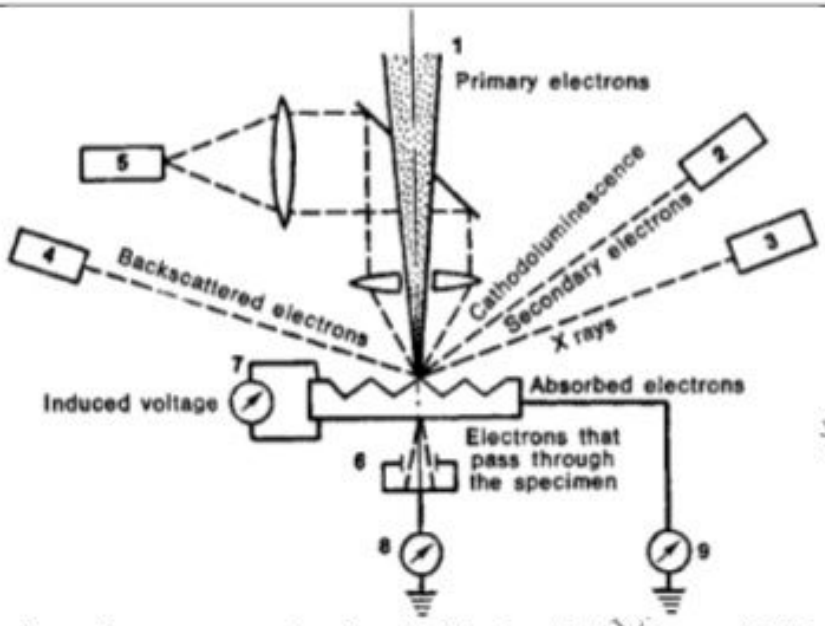


An electron microprobe operates under the principle that if a solid material is bombarded by an accelerated and focused electron beam, the incident electron beam has sufficient energy to liberate both matter and energy from the sample. These electron sample interactions mainly liberate heat, but they also yield both derivative electrons and x-rays. These quantized x-rays are characteristic of the element. EPMA analysis is considered to be "non-destructive" so it is possible to re-analyze the same materials more than one time.

APPLICATIONS OF EMPA

- Quantitative EMPA analysis is the most commonly used method for chemical analysis of geological materials at small scale.
- EPMA is also widely used for analysis of synthetic materials such as optical wafers, thin films, microcircuits, semi-conductors, and superconducting ceramics.

STRENGTHS AND LIMITATIONS OF ELECTRON PROBE MICRO-ANALYZER (EPMA)

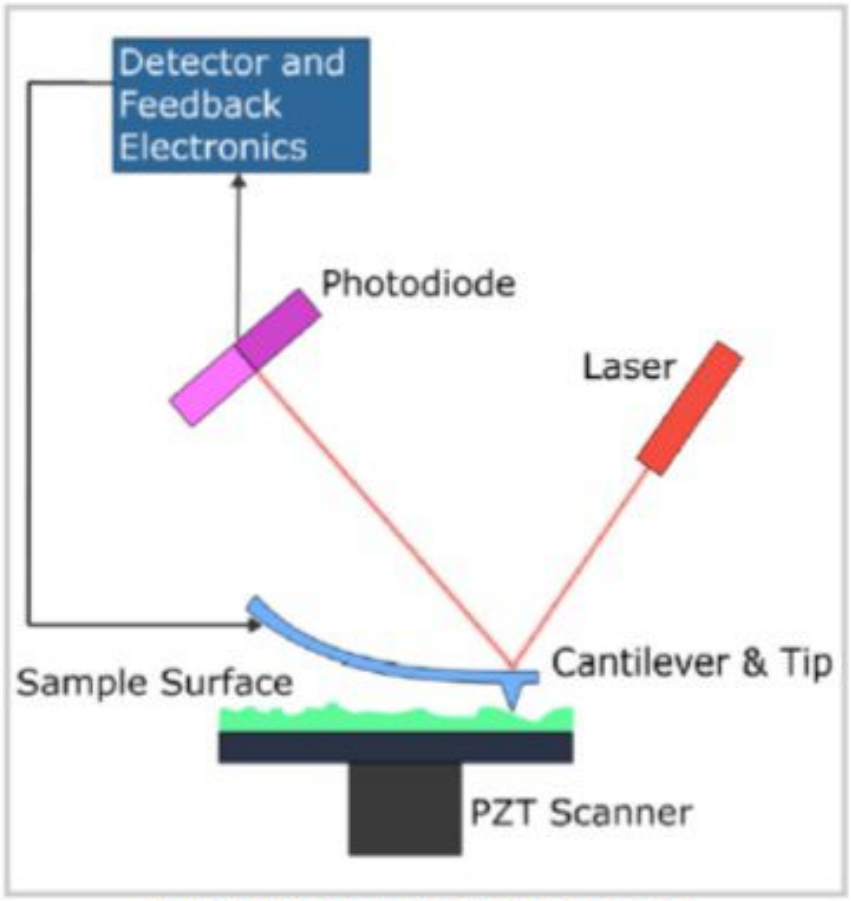
Strength's:-

- An electron probe is the primary tool for chemical analysis of solid materials at small spatial scales .
- Spot chemical analyses can be obtained in situ , which allows the user to detect even small compositional variations within textural context or within chemically zoned materials.

Limitations:-

- Electron probe unable to detect the lightest elements (H, He and Li).

  Probe analysis also cannot distinguish between the different valence states of Fe.



Scanning probe microscope

Electron Microprobe Analysis(EMPA)

An electron probe micro-analyzer is a micro beam instrument used primarily for thein situ non-destructive chemical analysis of minute solid samples. EPMA is also informally called an electron microprobe, or just probe. It is fundamentally the same as an SEM, with the added capability of chemical analysis.

Karnatak Law Society's
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Web: www.vdrit.org email: klsvdrit@yahoo.com

Scanning Probe Microscopy

What are scanning probe microscopes?

Scanning probe microscopes (SPMs) are a family of tools used to make images of nanoscale surfaces and structures, including atoms. They use a physical probe to scan back and forth over the surface of a sample. During this scanning process, a computer gathers data that are used to generate an image of the surface. In addition to visualizing nanoscale structures, some kinds of SPMs can be used to manipulate individual atoms and move them to make specific patterns. SPMs are different from optical microscopes because the user doesn't "see" the surface directly. Instead, the tool "feels" the surface and creates an image to represent it.

How do they work?

SPMs are a very powerful family of microscopes, sometimes with a resolution of less than a nanometer. (A nanometer is a billionth of a meter.)

An SPM has a probe tip mounted on the end of a cantilever. The tip can be as sharp as a single atom. It can be moved precisely and accurately back and forth across the surface, even atom by atom.

When the tip is near the sample surface, the cantilever is deflected by a force. SPMs can measure deflections caused by many kinds of forces, including mechanical contact, electrostatic forces, magnetic forces, chemical bonding, van der Waals forces, and capillary forces.

The distance of the deflection is measured by a laser that is reflected off the top of the cantilever and into an array of photodiodes (similar to the devices used in digital cameras). SPMs can detect differences in height that are a fraction of a nanometer, about the diameter of a single atom.

The tip is moved across the sample many times. This is why these are called "scanning" microscopes. A computer combines the data to create an image.

The images are inherently colorless because they are measuring properties other than the reflection of light. However, the images are often colorized, with different colors representing different properties (for example, height) along the surface.

Scientists use SPMs in a number of different ways, depending on the information they're trying to gather from a sample. The two primary modes are contact mode and tapping mode. In contact mode, the force between the tip and the surface is kept constant. This allows a scientist to quickly image a surface. In tapping mode, the cantilever oscillates, intermittently touching the surface. Tapping mode is especially useful when a scientist is imaging a soft surface.

There are several types of SPMs. Atomic force microscopes (AFMs) measure the electrostatic forces between the cantilever tip and the sample. Magnetic force microscopes (MFMs) measure magnetic forces. And scanning tunneling microscopes (STMs) measure the electrical current flowing between the cantilever tip and the sample.

AFM probes cannot normally measure steep walls or overhangs.

Cantilevers are more expensive

Applications

- With AFM, virtually any surface, whether insulator, conductor, organic or biological can be imaged
- Nanotechnology, Biological research

Advantages

- AFM provides a 3-dimensional surface profile
- Samples doesnot require (coatings)
- Does not need high vaccum
- Materials can also be analyzed in diff enviroments such in liquid under vaccum & at low temp.
- Provides a very high resolution
- AFM can be combined with a variety of optical microscopy techniques
- It can work in liquid environment, this makes it possible to study biological macromolecules & living organism

