XRD techniques:-

① Laue diffraction method:

It is very much useful for study of crystal symmetry.

② powder diffraction method:

It has large numbers of applications.

③ Rotating crystal method: used to align the crystals and measure lattice parameters and crystal structure.

Applications:

① ~~Study of d-spacing~~:

The glancing angle vs Intensity of diffracted beam can give different Information.

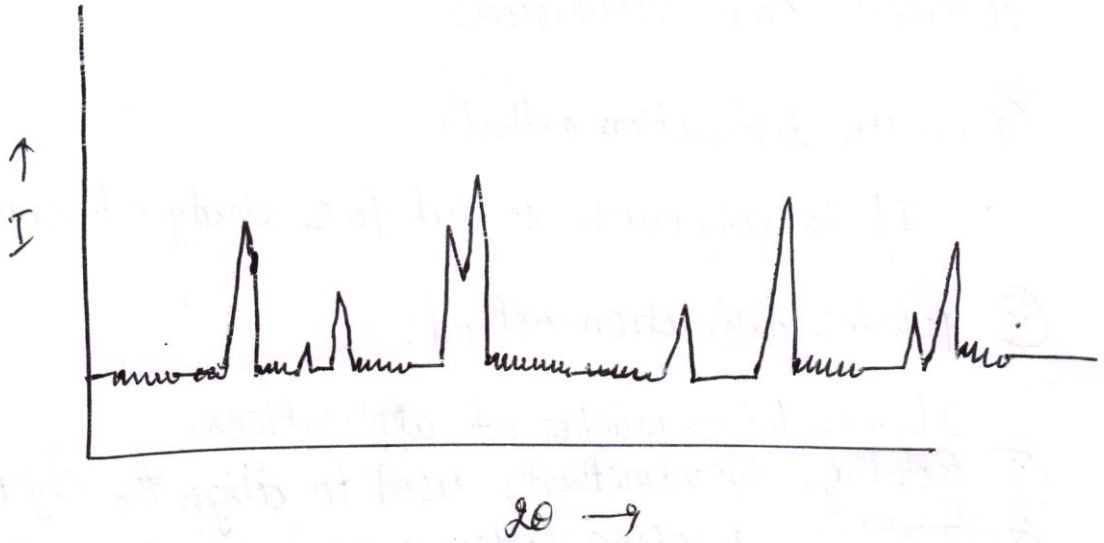
① study of d-Spacing:

② study of mixtures:

By measuring the relative intensities of non-overlapping lines the relative concentration of each component can be obtained

③ Study of Alloys:

If the alloy is used for study, for uniform composition a typical powder diffraction pattern is produced. If one of the components precipitates, separate lines corresponding to that component is observed.



