CHIT 4.2

Unit-I: Nanomaterials and Electron Microscopies

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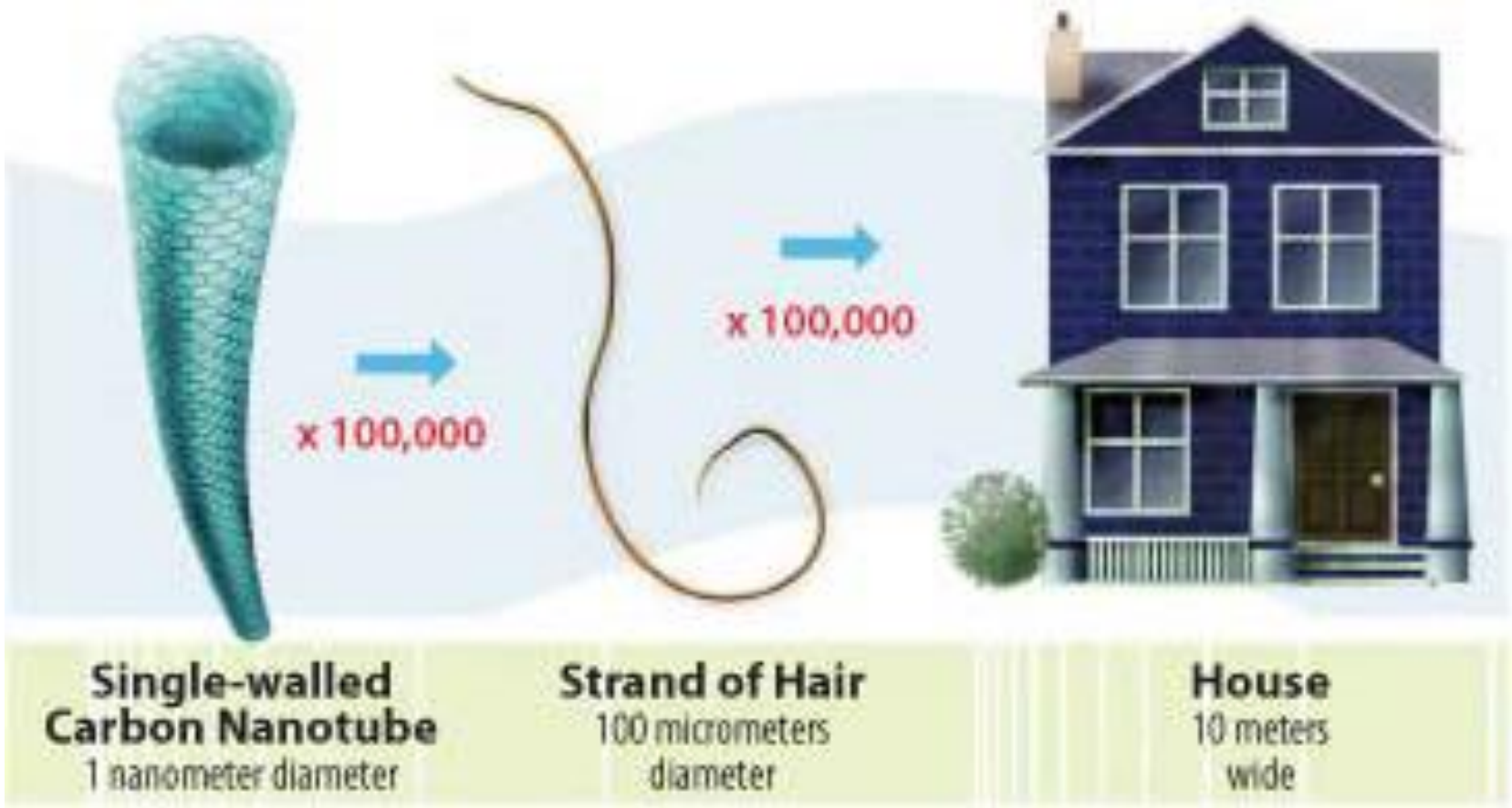
Nanomaterials

- Nanoscale materials are defined as a set of substances having at least one dimension is less than 100 nanometers. A nanometer is one millionth of a millimeter.
- *In Greek nano- means dwarf.*
- Nanomaterials are of interest because at this scale unique catalytic, optical, magnetic, electrical, and thermal properties emerge. These emergent properties have the potential application in electronics, medicine, sensors, drug development, water decontamination, information and communication technologies, and other fields.

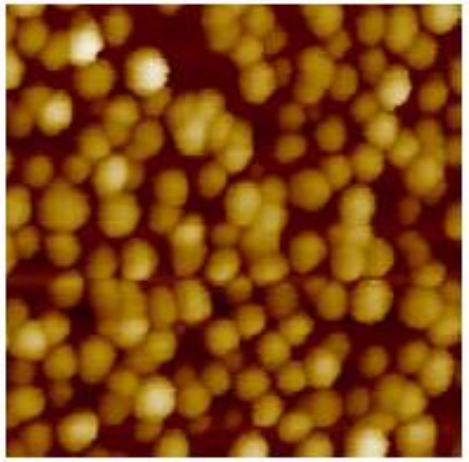
Advances in Nanomaterials

- One of the first scientific report is the colloidal gold particles synthesised by Michael Faraday in 1857. Nanostructured catalysts have also been investigated for over 70 years.
- By the early 1940's, precipitated and fumed silica nanoparticles were being manufactured and sold in USA and Germany as substitutes for ultrafine carbon black for rubber reinforcements.
- Nanosized amorphous silica particles have found large-scale applications in many every-day consumer products, ranging from non-diary coffee creamer to automobile tires, optical fibers and catalyst supports.
- In the 1960s and 1970's metallic nano-powders for magnetic recording tapes were developed.