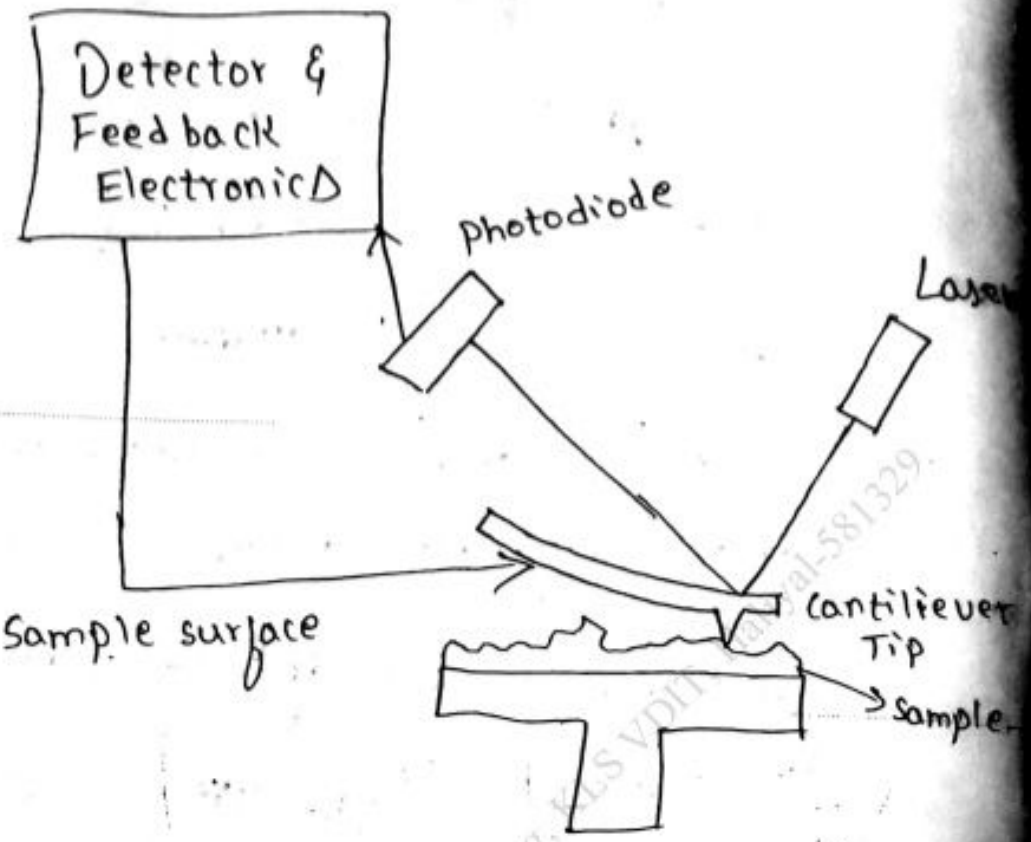
Disadvantages -

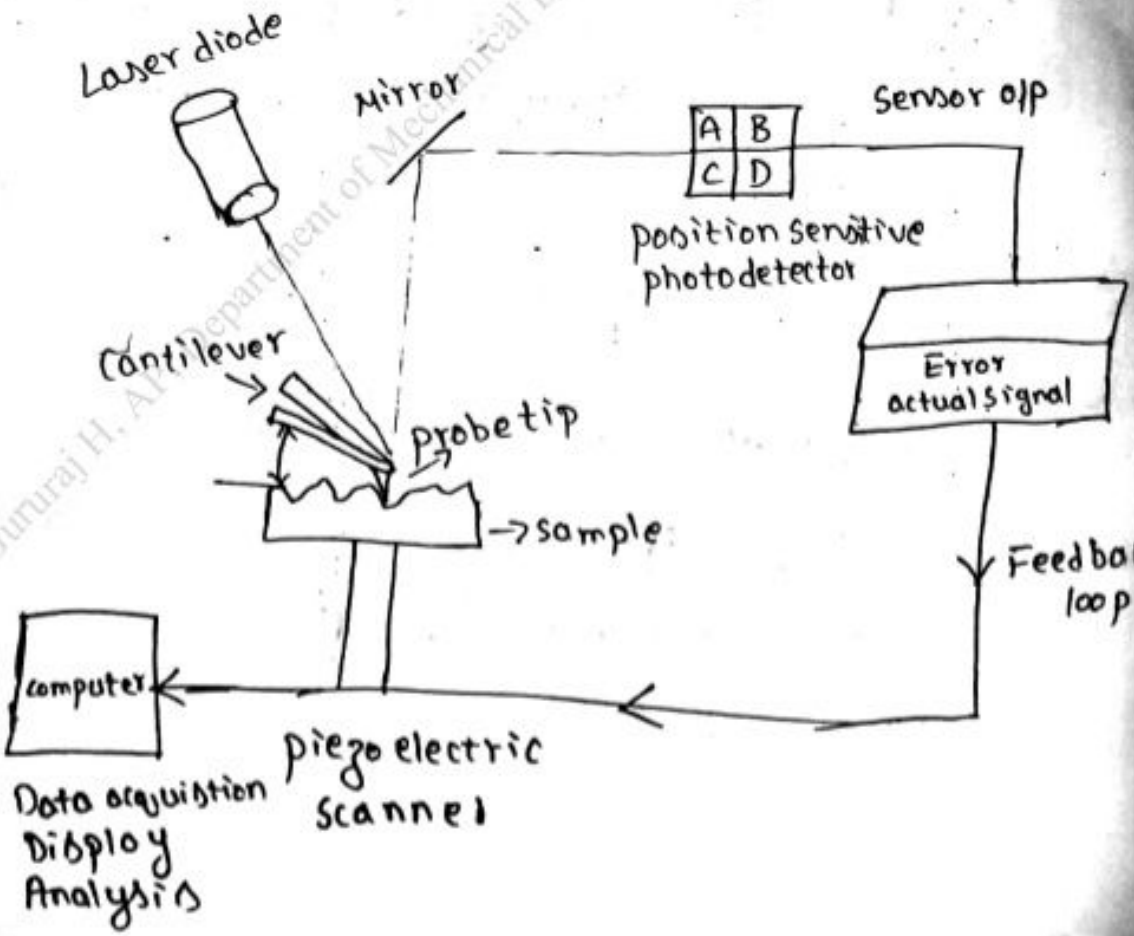
Scanning area is very small (150 x 150 micrometers)

Scanning speed is slow

Image distortions & Thermal drift

Images can also be affected by nonlinearity hysteresis & creep





Forces that are measured in AFM include mechanical contact force, vanderwaals forces, Capilliary forces, chemical bonding, electrostatic forces.

Imaging Mode

Contact mode

Non contact mode

Tapping Mode

Contact mode :- Tip is in intimate contact with the surface & scanns across the surface

Non contact mode :- Distance blw the tip & surface is continually adjusted so as to maintain a const deflection

Tapping mode → Stiff cantilever is brought within close proximity of the surface. During the oscillations, part of the tip intermittently touches or taps the surface.

Principle – An AFM uses a cantilever with a very sharp tip to scan over a sample surface. As the tip approaches the surface, the close-range attractive force b/w the surface & the tip causes the cantilever to deflect towards the surface. However, as the cantilever is brought even closer to the surface, such that the tip makes contact with it, increasingly repulsive force takes over & causes the cantilever to deflect away from the surface.

Working → AFM consists of a cantilever with a sharp tip (probe) at its end that is used to scan the specimen surface. The cantilever is typically silicon or silicon Nitride with a tip radius of ~~con~~ curvature on the order of Nanometers, when the tip is brought into proximity of a sample surface forces b/w the tip & the sample lead to deflection of the cantilever.

Atomic Force Microscopy (AFM)

It is a powerful microscopy Technology for studying samples at Nanoscale.

AFM generate images at "atomic resolution" with angstron scale resolution, height information, with minimum sample preporation

Atomic force microscopy / Scanning force Microscopy (AFM)

~~It~~ ~~(SFM)~~

Scanning probe Microscopy (SPM)

AFM is designed to measure local properties, such as height, friction, magnetism with a probe. To acquire an image the SPM raster-scan the probe over a small area of the sample, measuring the local property simultaneously.

als
smic
torms

Limitations

Peak overlay may occur & worsens fo
high angle reflections.

No depth profile information

se

For mixed materials, detection limit is

in

For unit cell determinations, indexing
patterns for non-isometric crystal sys
is complicated

X-Ray Diffraction → (Powerful nondestruc
Technique for chara
crystalline materia

for

It provides information
on structure, phases, preferred crystal orei
& other structural parameter. such as averag
siguous size, crystallinity, strain & crystal defects.
The peak intensities are determined by t
ed distribution of atoms with in the lattice, co
ight the x-ray diffraction pattern is the "fingerp
of perodic atomic arrangements in a given m
XRD pattern enables quick phase identifica
for a large variety of crystalline sample

Measuring residual stress in bulk metals & ceramics

Analysing films as thin as 50 angstroms for texture & phase behaviors

Determining crystalline minority phase

Determining percentage of material in crystalline form versus amorphous.

Strengths

Powerful & rapid (<20 min) technique for identification of an unknown material.

In most cases, it provides an unambiguous mineral determination.

Minimal sample preparation is required

Data interpretation is relatively straight forward

Non destructive

Characterization of Crystalline

Identification of fine grained minerals su
clays & mixed layer ~~ergs~~ clays that ar
difficult to determine optically

Determination of unit cell dimensions

Measurement of sample purity

Ideal uses Advantages

Phase identification for a large varie
of bulk & Thin film samples

Determine of modal amount of minero
(Quantitative Analysis)

Determining the thickness, roughness
density of the film using glancing
incidence X-ray reflectivity measure

For typical powder patterns, data is collected at 2θ from ~5° to 70° angles that are preset in the X-ray scan.

Applications

-> Identification/quantification of crystalline phase.

Measurement of average crystallite size, strain or micro strain effects in bulk & thin film samples

Quantification of prefered oreintation in Thin films

Determination of the ratio of crystalline to amorphous material in bulk materials & thin-film samples.

the incident X-rays impinging the
Sample & detector are rotated, the int
of the reflected X-ray is recorded.

When the geometry of the inciden
X-rays impinging the sample satisfies t
Bragg Equation, constructive interference
occurs & a peak in intensity occurs.

A detector records & processes thi
X-ray signal & converts the signal to
count rate which is then o/p to a device
such as a printer or computer maintor.

The geometry of an X-ray diffracton
is such that the sample rotates in the p
of the collimated X-ray beam at an angl
while the X-ray detector is mounted o
an arm to collect the diffracted X-rays
& rotates an angle 2θ

The instruement used to maintain
the angle & rotate the sample is
termed as Goniometer

Working

X-rays are generated in a cathode ray tube by heating a filament to produce electrons, accelerating the electrons toward a target by applying a voltage & bombarding the target material with electrons. when electrons have sufficient energy to dislodge inner shell electrons of the target material characteristic X-ray spectra are produced

These spectra consits of several components, the most common being K_α & K_β Copper is the most common target material for single crystal diffraction with CuK_α radiation = 1.5418 A°

These x-rays are collimated & directed onto a sample

As the sample & detector are rotated the intensity of the reflected X-ray is recorded. when the geometry of

a diffraction pattern on a detector
The resulting wave interference patter
is the basis of diffraction analysis
This analysis is called Bragg diffra

It describes the condition of θ for
constructive interference to be at its
strongest

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

n is a positive integer
λ is the wavelength of incident wav
d lattice spacing
θ diffraction maximum

n -> Any integer, d -> spacing b/w diff
pl
θ -> Incident angle
λ -> wavelength of the beam

X-rays are generated by a cathode rays tube, filtered to produce monochromatic radiation, collimated to concentrate & directed towards the sample. The interaction of incident rays with the sample produces constructive interference when conditions satisfy Bragg's law

Bragg's law

Bragg's law gives the angles for coherent & incoherent scattering from a crystal lattice.

The scattering neutron waves from the nuclei or by a coherent spin interaction with an unpaired electron. These re-emitted wave fields interfere with each other either constructively or destructively (overlapping waves either add up together to produce stronger peaks or are subtracted from each other to some degree) producing

ay)
sition

Instrumentation

X-ray tube

High velocity of electrons be
on metal target, x-rays are prod

Collimator

close metal plates separated b
gap. Use is to produce narrow be

ways

t

Monochromator

Absorbs the undesirable rad
& allows required wavelength to p

a

Filter eg :- Zirconium
Crystal :- chloride, Lithium

f

Detectors

photographic methods
Counter methods

sions.

n

Goniometer - Instrument used
maintain the angle & rotate the s

The Quantum of radiation (x-ray) is emitted corresponding to this transition time scale is approximately $10^{-18} - 10^{-14}$

Emitted radiation is called x-rays

Production of x-rays

x-rays are obtained ~~by~~ in three ways

1) By bombardment of metal target with a beam of high Energy electrons

2) By exposure of a substance to a primary beam of x-ray in order to generate a secondary beam of x-ray fluorescene

3) By use of radioactive source decay process result in x-ray emissions.

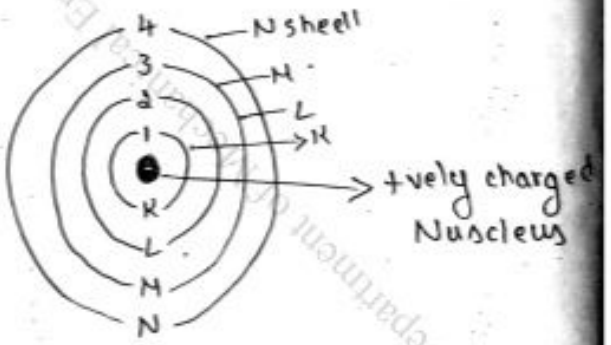
x-rays are produced whenever high speed electrons collide with a metal target

crystal can be determined, as well
chemical bonds, their disorders &
other information.