~~④ Study of alloys:-~~

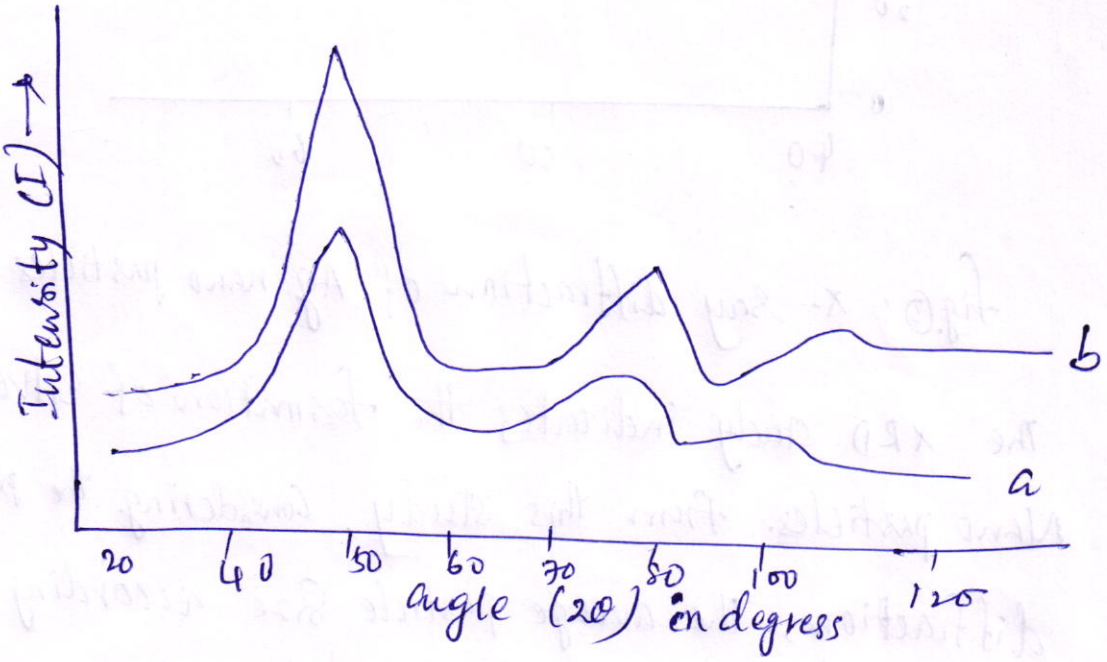
~~If an alloy is used for the study,~~

④ Stress determination in metals:-

If there is a stress in metal, it changes the d-spacing. This results in change of angle of diffraction core. By measuring this change, accurate measurements of stress is possible.

(5) Determination of particle size:-

When the size of the crystallite ~~dcrease~~ decreases, the angular spread of X-ray diffraction increases. Hence width of the observed diffraction pattern also increases. By measuring the full width at half maximum [FWHM], the mean particle size of the Sample can be measured.



fig(2): (a) XRD patterns of nano crystals Corresponding to grain size

(a) about 1-5 nm. and
(b) about 2-20 nm.

from above fig: we find that with decrease of crystal size, the width of diffraction pattern increases.

Scherres formula for Estimation of particle size.

For estimation of particle size, X-Ray diffraction (XRD) is used.

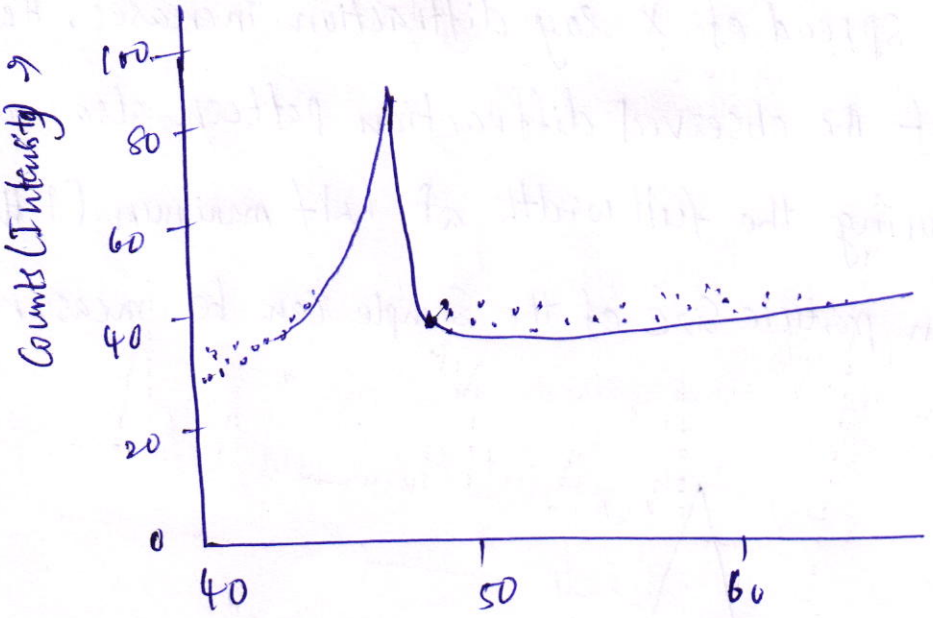


fig ③: x-ray diffraction of Ag nano particles.

The XRD study indicates the formation of Silver (Ag) Nano particles. From this study, considering the peak of diffraction, The average particle size according to Debye-scherres formula.

$$D = \frac{0.9\lambda}{W\cos\theta}$$

where λ → wavelength of x-rays.