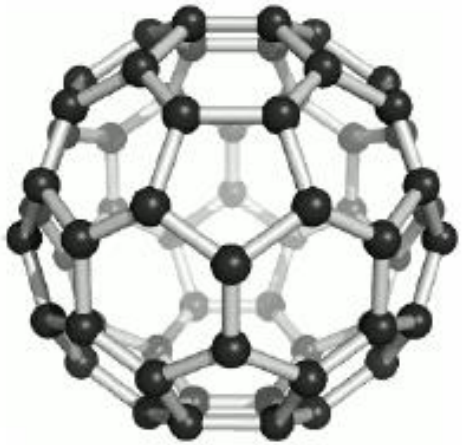


Nanotechnologies **are the design, synthesis, characterisation, and application of structures/ devices by controlling shape and size at nanometre scale.**

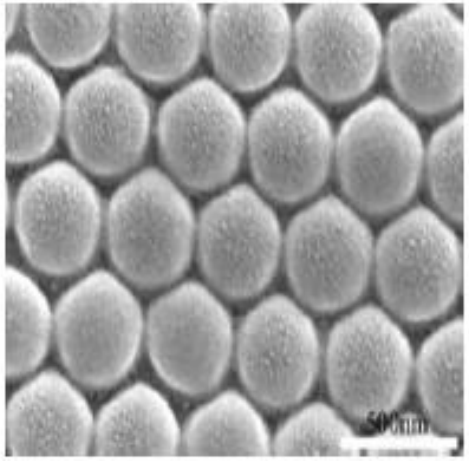
Nanomaterials with a variety of morphologies



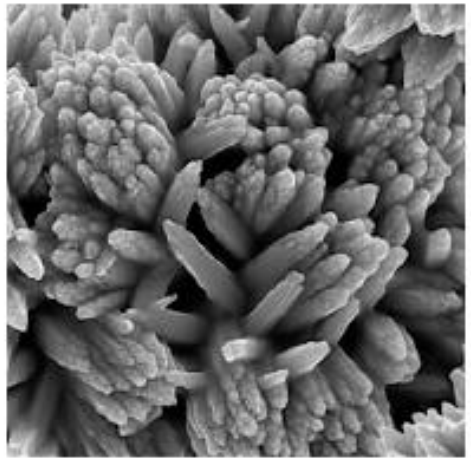
Au nanoparticle



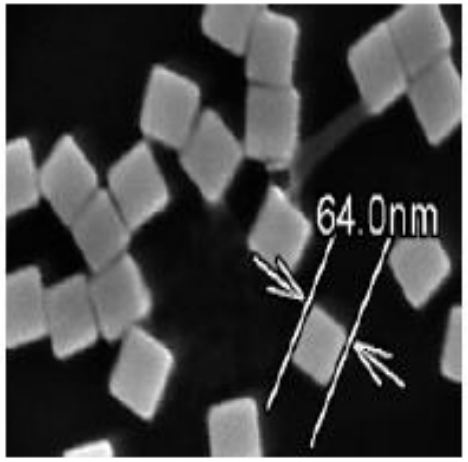
Buckminsterfullerene



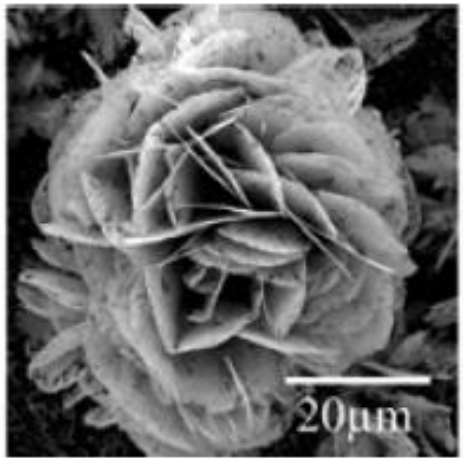
FePt nanosphere



Titanium nanoflower



Silver nanocubes



SnO2 nanoflower

Nanomaterials

- **The first ever concept of nanomaterials was presented in 1959 by professor of physics Dr. Richard P. Feynman.**
- **Invention of the scanning tunneling microscope in 1981 and the discovery of fullerene in 1985 resulted in the emergence of nanotechnology.**

Nanomaterials

Classification of Nanomaterials

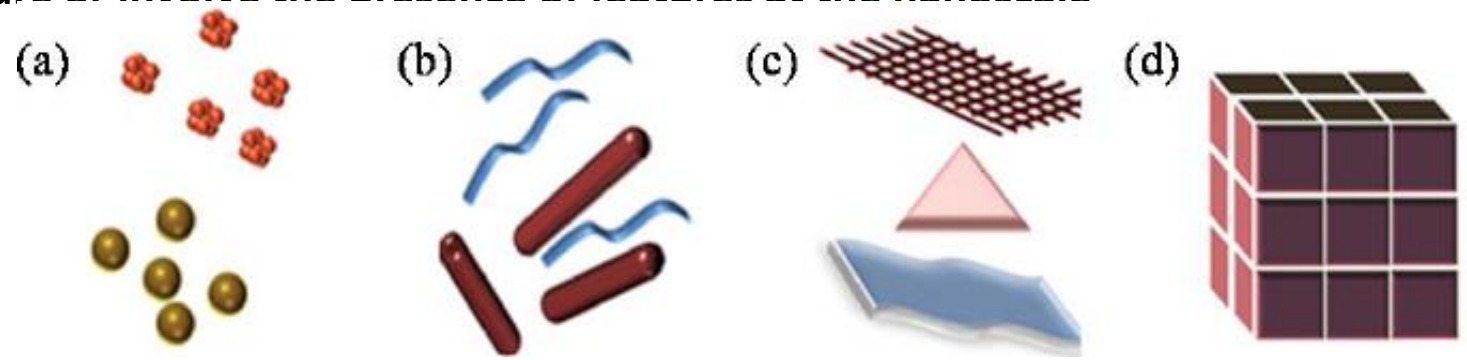
Classification is based on the number of dimensions of a material, which are not confined to the nanoscale range (<100 nm).

1) Zero-dimensional nanomaterials: Materials wherein all the dimensions are measured within the nanoscale (no dimensions are larger than 100 nm). The most common representation of zero-dimensional nanomaterials are nanoparticles Fullerenes, activated carbon, nanoporous silicon

2) One-dimensional nanomaterials: One dimension is outside the nanoscale i.e. 100nm. This leads to needle like-shaped nanomaterials. Eg: nanotubes, nanorods, and nanowires.