X-ray are electromagnetic radiati
wavelength in the range 0.1 – 100 A° (a

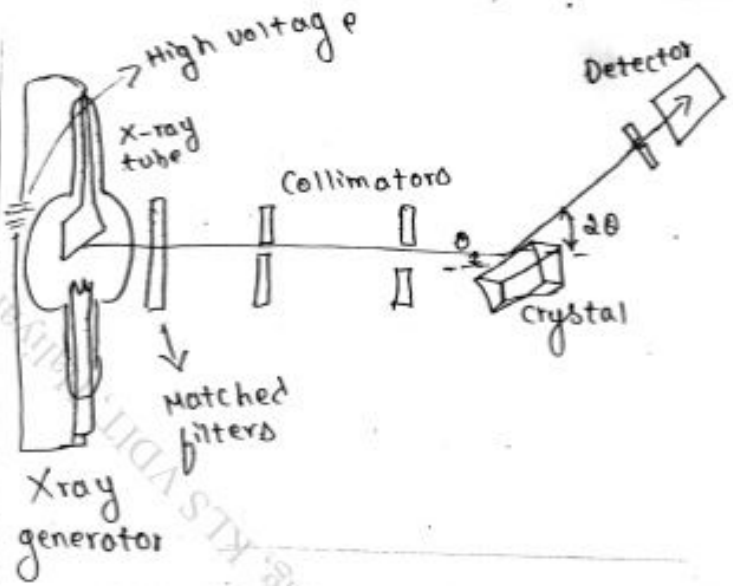
Principle

In every atom the electrons are ar
in layers or shells like KLMN shells.

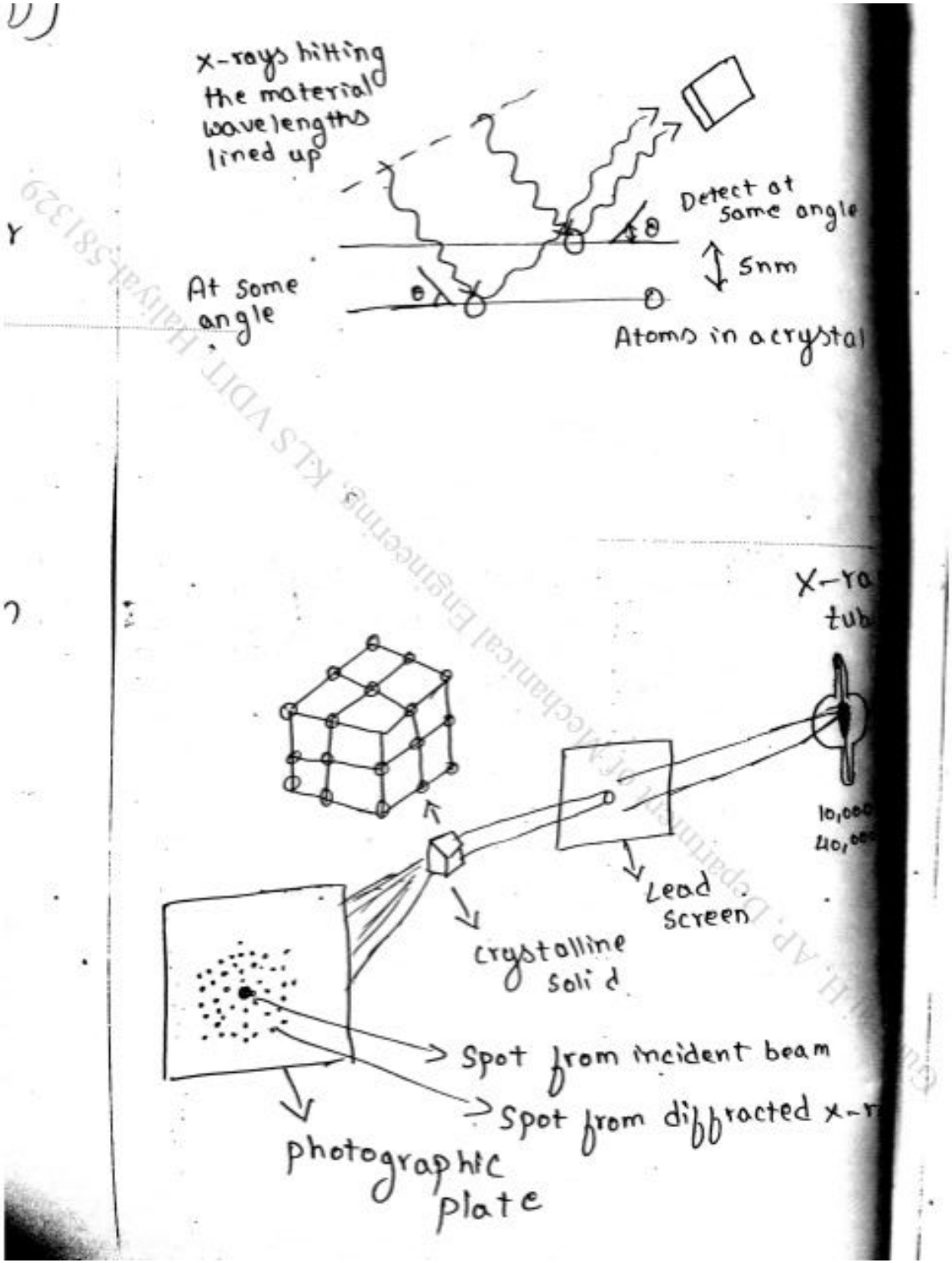


When the atom is bombarded with an
electron, eject one of the electron from
the inner shell.

The electrons migrate from the outer
shell to the inner shell to fill the gap
with higher energy



XRD is a tool used for identifying the atomic & molecular structure of a crystal, in which the crystalline atoms cause a beam of incident x-rays to diffract into many specific directions. By measuring the angles & intensities of these diffracted beams a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal, from this electron density the mean position of the atoms in the

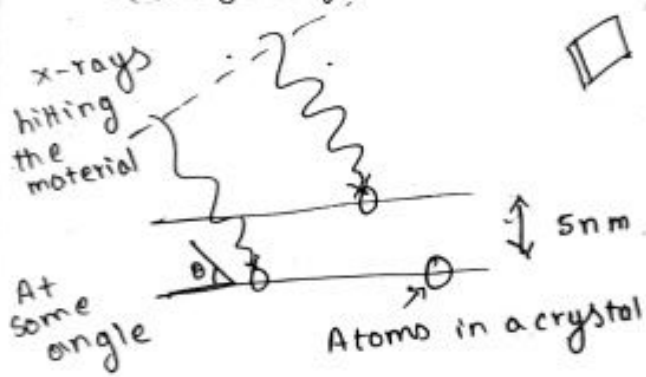

X-rays hitting the material wavelengths lined up
Detect at same angle
θ
5nm
At some angle
θ
Atoms in a crystal
X-ra
tub
10,000
40,000
Lead screen
crystolline soli d
Spot from incident beam
Spot from diffracted x-r
photographic plate

X-ray diffractometry (XRD)

X-ray diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material & can provide information on unit cell dimensions

The analyzed material is finely ground homogenized, & average bulk composition is determined.

X-ray Diffraction



Sample preparation on TEM

Fixation → fixed with chemical products

Rinsing & staining → treated with heavy metal compounds

Dehydration – Dehydrated with organic solvent / acetone or ethanol

Embedding in resin – material is gradually infiltrated with the ~~soft~~ still unpolymerised resin

Trimming of resin block & ultrathin sectioning

Collection of sections on grid

Thin sample (< 50nm)

Detailed image 1 nanometer in size

Disadvantages

- TEM are very large & very expensive
- Laborious Sample preparation
- operation & Analysis is requires special training
- Samples are limited to those that are electron transparent.
- TEM require special housing & maintenance

Applications

- life science, medical, biological, material research forensic analysis
- TEM provide topographical, morphological, compositional & crystalline information
- study of crystals metals, & To identify flaws, fractures & damages to micro-sized object
- View samples on a molecular level
- Semiconductor analysis, & production & manufacturing of computer & silicon chips.

- High electron beam bombardment
- Lenses focus it onto the specimen
- Electrons are used for image construct
- Image is constructed by the transmitted electrons
- Thicker region occlude more beam

Advantages

- offers most powerful magnification, potentially over one million times or more.
- provide information on element & compound structu
- Images are high quality & detailed
- It provides information about morpholo crystallinity, particle size distribution & elemental composition of the sample

Working

Tungsten filament – Generates a beam of electrons that is then focused on the specimen by the condenser

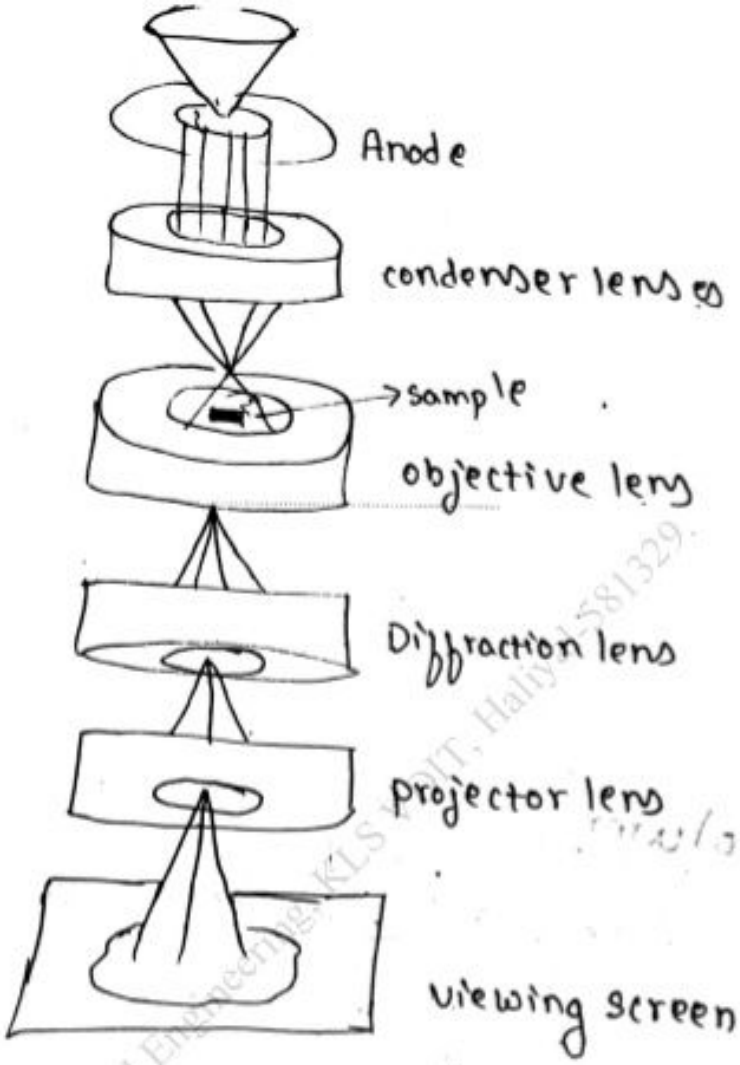
Magnetic lens – are used to focus the beam

The column containing the lenses & specimen must be under high vaccum to obtain a clear image because electrons are deflected by collisions with air molecules

Magnetic lenses :- Form the enlarged visible image of the specimen on a fluroscent screen

photographic film :- The screen can also be moved aside & the image captured on photographic film as a permanent record.