W → is FWHM

θ → diffraction angle.

D → particle size.

The average particle size of Ag is 14nm.

PHYSICAL VAPOUR DEPOSITION:

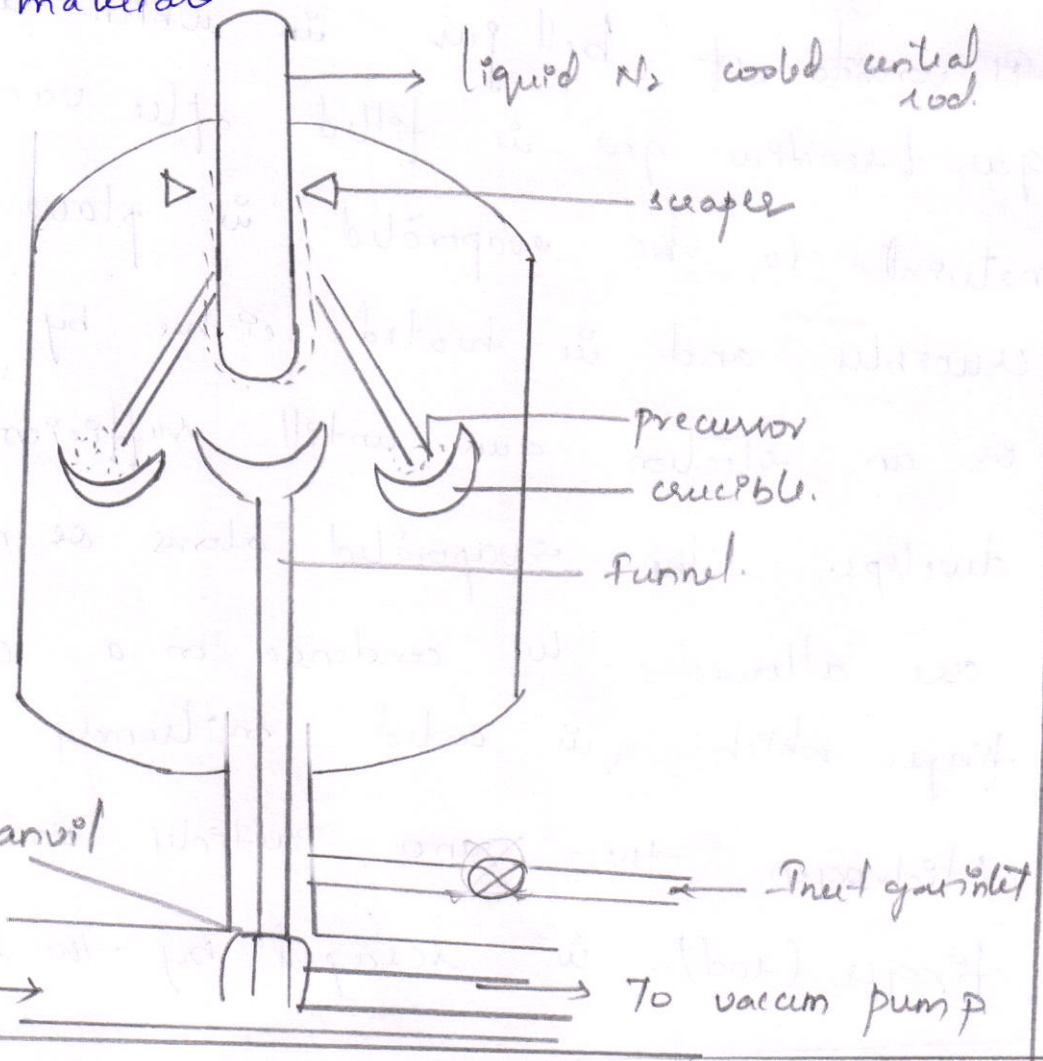
The material of interest are evaporated and hence are used to obtain in the gas phase. The gas phase atoms / molecules are used to obtain the nanostructured materials by evaporation method and sputtering technique.