3) Two-dimensional nanomaterials: Two of the dimensions are not confined to the nanoscale. 2-D nanomaterials exhibit plate-like shapes. Eg: nanofilms, nanolayers, and nanocoatings, Graphene

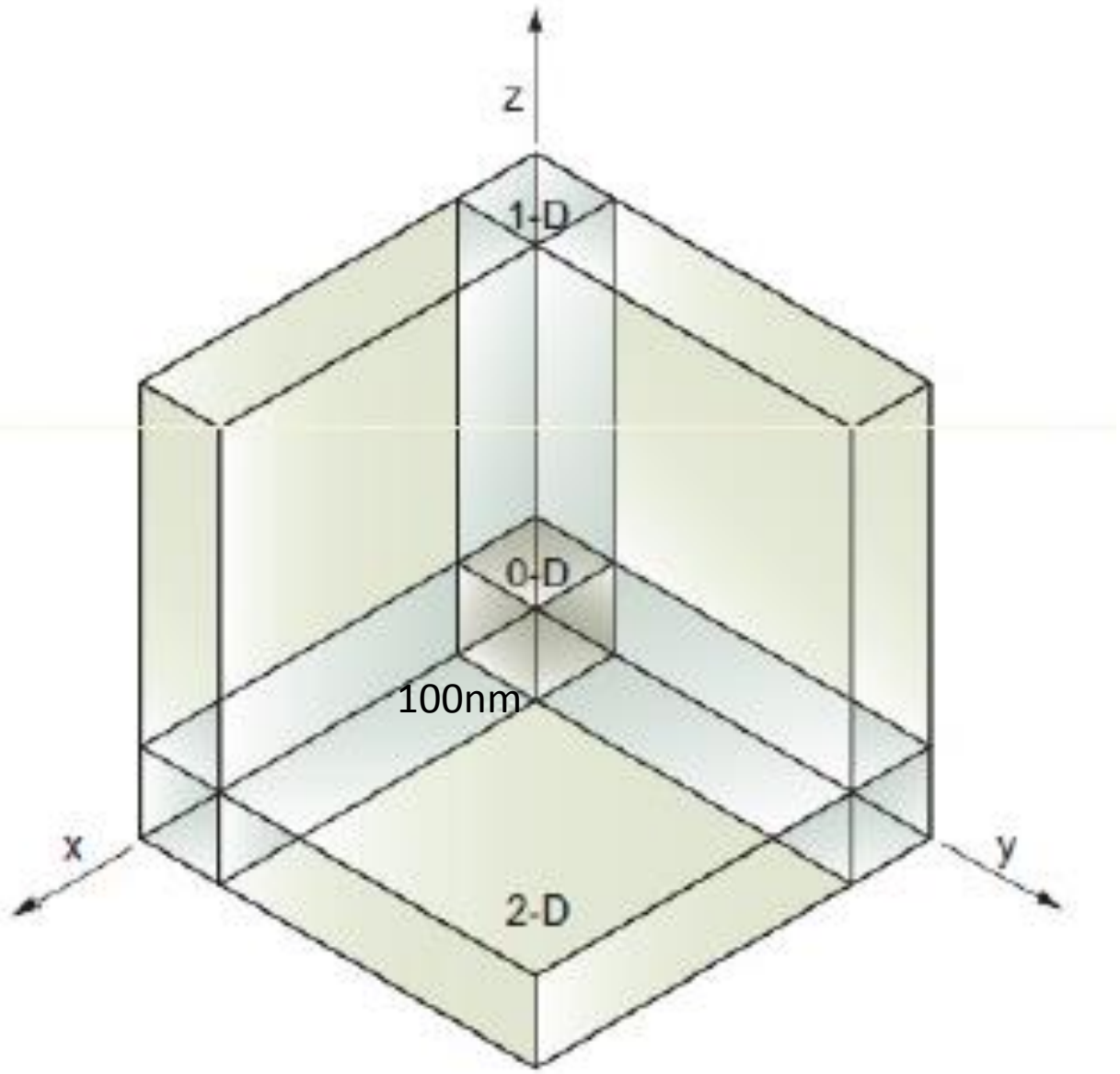
4) Three-dimensional nanomaterials: Bulk nanomaterials are materials that are not confined to the nanoscale in any dimension. These materials are thus characterized by having three arbitrarily dimensions above 100 nm. Materials possess a nanocrystalline structure or involve the presence of features at the nanoscale



Classification of Nanomaterials (a) 0D spheres and clusters, (b) 1D nanofibers, wires, and rods, (c) 2D films, plates, and networks, (d) 3D nanomaterials.

Nanomaterials

Three-dimensional space showing the relationships among 0-D, 1-D, 2-D, and 3-D nanomaterials.



0-D: All dimensions at the nanoscale

1-D: Two dimensions at the nanoscale, one dimension at the macroscale

2-D: One dimension at the nanoscale, two dimensions at the macroscale

3-D: No dimensions at the nanoscale, all dimensions at the macroscale

Nanomaterials

Classification based on pore dimensions:

A useful way to classify nanoporous materials is by the diameter size of their pores, since most of the properties, which are interesting for the applications of adsorption and diffusion are dependent on this parameter.

According to IUPAC definition, nanoporous materials are classified in three main groups depending on their pore dimension

Microporous materials (d<2 nm):

- **These materials have very narrow pores. They can host only small molecules, such as gases or linear molecules, and generally show slow diffusion kinetics and high interaction properties.**
- **They are generally used in gas purification systems, membrane filters or gas-storage materials.**

Example: naturally occurring clay materials, MOF's.

Mesoporous materials (2<d<50 nm):

- **These materials have pores with diameter size enough to host some big molecules, for example aromatic systems or large polymeric monomers.**
- **Diffusion kinetics of the adsorbed molecules is often due to capillarity, with an initial interaction with the pore wall followed by pore filling. These systems can be used as nano-reactors for the polymerization or adsorbing systems for liquids or vapours.**

Example: MCM-41 (Mobil composition of matter No. 41 developed by Mobil Oil Corporation), MCM48, SBA15 and carbon mesoporous materials, MOF's etc.