rays



trons

s

ns

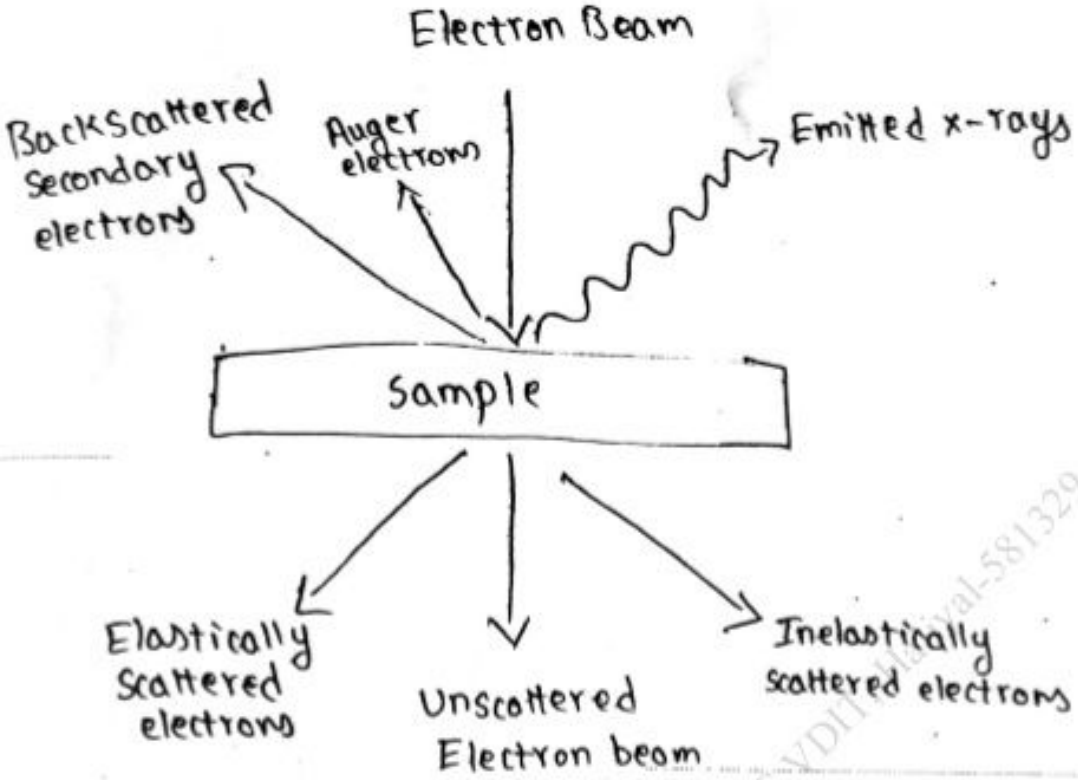
Magnification – 2,000,000X

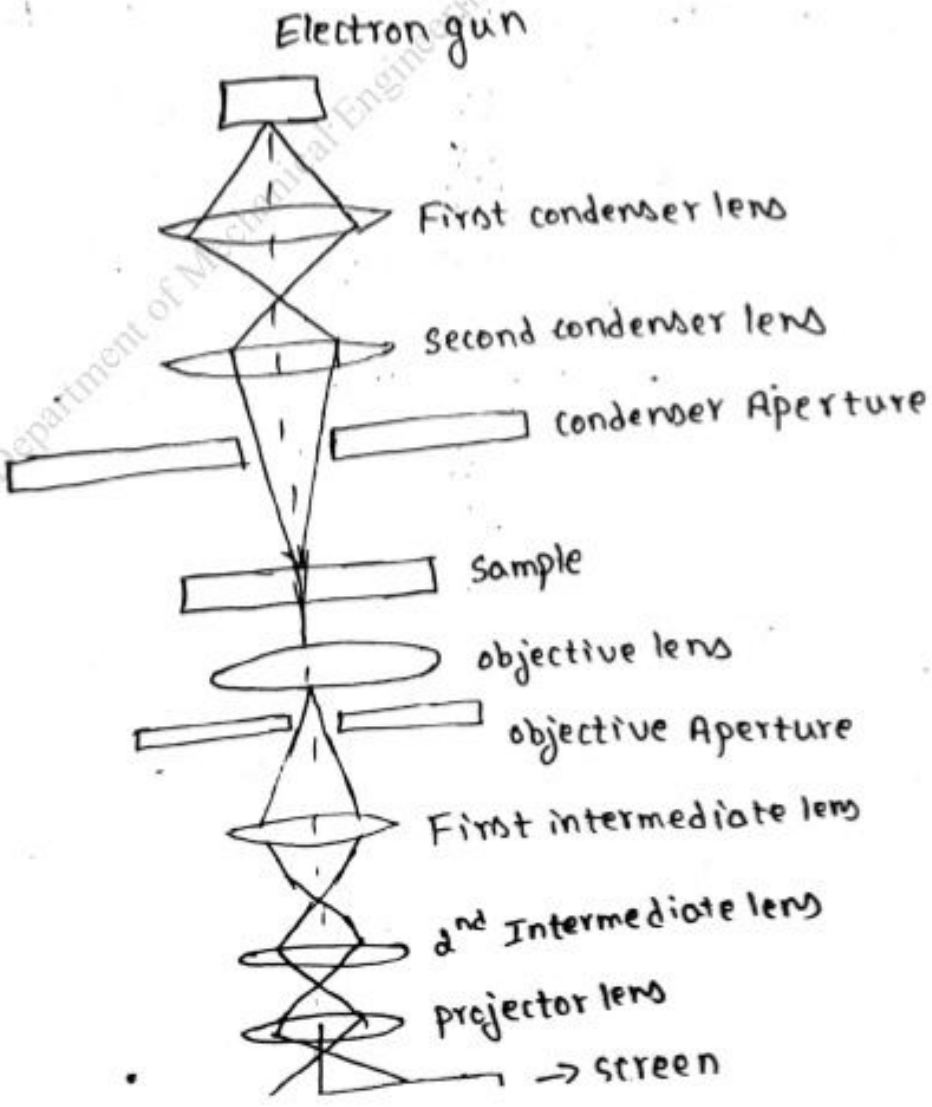
perture

ure

lens

y





A sophisticated system of electromagne lenses focuses the scattered electrons into an image or a diffraction pattern, or a nano-analytical spectrum

Imaging Mode - provides a highly magnifie view of the micro- & nanostructure

Diffraction Mode - Displays accurate informat about the local crystal structure

Nanoanalytical modes - Represents which elements are present in the tiny volume of material.

De Broglie equation

$$\lambda_e \approx \frac{h}{\sqrt{2m_0E\left(1+\frac{E}{2m_0c^2}\right)}}$$

h - planks's const m_0 - rest mass of electron

c - speed of light

Transmission Electron Microscope (TEM)

TEM is a microscopy technique in which a beam of electrons is transmitted through an ultra - thin specimen,

TEM is based on "Transmitted Electrons"

- Very high resolution

In 1986 "Ruska (scientist)" was awarded the Nobel prize in physics for the development of TEM

Principle:- TEM uses high energy electrons (up to 300 KV accelerating voltage) which are accerlerated to nearly the speed of a light. The electron beam behaves like a wavefront with wavelength about a million times shorter than ~~wavelength~~ lightwaves

When an electron beam passes through a thin-section specimen of a material electrons are scattered

— SEM operators & researchers are advised to observe safety precautions (exposure to x-rays, high radiation needs safety)

— only knowledgeable experience researchers being able to identify the actual data & as well as preparation skill.

- structural analysis
- Powder morphology. particle size & analysis
- Delamination investigation
- Examination of surface morphology

SEM Disadvantage

- SEM are expensive, large & must be housed in an area free of any possible electric, magnetic or vibration interference
- Special training is required to operate an SEM
- Maintenance is high, involves keeping a steady voltage, currents to electromagnetic coils & circulation of cool water
- Risk of radiation exposure associated with the electrons that scatter from beneath the surface

- Provide Qualitative Chemical analysis
- Identify crystalline structures.
- Semiconductor inspection
- Examine microchips of computors
- Essential Research tool in fields such as life science, biology, gemology metallurgy, medical & forensic science

SEM Advantages

- Easy to operate with proper training & advanced computer Technology & associated software make operation user friendly
- Works fast, EDX analyses is completed in less than 5 minutes
- Generation of data in digital form
- Minimum preparation actions

original object is scanned onto a monitor for viewing.

SEM use scanning coils, ~~one of~~ which create a magnetic field using fluctuating voltage, to manipulate the electron beam. The scanning coils are able to move the beam precisely back & forth over a defined section of an object. If a researcher wants to increase the magnification of an image, he or she simply sets the electron beam to scan a smaller area of the sample.

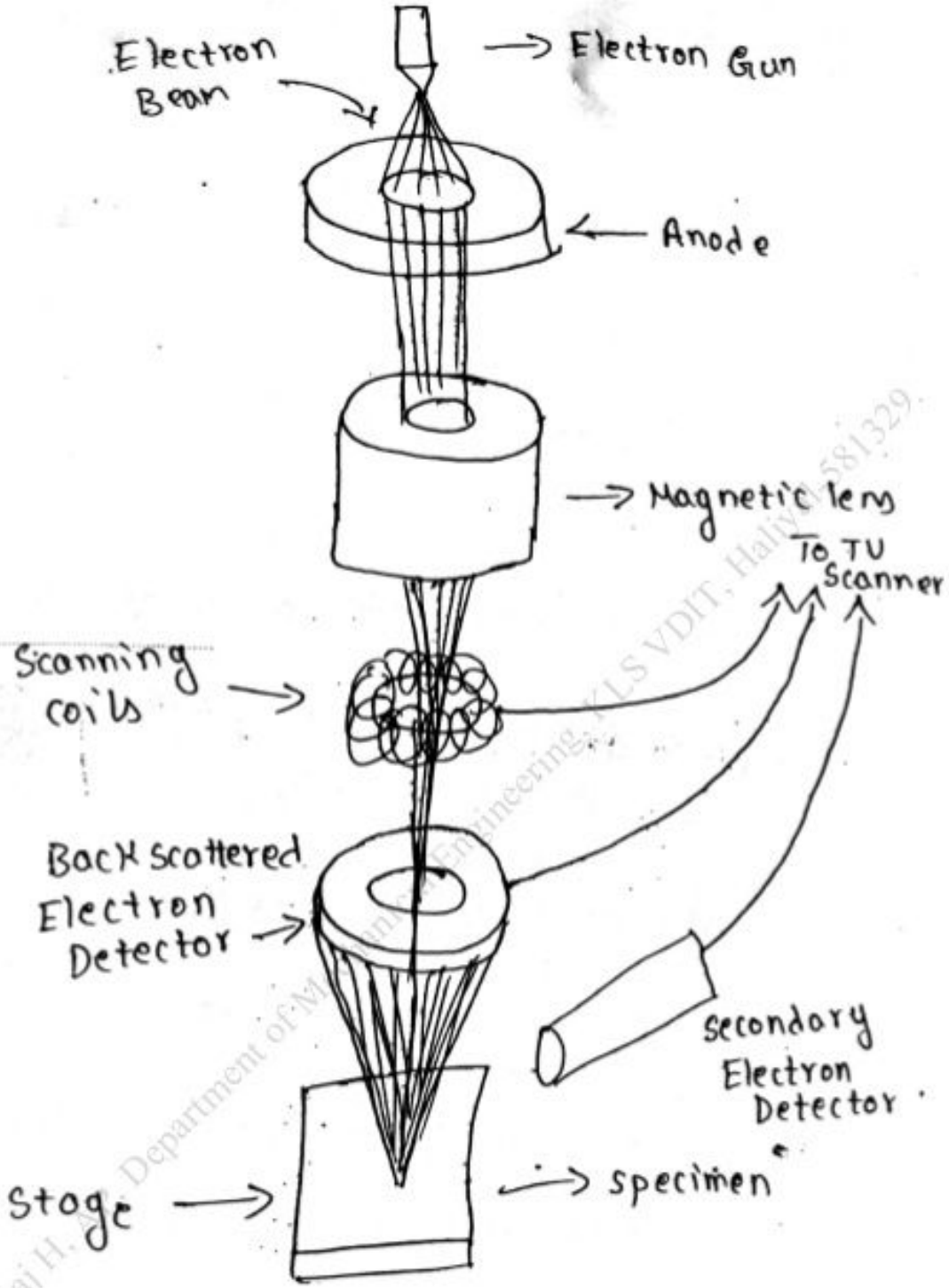
SEM Applications

- Characterizations of solid Materials
- Topographical, Morphological & Compositional information
- SEM can detect & analyze surface fracture
- Provide information in microstructure
- examine surface contaminations
- Variation in chemical compositions.