By - i) - Evaporation method:

The schematic representation of the experimental set up used for synthesis of nano materials by evaporation shown in fig. It consists of bell jar in which an inert gas / reactive gas is filled after vaccum. The material to be evaporated is placed in the crucible and is heated either by resistance or an electron gun untill sufficient vapour develops. The evaporated atoms or molecules are allowed to condense on a cooled finger which is cooled externely by liquid Nitrogen the nano particles on the cooled finger (rod) is scraped by the scrapper

and collected to the piston anvil through a funnel. The piston anvil is used to obtain the compacted nano powder. the desired purity of the Nano powder is obtained since the evaporation is done at the vacuum chamber with pressure of an inert gas. this method is more suitable for Nano conductive materials or highly melting materials.

PHYSICAL VAPOUR DEPOSITION TECHNIQUE



SPUTTERING:

In case of compound materials the material will disassociate before evaporation and hence, the proportion of the constituents stiochiometry not maintained in the final products. ∴ It is advisable to use the sputtering technique for the deposition of stiochimetic products.

An inert gas like argon is incident on the target material the atoms or molecules in the ionised form hit the target material and knock out the surface material. The knocked out atoms are deposited on the second solid surface is known as substrate. The removal of atoms from the first solid stab i.e, target is known as erosion.

GLOW DISCHARGE:

The cross sectional view of the experimental set up used for glow discharge i.e, dc sputtering is shown in fig ②. The target is held at the cathode while the substrate is held at anode after attaining a suitable pressure in the chamber the argon gas is passed into the chamber at pressure of α (0.1) Torr.

When a suitable current flows over the electrode. The observed current is due to the presence of the ions and electrons that exist in gas and secondary electrodes which leave the target after bombardment. As the voltage increase the above contribution also increase. However at certain high voltage plasma region is obtained. The plasma region consists of mixture of particles like electrons, ions, neutrons and protons.

Characteristics of XRD:

When new materials are synthesized one should know about its elements, composition, crystal structure and symmetry etc. One of the most useful characterization technique is X-ray diffraction technique.

Different X-ray techniques:

1. Laue diffraction method: It is very much useful for study of crystal symmetry & orientation. In this method we can use only single crystal.

2. Powder diffraction method:

It has large no. of applications.

3. Rotating crystal method:

It is used to align crystal and measure lattice parameter and crystal structure.

The glancing angle vs Intensity of diffra
-cted beam can give different information

1. Study of 'd' spacing:

* The relative intensities of strongest lines are measured and compare with the pattern of known compounds using powder diffraction pattern.

2. Study of mixtures:

* If a mixture is used for the study, measuring the relative intensities of non-overlapping lines the relative concentration of each component can be obtained.

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 fig (1)
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 rigid 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.