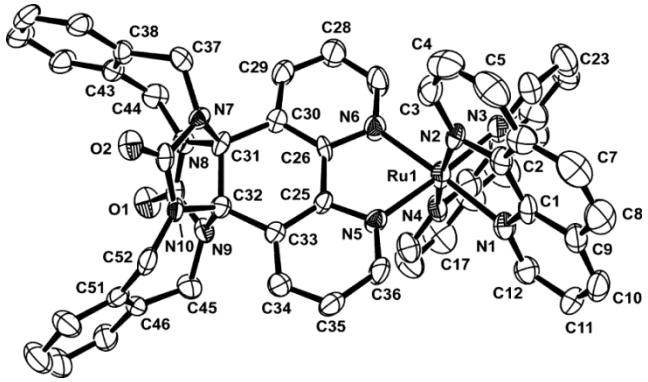
Macroporous systems (d>50 nm):

- **Pores of these materials could host very large molecules, such as poly-aromatic systems or small biological molecules.**

- **These materials are principally used as matrices to store functional molecules, and as sensing materials.**

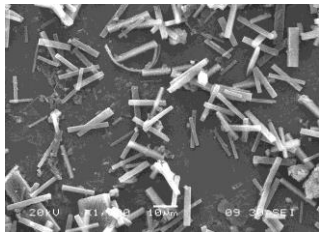
Example: Carbon micro tubes, Porous gels and porous glasses

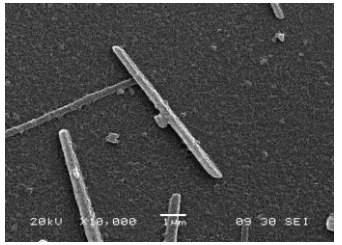
Self-association of Complexes in Water

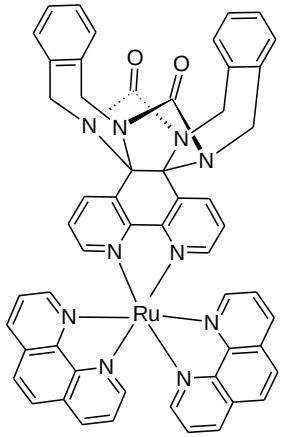


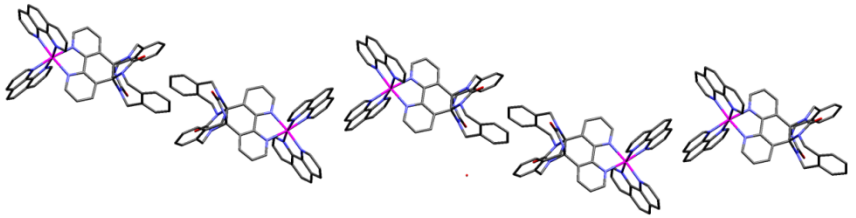
ORTEP diagram of $[Ru(phen)_2(bxbg)]^{2+}$ cation