The Principal images produced in the SEM are of Three types

1) Secondary electron images
2) Backscattered electron images
3) Elemental X-ray Maps.

As the electron beam traces over the sample it interacts with the surface of the sample dislodging secondary electrons from the surface of the specimen in unique patterns. A secondary electron detector attracts those scattered electrons & depending on the number of electrons that reach the detector, registers different levels of brightness on a monitor. Additional sensors detect backscattered electrons (electrons that reflect off the specimen's surface) & X-rays (emitted from beneath the specimen's surface). Dot by dot, row by row, an image of the


Electron Beam
Electron Gun
Anode
Magnetic lens
To TV Scanner
Scanning coils
Back scattered Electron Detector
Secondary Electron Detector
Stage
Specimen

Instrumentation – Heated filament as a source of electron beam

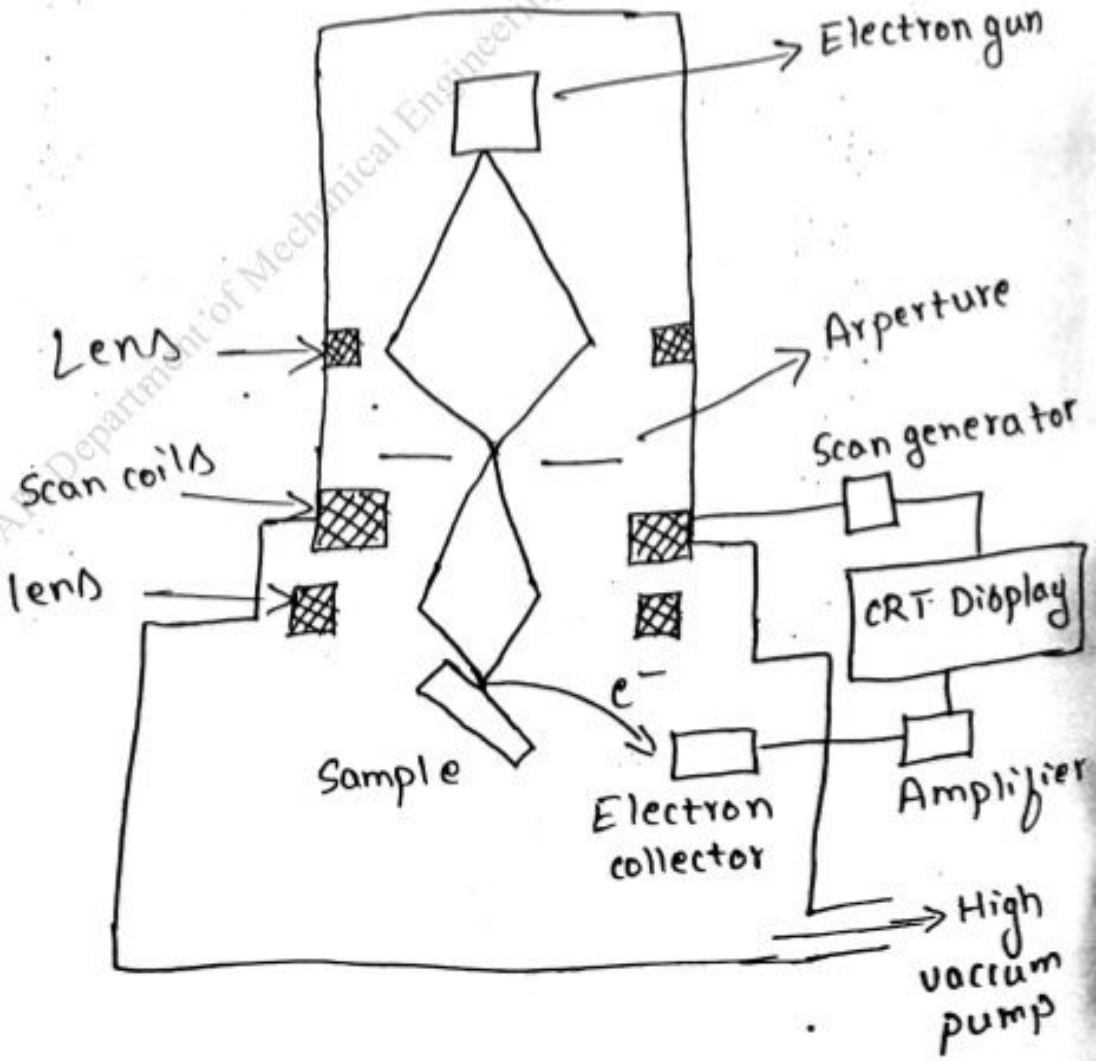
Condenser lenses

Evacuated chamber

Electron detector

Amplifier

CRT with image forming electronics



Scanning Electron Microscope (SEM)

Scanning Electron Microscope produces images of a sample by scanning it with a focused beam of electrons.

The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface Topography & composition.

Principle → An electron beam is focused onto the sample surface kept in a vaccum by electro magnetic lenses. The beam is scanned over the surface of the sample.

The scattered electron from the sample is then fed to the detector & then to a cathode ray tube through an amplifier where the images are formed, which gives the information on the surface of the sample.

Applications

Microelectronics

Nanophysics

Biotechnology

Medical diagnosis

Advantages

Medium cost, simple devices

Fast & adaptable to all kinds of sample systems

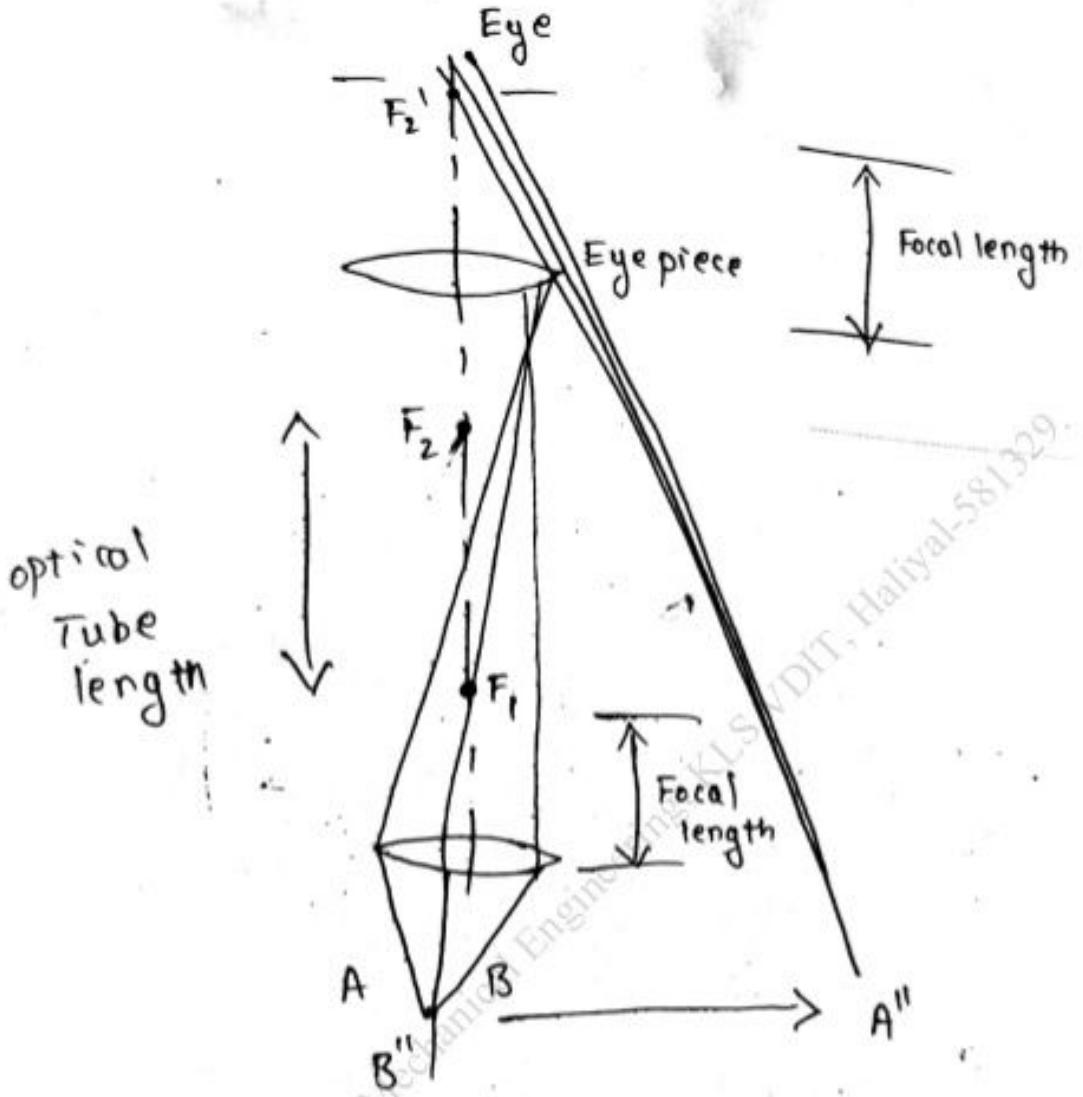
Easy to be integrated with digital cameras/camcorder systems for data storage & analysis.

Disadvantage

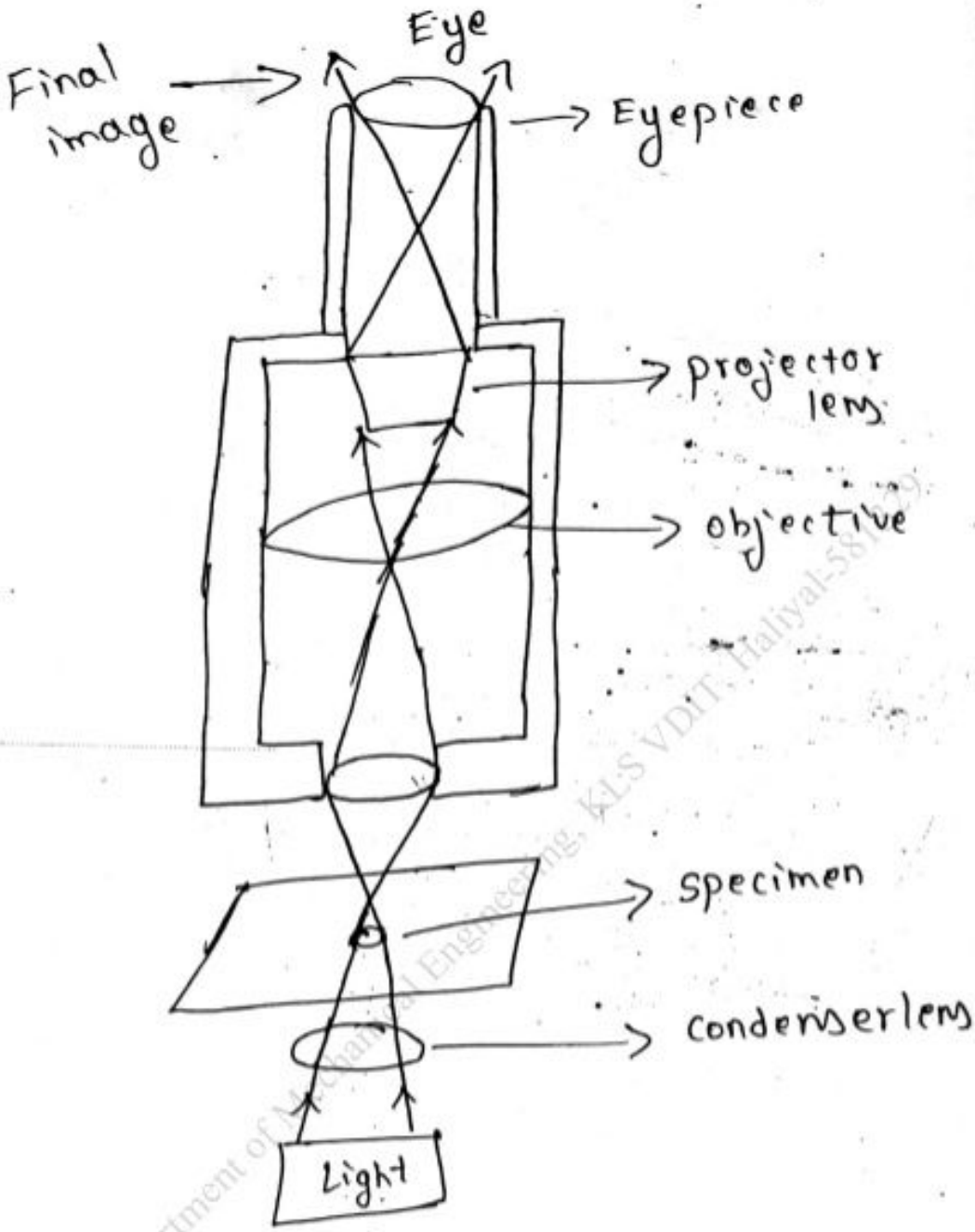
High level of Magnification can not be acheived.