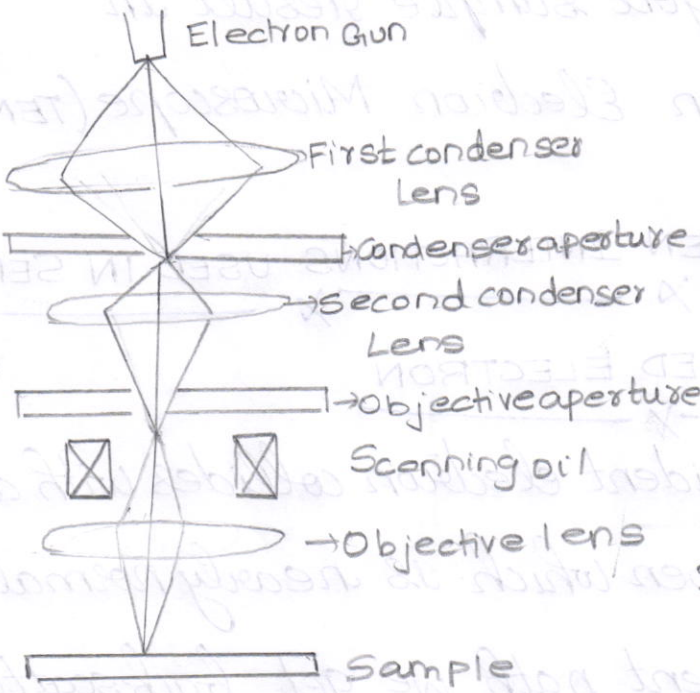


Fig (1) Scanning Electron Microscope

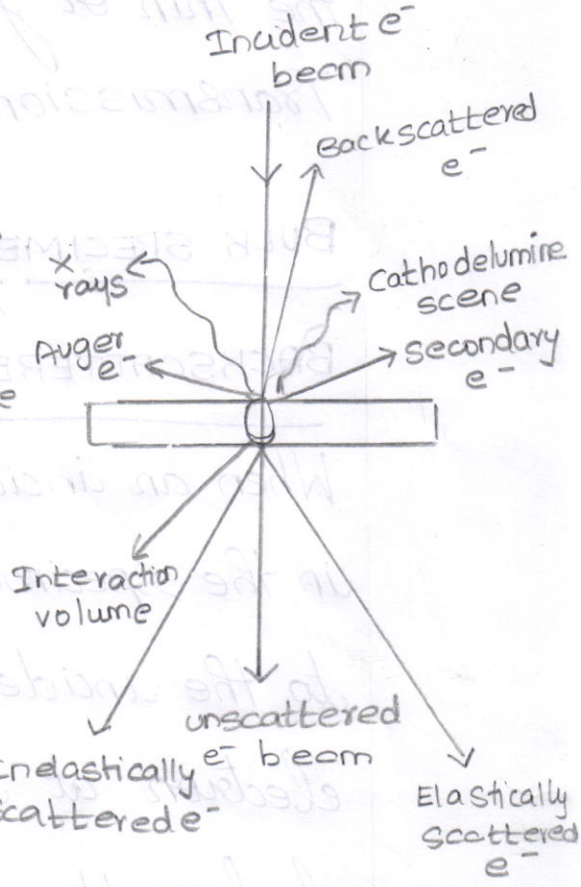


Fig (2) Specimen Interaction

SPECIMEN INTERACTION

Specimen interaction results in salient features of an electron microscope. When the energetic electrons strike the sample, various interactions occur (Fig 2). The interactions occurring on the top side of the thick or bulk sample results in Scanning Electron Microscope (SEM) while the interactions occurring on the bottom side of the thin or foil sample result in Transmission Electron Microscope (TEM)

BULK SPECIMEN INTERACTIONS USED IN SEM

BACKSCATTERED ELECTRON

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

(5)

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

When an incident electron passes very near 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 (~5eV) and is called secondary electrons. ~~Since the emitted secondary~~ electrons Each incident electrons can produce several secondary electrons. Since the emitted secondary electrons have low energy, only the secondaries that are very near the surface

(<100nm) 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 Augar electrons They have a characteristic energy, unique to each element from which they are emitted 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 ~ 1micrometer 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 application are