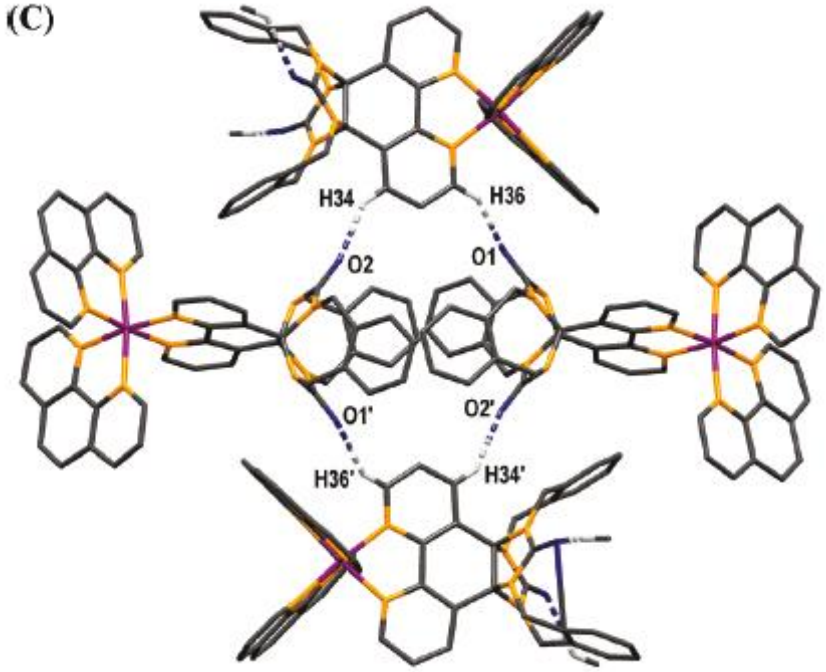
SEM images of aggregates

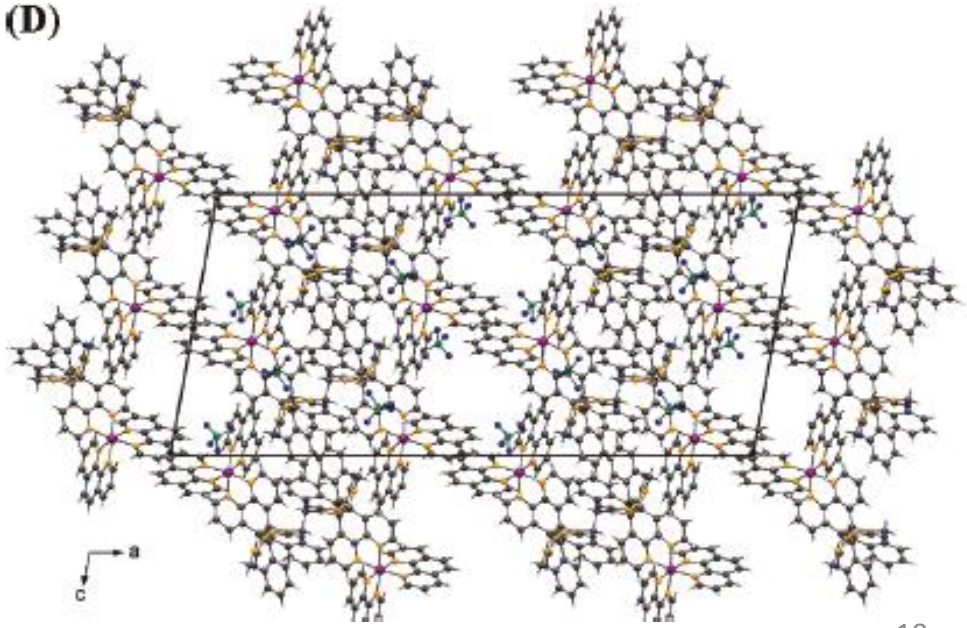


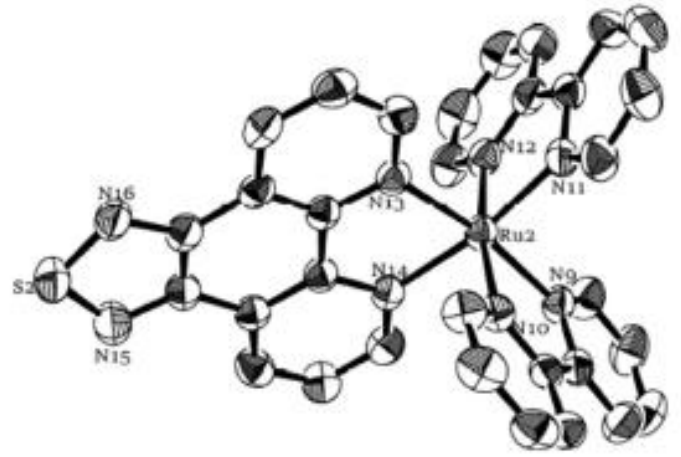