Low resolution

Principle



It create a magnified image by combing an objective lens & making an inverted real image, & magnifies the image further more with an eyepiece to allow the user to observe it by naked eye.

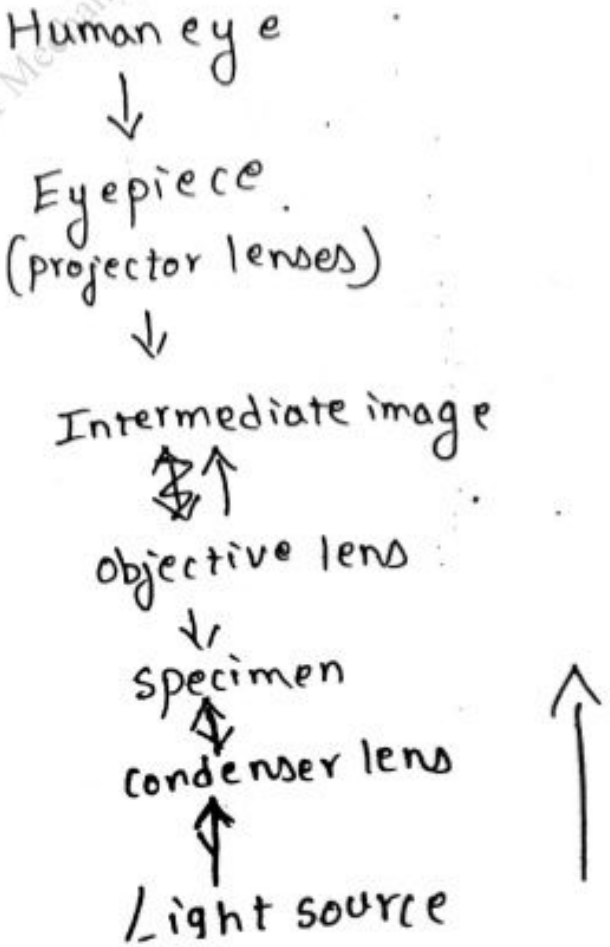


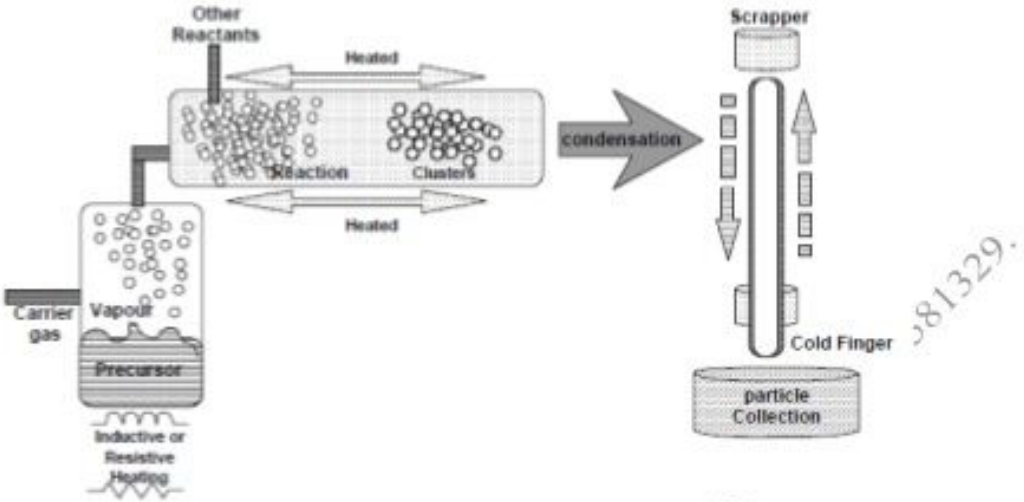
The function is to create a magnified image of a specimen consists of three basic functions of obtaining a clear sharp image, changing a magnification & bringing to focus.

Optical Microscopy

It is a type of Microscope which uses visible light & a system of lenses to magnify images of small samples.

Image from an optical microscope can be captured by normal light sensitive cameras to generate a micrograph.





A schematic of a typical CVC reactor

Because CVC processing is continuous, the production capabilities are much larger than in GPC processing. Quantities in excess of 20 g/hr have been readily produced with a small scale laboratory reactor. A further expansion can be envisaged by simply enlarging the diameter of the hot wall reactor and the mass flow through the reactor.

Chemical Vapour Condensation(CVC)

As shown schematically in Figure, the evaporative source used in GPC is replaced by a hot wall reactor in the Chemical Vapour Condensation or the CVC process. Depending on the processing parameters nucleation of nanoparticles is observed during chemical vapour deposition (CVC) of thin films and poses a major problem in obtaining good film qualities. The original idea of the novel CVC process which is schematically shown below where, it was intended to adjust the parameter field during the synthesis in order to suppress film formation and enhance homogeneous nucleation of particles in the gas flow. It is readily found that the residence time of the precursor in the reactor determines if films or particles are formed. In a certain range of residence time both particle and film formation can be obtained.

Adjusting the residence time of the precursor molecules by changing the gas flow rate, the pressure difference between the precursor delivery system and the main chamber occurs. Then the temperature of the hot wall reactor results in the fertile production of nanosized particles of metals and ceramics instead of thin films as in CVD processing. In the simplest form a metal organic precursor is introduced into the hot zone of the reactor using mass flow controller. Besides the increased quantities in this continuous process compared to GPC has been demonstrated that a wider range of ceramics including nitrides and carbides can be synthesised. Additionally, more complex oxides such as $BaTiO_3$ or composite structures can be formed as well. Appropriate precursor compounds can be readily found in the CVD literature.

The extension to production of nanoparticles requires the determination of a modified parameter field in order to promote particle formation instead of film formation. In addition to the formation of single phase nanoparticles by CVC of a single precursor the reactor allows the synthesis of

1. mixtures of nanoparticles of two phases or doped nanoparticles by supplying two precursors at the front end of the reactor, and
2. coated nanoparticles, i.e., n-ZrO_2 coated with n-Al_2O_3 or vice versa, by supplying a second precursor at a second stage of the reactor. In this case nanoparticles which have been formed by homogeneous nucleation are coated by heterogeneous nucleation in a second stage of the reactor.

gas flow by thermophoretic forces and deposited loosely on the surface of the collection device as a powder of low density and no agglomeration.

Subsequenly, the nanoparticles are removed from the surface of the cylinder by means of a scraper in the form of a metallic plate. In addition to this cold finger device several techniques known from aerosol science have now been implemented for the use in gas condensation systems such as corona discharge, etc. These methods allow for the continuous operation of the collection device and are better suited for larger scale synthesis of nanopowders.

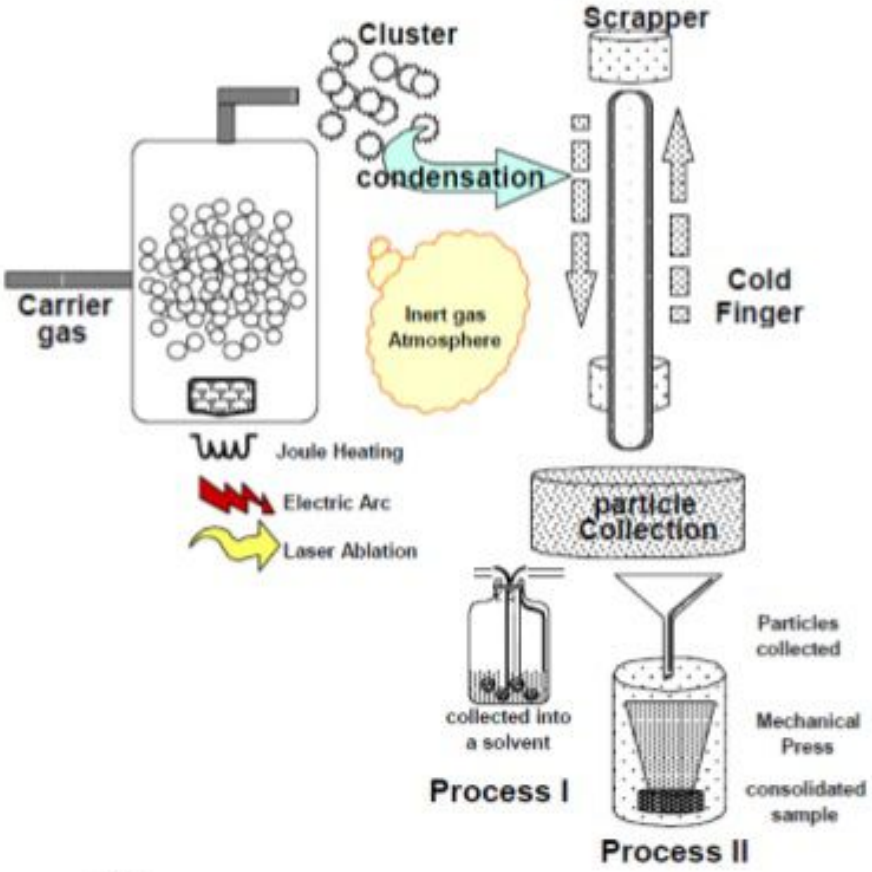
However, these methods can only be used in a system designed for gas flow, i.e. a dynamic vacuum is generated by means of both continuous pumping and gas inlet via mass flow controller. A major advantage over convectional gas flow is the improved control of the particle sizes. It has been found that the particle size distributions in gas flow systems, which are also lognormal, are shifted towards smaller average values with an appreciable reduction of the standard deviation of the distribution. Depending on the flow rate of the He-gas, particle sizes are reduced by 80% and standard deviations by 18%.