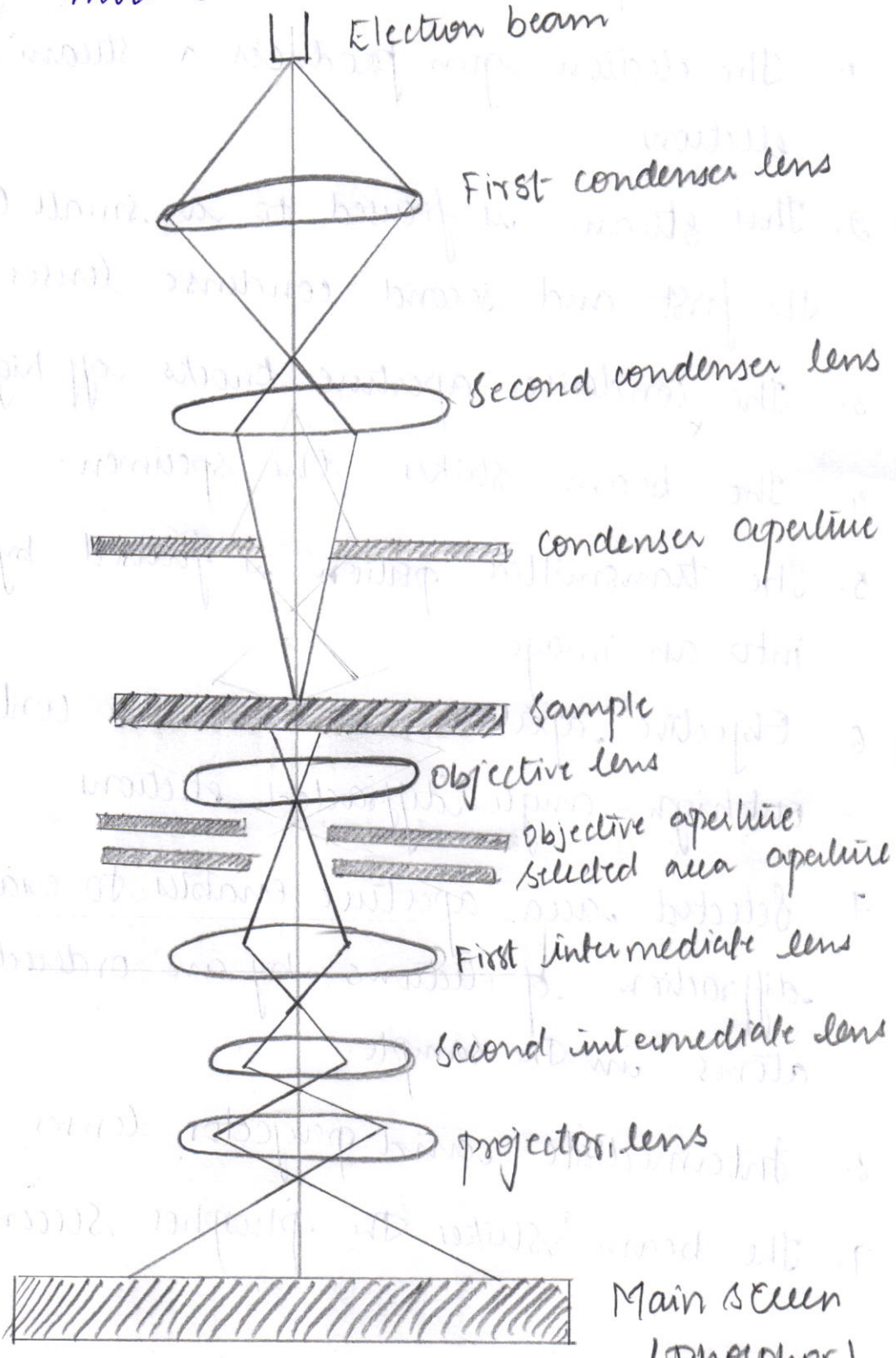
1) to view the surface of the device
2) to failure analysis
3) cross-sectional analysis to determine the device dimensions such as MOSFET channel length or junction depth
4) on-line inspection of wafer processing production
5) inspection of integrated-circuits etc.

TRANSMISSION ELECTRON MICROSCOPE (TEM):

A schematic representation of a TEM is shown in fig 19. Each component/part is labelled and their functions are briefed below.

1. The election gun produces a stream of monochromatic elections.
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 elections.
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 elections.
7. Selected area aperture enables to examine the periodic diffraction of elections 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.



THIN SPECIMEN INTERACTIONS USED IN TEM:

Unscattered electrons:

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

Elastically scattered Electrons:

These are electron 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 electron follow Braggs 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, loosing 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 particle studied using XRD in section 9.8. The Ag nano particles are spherical in shape with a smooth surface morphology the diameter of the nanoparticles 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.

APPLICATIONS:

TEM gives the following useful informations:

1. MORPHOLOGY:

The size, shape and arrangment of particles as well as their relationship to one another on the scale of atomic diameters.

2. CRYSTALLOGRAPHIC INFORMATION:

The arrangment of atoms in the specimen and their degree of order, detection of atomic-scale defects a few nanometers in diameter.

3. COMPOSITIONAL INFORMATION:

The elements and compounds the sample is composed and their relative ratios.