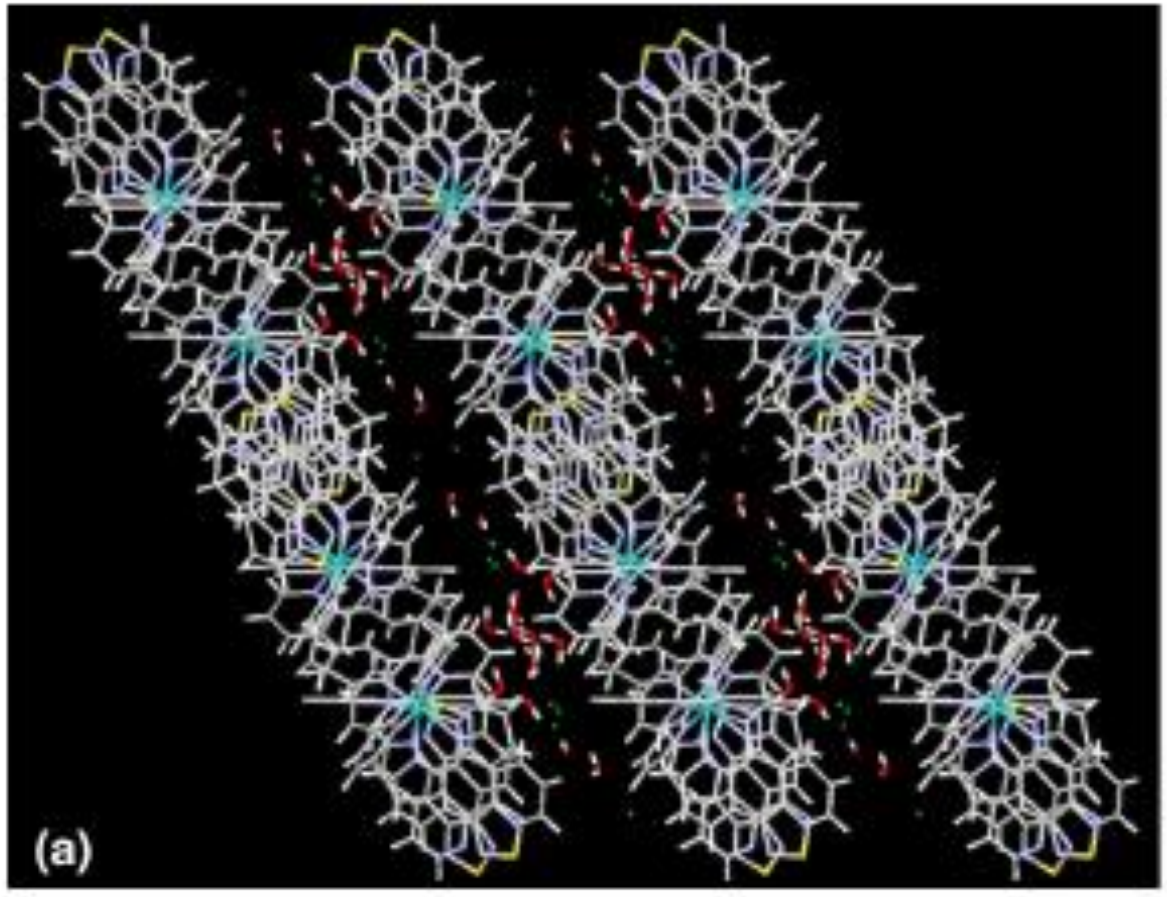


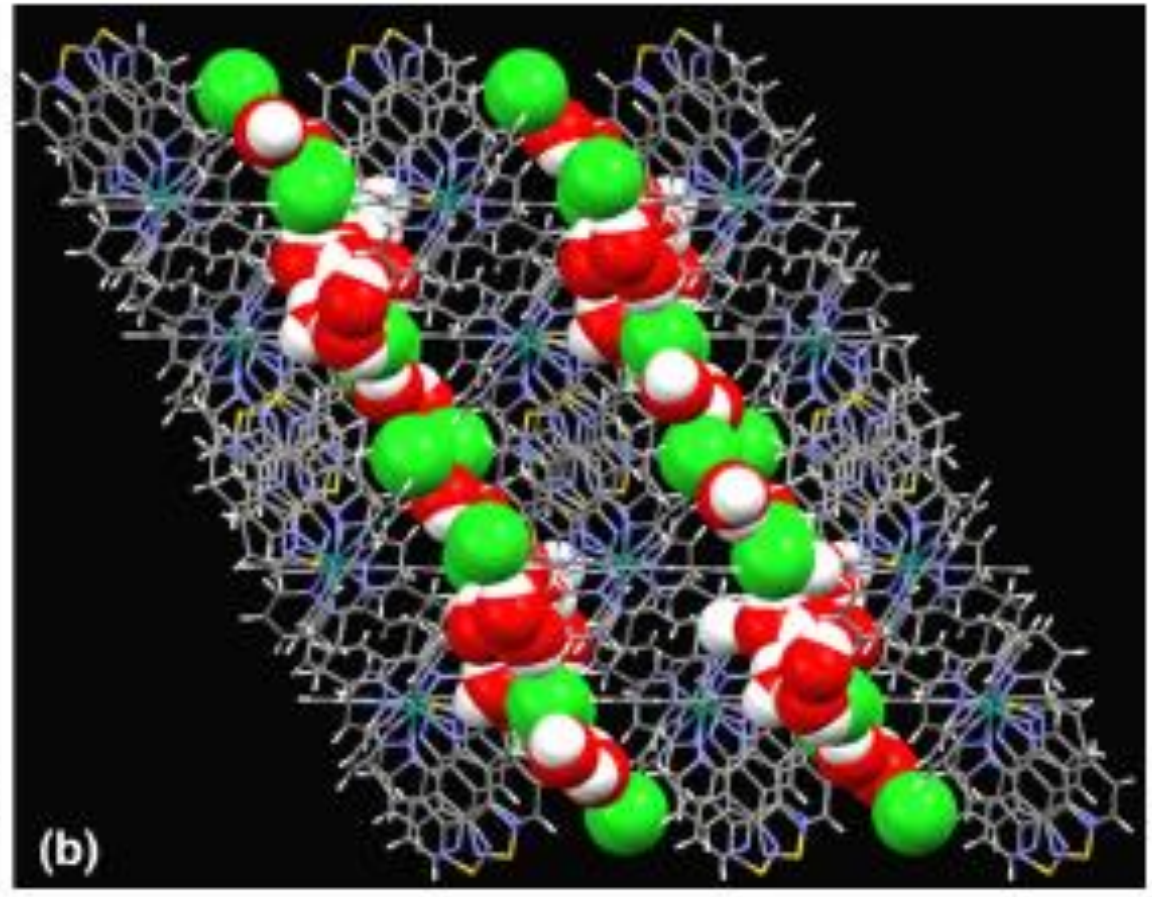







N16
N13
N12
N11
Ru2
N14
N9
S2
N10
N15


(a)


(b)