The synthesis of nanocrystalline pure metals is relatively straightforward as long as evaporation can be done from refractory metal crucibles (W, Ta or Mo). If metals with high melting points or metals which react with the crucibles, are to be prepared, sputtering, i.e. for W and Zr, or laser or electron beam evaporation has to be used. Synthesis of alloys or intermetallic compounds by thermal evaporation can only be done in the exceptional cases that the vapour pressures of the elements are similar. As an alternative, sputtering from an alloy or mixed target can be employed. Composite materials such as Cu/Bi or W/Ga have been synthesised by simultaneous evaporation from two separate crucibles onto a rotating collection device. It has been found that excellent intermixing on the scale of the particle size can be obtained.

However, control of the composition of the elements has been difficult and reproducibility is poor. Nanocrystalline oxide powders are formed by controlled postoxidation of primary nanoparticles of a pure metal (e.g. Ti to TiO2) or a suboxide (e.g. ZrO to ZrO2). Although the gas condensation method including the variations have been widely employed to prepared a variety of metallic and ceramic materials, quantities have so far been limited to a laboratory scale. The quantities of metals are below 1 g/day, while quantities of oxides can be as high as 20 g/day for simple oxides such as CeO2 or ZrO2. These quantities are sufficient for materials testing but not for industrial production. However, it should be mentioned that the scale-up of the gas condensation method for industrial production of nanocrystalline oxides by a company called nanophase technologies has been successful.

Gas Condensation Processing (GPC)

In this technique, a metallic or inorganic material, e.g. a suboxide, is vaporised using thermal evaporation sources such as crucibles, electron beam evaporation devices or sputtering sources in an atmosphere of 1-50 mbar He (or another inert gas like Ar, Ne, Kr). Cluster form in the vicinity of the source by homogenous nucleation in the gas phase and grow by coalescence and incorporation of atoms from the gas phase.



Schematic representation of typical set-up for gas condensation synthesis of nanomaterials followed by consolidation in a mechanical press or collection in an appropriate solvent media.

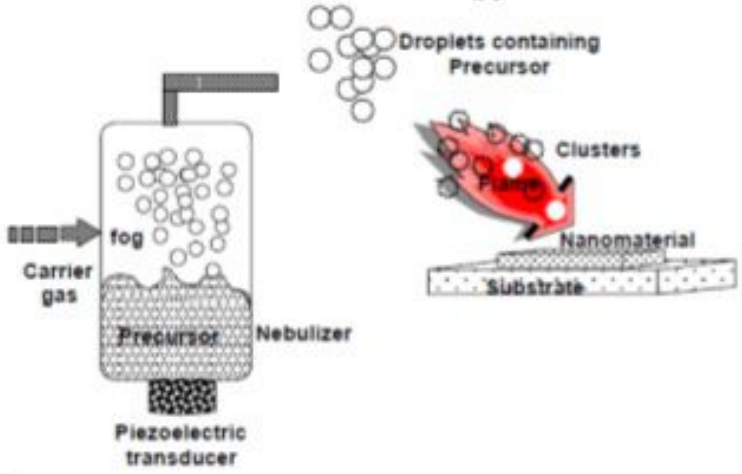
The cluster or particle size depends critically on the residence time of the particles in the growth system and can be influenced by the gas pressure, the kind of inert gas, i.e. He, Ar or Kr, and on the evaporation rate/vapour pressure of the evaporating material. With increasing gas pressure, vapour pressure and mass of the inert gas used the average particle size of the nanoparticles increases. Lognormal size distributions have been found experimentally and have been explained theoretically by the growth mechanisms of the particles. Even in more complex processes such as the low pressure combustion flame synthesis where a number of chemical reactions are involved the size distributions are determined to be lognormal.

Originally, a rotating cylindrical device cooled with liquid nitrogen was employed for the particle collection: the nanoparticles in the size range from 2-50 nm are extracted from the

Because of its inherent simplicity, it is possible to scale up this process from laboratory (mg/day) to industrial scales (tons/day).

Flame assisted ultrasonic spray pyrolysis

In this process, precusrsors are nebulized and then unwanted components are burnt in a flame to get the required material, eg. ZrO2 has been obtained by this method from a precursor of Zr(CH3 CH2 CH2O)4. Flame hydrolysis that is a variant of this process is used for the manufacture of fused silica. In the process, silicon tetrachloride is heated in an oxy-hydrogen flame to give a highly dispersed silica. The resulting white amorphous powder consists of spherical particles with sizes in the range 7-40 nm. The combustion flame synthesis, in which the burning of a gas mixture, e.g. acetylene and oxygen or hydrogen and oxygen, supplies the energy to initiate the pyrolysis of precursor compounds, is widely used for the industrial production of powders in large quantities, such as carbon black, fumed silica and titanium dioxide. However, since the gas pressure during the reaction is high, highly agglomerated powders are produced which is disadvantageous for subsequent processing. The basic idea of low pressure combustion flame synthesis is to extend the pressure range to the pressures used in gas phase synthesis and thus to reduce or avoid the agglomeration. Low pressure flames have been extensively used by aerosol scientists to study particle formation in the flame.



Flame assisted ultrasonic spray pyrolysis

A key for the formation of nanoparticles with narrow size distributions is the exact control of the flame in order to obtain a flat flame front. Under these conditions the thermal history, i.e. time and temperature, of each particle formed is identical and narrow distributions result. However, due to the oxidative atmosphere in the flame, this synthesis process is limited to the formation of oxides in the reactor zone.

Applications:

It can be used in ceramics manufacturing processes, as an investment casting material, or as a means of producing very thin films of metal oxides for various purposes.

Other elements (metals, metal oxides) can be easily incorporated into the final product and the silicalite sol formed by this method is very stable.

Other products fabricated with this process include various ceramic membranes for microfiltration, ultrafiltration, nanofiltration, pervaporation and reverse osmosis.

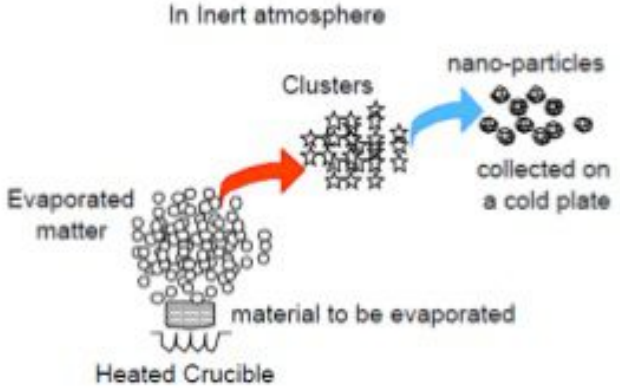
Gas Phase synthesis of Nano-materials

synthesis methods of nanoparticles in the gas phase are based on homogeneous nucleation in the gas phase and subsequent condensation and coagulation.

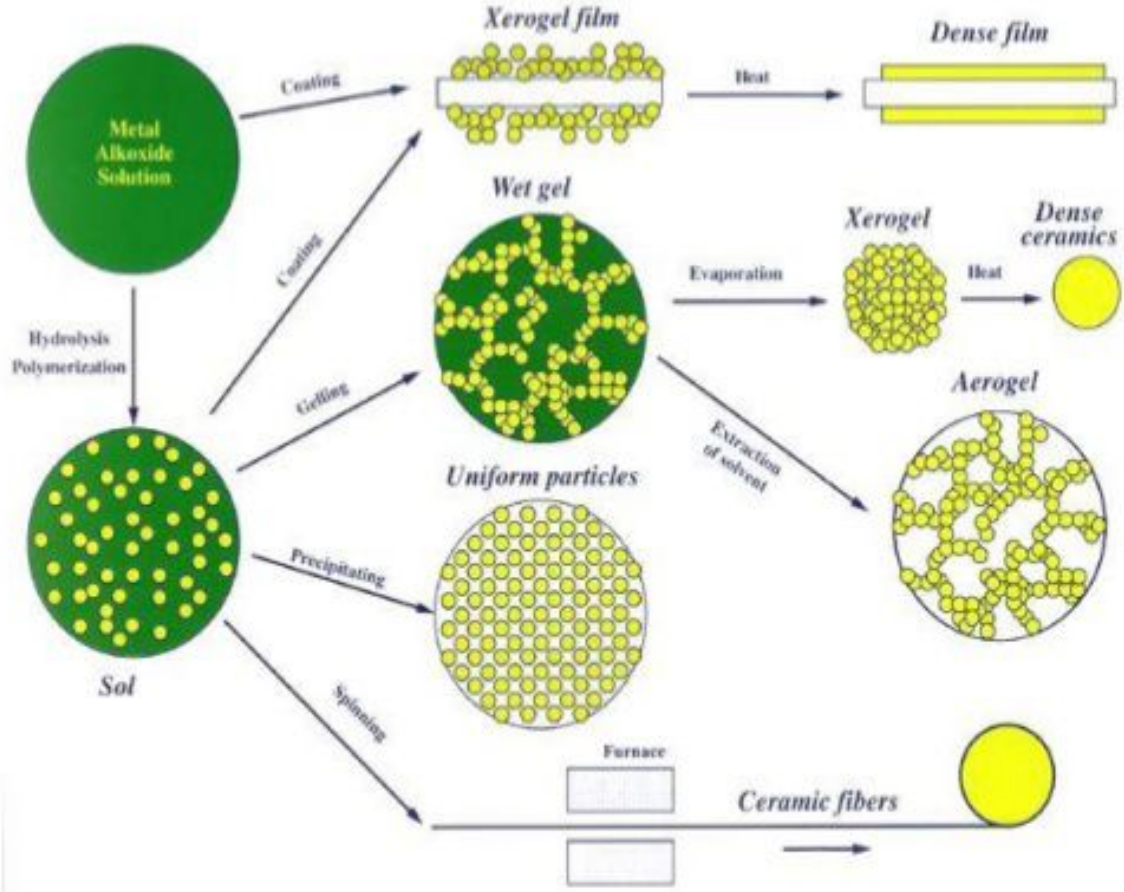
Furnace

The simplest fashion to produce nanoparticles is by heating the desired material in a heat resistant crucible containing the desired material. This method is appropriate only for materials that have a high vapour pressure at the heated temperatures that can be as high as 2000°C. Energy is normally introduced into the precursor by arc heating, electronbeam heating or Joule heating. The atoms are evaporated into an atmosphere, which is either inert (e.g. He) or reactive (so as to form a compound). To carry out reactive synthesis, materials with very low vapour pressure have to be fed into the furnace in the form of a suitable precursor such as organometallics, which decompose in the furnace to produce a condensable material. The hot atoms of the evaporated matter lose energy by collision with the atoms of the cold gas and undergo condensation into small clusters via homogeneous nucleation. In case a compound is being synthesized, these precursors react in the gas phase and form a compound with the material that is separately injected in the reaction chamber. The clusters would continue to grow if they remain in the supersaturated region. To control their size, they need to be rapidly removed from the supersaturated environment by a carrier gas. The cluster size and its distribution are controlled by only three parameters:

1) the rate of evaporation (energy input)
2) the rate of condensation (energy removal), and
3) the rate of gas flow (cluster removal).



Schematic representation of gas phase process of synthesis of single phase nanomaterials from a heated crucible



Advantages of Sol-Gel Technique:

Can produce thin bond-coating to provide excellent adhesion between the metallic substrate and the top coat.
Can produce thick coating to provide corrosion protection performance.
Can easily shape materials into complex geometries in a gel state.
Can produce high purity products because the organo-metallic precursor of the desired ceramic oxides can be mixed, dissolved in a specified solvent and hydrolyzed into a sol, and subsequently a gel, the composition can be highly controllable.
Can have low temperature sintering capability, usually 200-600°C.
Can provide a simple, economic and effective method to produce high quality coatings.