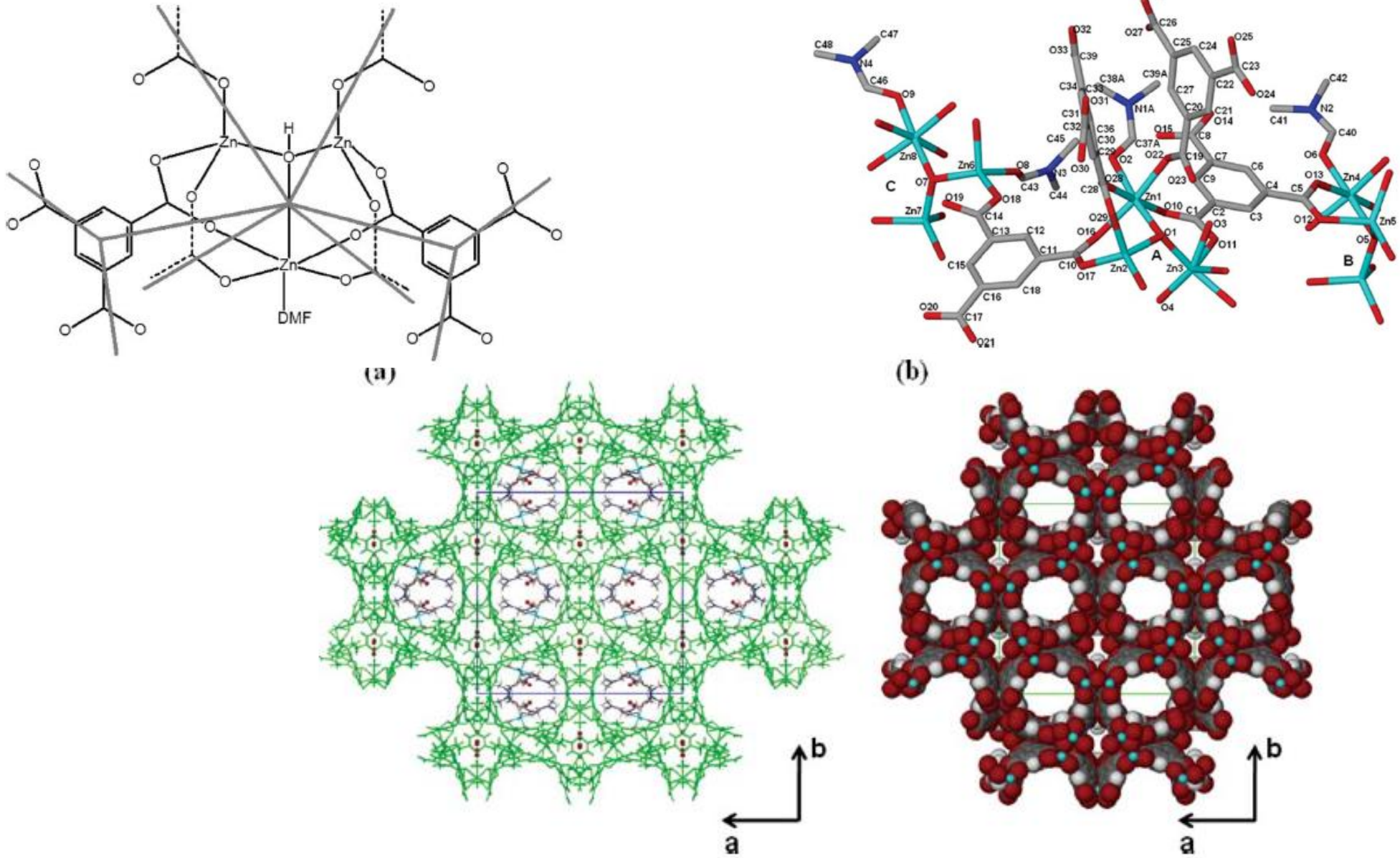
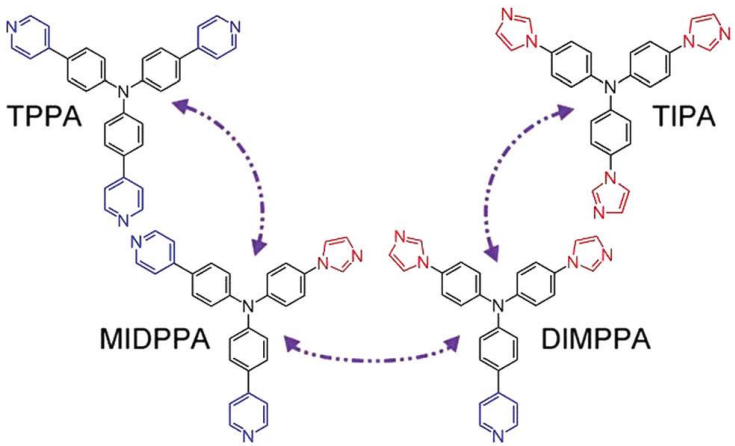
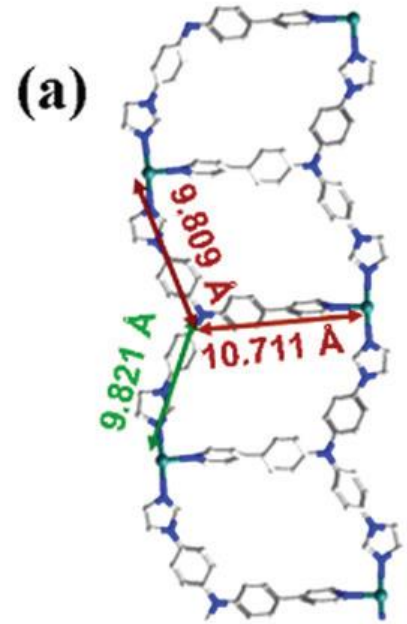
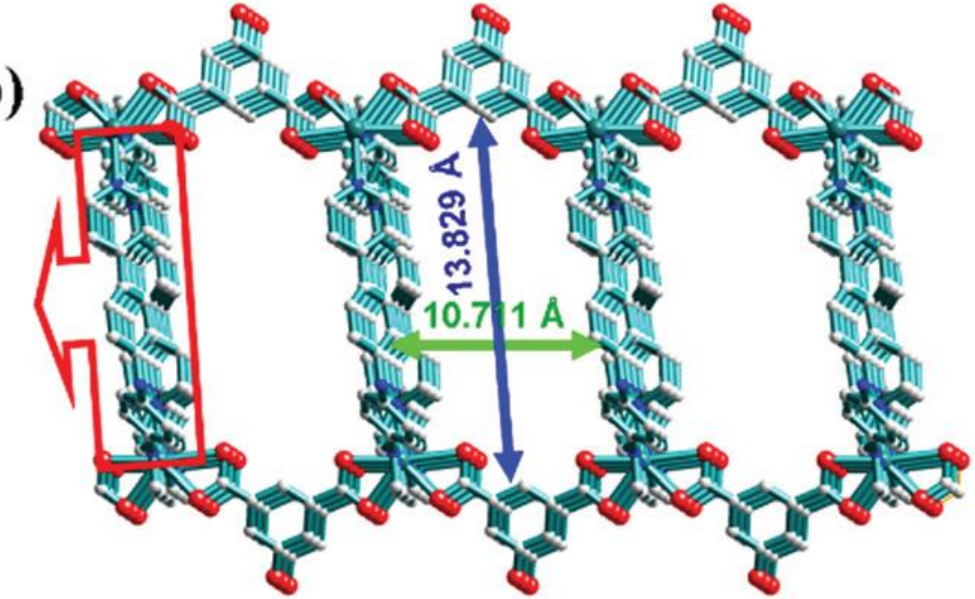
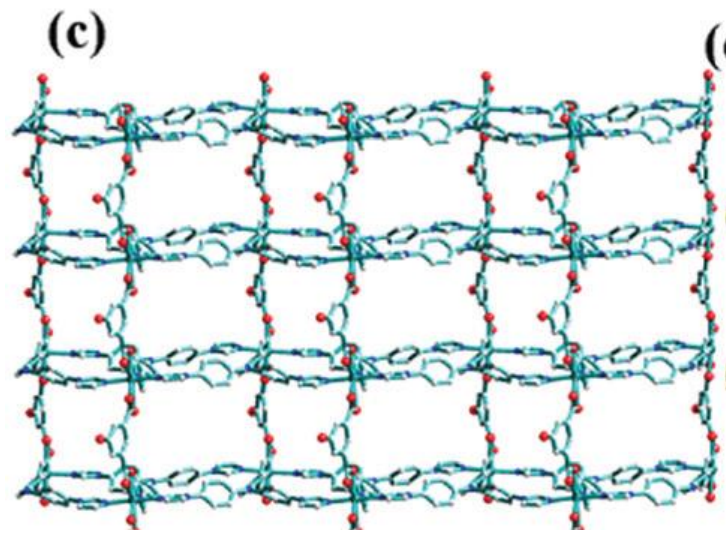


Fig. 3 (a) Packing diagram of **1** viewed along [001], framework shown in green. (b) Packing diagram of **1** viewed along [001] with the framework shown with van der Waals radii and counter ion and guest molecules omitted.









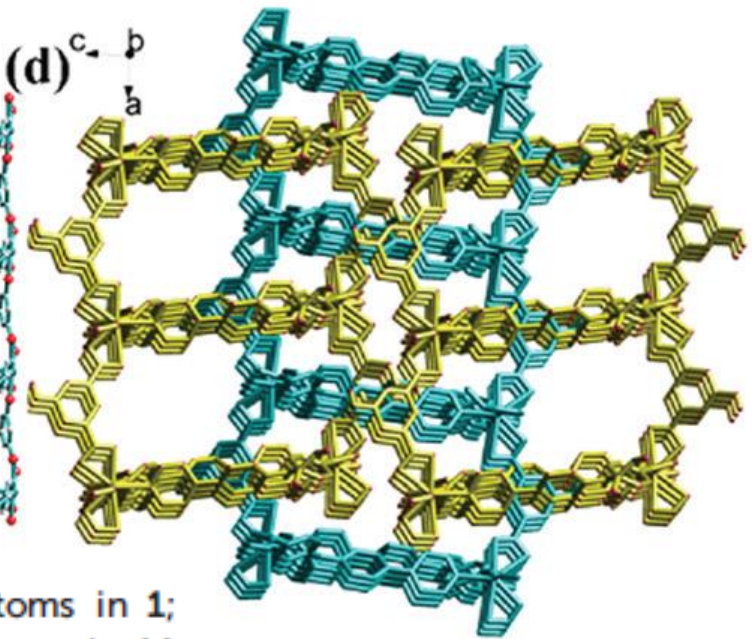


Fig. 2 (a) 1D chains constructed by DIMPPA and Cd^{2+} atoms in **1**; (b) single network of **1** along the *b* axis; (c) a view of the single network of **1** along the *c* axis; (d) 2D → 3D structure of **1** *via* parallel polycatenation.