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Wet Chemical Synthesis of Nano-materials- sol-gel process

WET CHEMICAL TECHNIQUE (Chemical solution deposition technique)

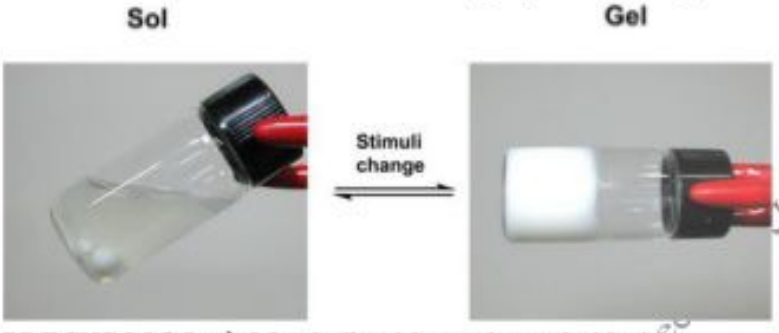
Produce high purity and homogeneous nanomaterials, particularly metal oxide nanoparticles

Starting material from a chemical solution leads to the formation of colloidal suspensions known as SOL.

The SOL evolves towards the fomation of inorganic network containing a liquid phase called the GEL. The removal of liquid phase from the Sol yields the Gel.

The particle size and shape are controlled by the Sol/Gel transitions.

The thermal treatment (firing/calcinations) of the gel leads to further polycondensation Reaction and enhances the mechanical properties of the products (i.e.) oxide nanoparticles.



PRECURSORS → Metal alkoxides and metal chlorides

Starting material is washed with water and dilute acid in alkaline solvent.

The material undergoes hydrolysis and polycondensation reaction which leads to the formation of colloids.

Colloid System composed of solid particles is dispersed in a solvent containing particles of size from 1nm to 1mm

The SOL is then evolved to form an inorganic network containing a liquid phase (GEL).

The Sol can be further processed to obtain the substrate in a film, either by dip coating or Spin-coating or case into a contained with desired shape or powders by calcination.

The chemical reaction which takes place in the Sol-Gel metal alkoxides M(OR)2 during the hydrolysis and condensation is given by

$$M\text{-}O\text{-}R + H_2O \rightarrow M\text{-}OH + R\text{-}OH \quad \text{(Hydrolysis)}$$

$$M\text{-}O\text{-}H + R\text{-}O\text{-}M \rightarrow M\text{-}O\text{-}M + R\text{-}OH \quad \text{(Condensation)}$$

In essence, the sol-gel process usually consists of 4 steps:

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

(2) The deposition of sol solution produces the coatings on the substrates by spraying, dipping or spinning.

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

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

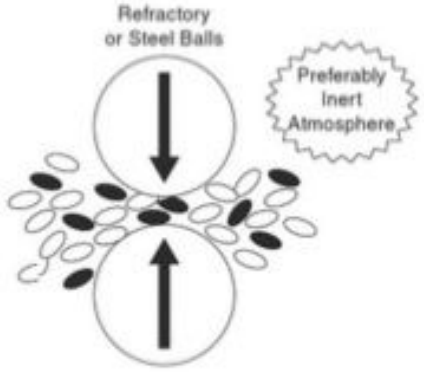
Popular, simple, inexpensive and extremely scalable material to synthesize all classes of nanoparticles.

Can produce amorphous or nanocrystalline materials.

MECHANICAL ATTRITION MECHANISM is used to obtain nanocrystalline structures from either single-phase powders or amorphous materials.

Can use either refractory balls or steel balls or plastic balls depending on the material to be synthesized.

When the balls rotate at a particular rpm, the necessary energy is transferred to the powder which in turn reduces the powder of coarse grain-sized structure to ultrafine nanorange particle.



The energy transferred to the powder from the balls depends on many factors such as

Rotational Speed of the balls

Size of the balls

Number of the Balls

Milling time

Ratio of ball to powder mass

Milling medium /atmosphere

Cryogenic liquids can be used to increase the brittleness of the product

One has to take necessary steps to prevent oxidation during milling process

The selection of ball material indluences the type of material obtained.

Eg) harder material balls, synthesize softer materials

Alpha-alumina and zirconia are widely used ball materials due to their high grinding resistance values.

ADVANTAGES OF BALL MILLING

Scaling can be achieved upto tonnage quantity of materials for wider applications

DISADVANTAGES OF BALL MILLING

Contamination of the milling media

Non-metal oxides require an inert medium, and vacuum or glove box to use powder particles.

So The milling process is restrictive.

5 grand challenges for nanotechnology

The five main challenges are to develop instruments to assess exposure to engineered nano-materials in the air and water and we think that that challenge will take three to ten years. The emergence of new nano-technologies we feel that there is a very real need to monitor exposure to humans in the air and within water. The challenge becomes increasingly difficult in more complex matrices like food.

The second challenge would be to develop and validate methods to evaluate the toxicity of engineered nano-materials within the next 5 to 15 years.

To develop models for predicting the potential impact of engineered nano-materials on the environment and human health.

The next challenge would be to develop reverse systems to evaluate impact on the environment and the health impact of engineered nano-materials over their entire life span, which speaks to the life cycle issue.

The fifth is more of a grand challenge to develop the tools to properly assess risk to human health and to the environment.

Nano-materials Synthesis and Processing

Methods for creating Nanostructures

Methods for fabricating nanomaterials can be generally subdivided into two groups: **top-down** methods, and **bottom-up** methods.

In the first case nanomaterials are derived from a bulk substrate and obtained by progressive removal of material, until the desired nanomaterial is obtained. A simple way to illustrate a top-down method is to think of carving a statue out of a large block of marble. Printing methods also belong to this category.

Bottom-up methods work in the opposite direction: the nanomaterial, such as a nanocoating, is obtained starting from the atomic or molecular precursors and gradually assembling it until the desired structure is formed.

In both methods two requisites are fundamental: control of the fabrication conditions (e.g. energy of the electron beam) and control of the environment conditions (presence of dust, contaminants, etc.). For these reasons, nanotechnologies use highly sophisticated fabrication tools that are mostly operated in a vacuum in clean-room laboratories.

Processes for producing ultrafine powders- Mechanical grinding

Ball-milling of elemental powders has been thoroughly investigated in various conditions of energy transfer to identify the mechanisms by which materials deform to produce nanometer-sized grains, characterize the intergranular and intragranular defects of nanograined ground powders, and measure the resulting changes in properties with respect to those of coarse-grained elements, for instance mechanical, magnetic, hydrogen storage capacity

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Emergence of Nanotechnology

The emergence of nanotechnology has led to the design, synthesis, and manipulation of particles in order to create a new opportunity for the utilization of smaller and more regular structures for various applications. In recent years, nano-sized metal oxide particles have gotten much attention in various fields of application due to its unique optical, electrical, magnetic, catalytic and biomedical properties as well as their high surface to volume ratio and specific affinity for the adsorption of inorganic pollutants and degradation of organic pollutants in aqueous systems.

Bottom up and Top-down approaches

There are two general approaches to the synthesis of nanomaterials and the fabrication of nanostructures.

Bottom-up approach

These approaches include the miniaturization of materials components (up to atomic level) with further self-assembly process leading to the formation

During self-assembly the physical forces operating at nanoscale are used to combine basic units into larger stable structures.

Typical examples are quantum dot formation during epitaxial growth and formation of nanoparticles from colloidal dispersion.

Nanomaterials are synthesized by assembling the atoms/molecules together.

Instead of taking material away to make structures, the bottom-up approach selectively adds atoms to create structures.

Eg) Plasma etching, Chemical vapour deposition

Top-down approach

These approaches use larger (macroscopic) initial structures, which can be externally-controlled in the processing of nanostructures.

Typical examples are etching through the mask, ball milling, and application of severe plastic deformation.

Nanomaterials are synthesized by breaking down of bulk solids into nanosizes

Top-down processing has been and will be the dominant process in semiconductor manufacturing.

Eg) Ball Milling, Sol-Gel, lithography

challenges in Nanotechnology

The challenges arising from nanotechnology is largely on target.

No single person can provide the answers to the challenges that bring nanotechnology, nor can any single group or intellectual discipline. However, those who know the technology best (those who create it) must ultimately prepare the agenda for broad discussion, and participate fully in creation of relevant policy. In the realm of nanotechnology, public policy and science have become inseparable.

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NANO MATERIALS

Nano means small (10^-9 m) but of high potency, and emerging with large applications piercing through all the discipline of knowledge, leading to industrial and technological growth. In other words nano-sized structure needs to be magnified over 10 million times before we can easily appreciate its fine detail with the naked eye. Nanotechnology is already having its impact on products as diverse as novel foods, medical devices, chemical coatings, personal health testing kits, sensors for security systems, water purification units for manned space craft, displays for hand-held computer games, and high-resolution cinema screens. Nanotechnology is expected to have an impact on nearly every industry. The U.S. National Science Foundation has predicted that the global market for nanotechnologies will reach $1 trillion or more within 20 years.

WHAT IS NANO TECHNOLOGY?

Nanotechnology is a catch-all phrase for materials and devices that operate at the nanoscale. In the metric system of measurement, "Nano" equals a billionth and therefore a nanometer is one-billionth of a meter. References to nano materials, nanoelectronics, nano devices and nano powders simply mean the material or activity can be measured in nanometers. To appreciate the size, a human red blood cell is over 2,000 nanometers long, virtually outside the nanoscale range!

Nanotechnology is a multidisciplinary science that has its roots in fields such as colloidal science,device physics and supramolecular chemistry.

NANOTECHNOLOGY is a fundamental, enabling technology, allowing us to do new things in almost every conceivable technological discipline. Nano means small (10^-9 m) but of high potency, and emerging with large applications piercing through all the discipline of knowledge, leading to industrial and technological growth.

Nanotechnology is:

- Comprised of nanomaterials with at least one dimension that measures between approximately 1 and 100 nm
- Comprised of nanomaterials that exhibit unique properties as a result of their nanoscale size
- Based on new nanoscale discoveries across the various disciplines of science and engineering
- The manipulation of these nanomaterials to develop new technologies/applications or to improve on existing ones
- Used in a wide range of applications from electronics to medicine to energy and more

Nanotechnology is the creation of useful or functional materials, devices and systems through control of matter on the nanometer length scale and exploitation of novel phenomena and properties which arise because of the nanometer length scale.

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Module 4

NANO MATERIALS & CHARACTERIZATION TECHNIQUES:

Introduction: Importance of Nano-technology, Emergence of Nanotechnology, Bottomup and Top-down approaches, challenges in Nanotechnology

Nano-materials Synthesis and Processing: Methods for creating Nanostructures; Processes for producing ultrafine powders- Mechanical grinding; Wet Chemical Synthesis of Nano-materials- sol-gel process; Gas Phase synthesis of Nano-materials- Furnace, Flame assisted ultrasonic spray pyrolysis; Gas Condensation Processing (GPC), Chemical Vapour Condensation (CVC).

Optical Microscopy - principles, Imaging Modes, Applications, Limitations.

Scanning Electron Microscopy (SEM) - principles, Imaging Modes, Applications, Limitations.

Transmission Electron Microscopy (TEM) - principles, Imaging Modes, Applications, Limitations.

X- Ray Diffraction (XRD) - principles, Imaging Modes, Applications, Limitations.

Scanning Probe Microscopy (SPM) - principles, Imaging Modes, Applications, Limitations.

Atomic Force Microscopy (AFM) - basic principles, instrumentation, operational modes, Applications, Limitations.

Electron Probe Micro Analyzer (EPMA) - Introduction, Sample preparation, Working procedure, Applications, Limitations.