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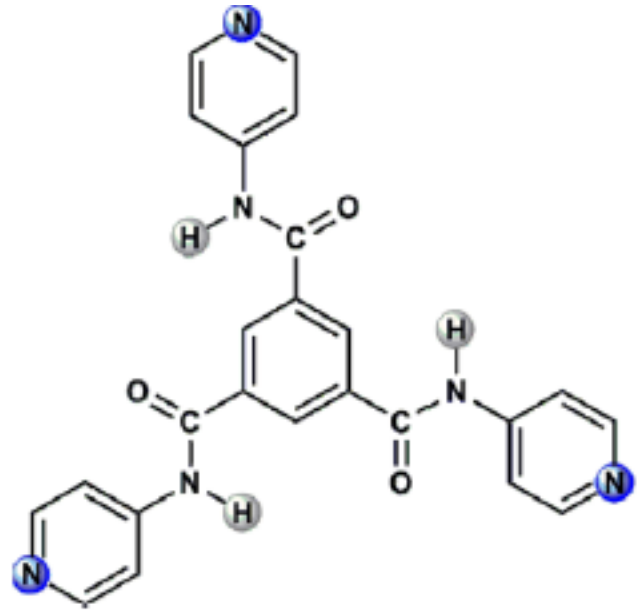
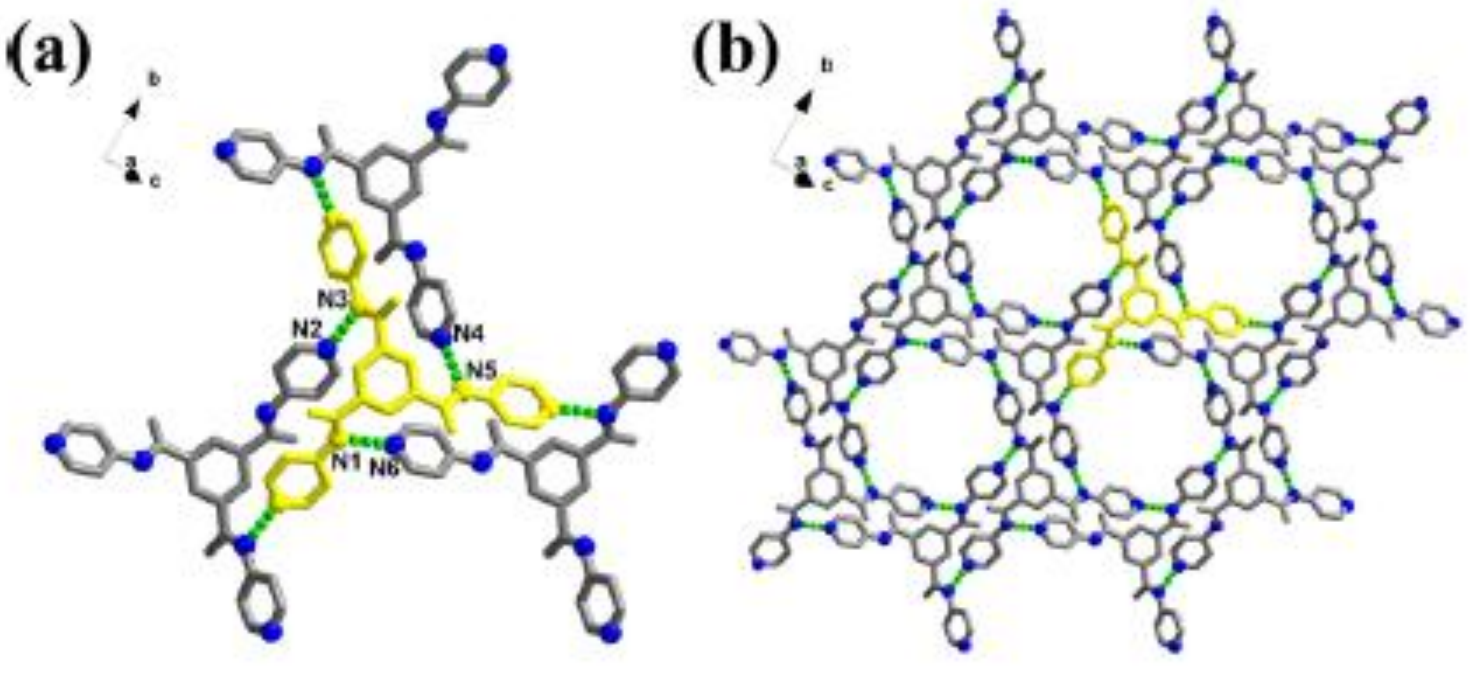
A Microporous Hydrogen-Bonded Organic Framework: Exceptional Stability and Highly Selective Adsorption of Gas and Liquid





Properties and applications of Nanoporous materials

- Nanoporous materials consist of a regular organic or inorganic framework supporting a porous structure.
- Typical examples of nanoporous solids are zeolites, activated carbon, metal–organic frameworks, ceramics, silicates, aerogels, pillared materials, various polymers and inorganic porous hybrid materials.
- In recent years, nanoporous materials have been recognized as promising candidates for the multifunctional applications such as catalysis, ion-exchange, gas storage, low density magnetic storage, etc.
- Nanoporous materials have the surface area of 500-1000m^2/gm, which enhances the catalytic activity.
- Since they have very low thermal conductivity values, they are used in thermal insulators.
- Because of high porosity (90-99%), they are extensively used in membrane technology.

Characterization techniques of nanomaterials

S. No.	Techniques	Information acquired
1.	Scanning Electron Microscopy (SEM) with Energy-dispersive X-ray spectroscopy	Surface topography (up to 10nm) and composition
2.	Transmission Electron Microscopy (TEM)	Surface morphology (up to 0.2nm)
3.	Atomic Force Microscopy	Identification of individual surface atoms
4.	Particle Size Analyzer	Particle Size distribution
5.	FT-Raman Spectra	Distinguish single walled carbon nanotubes and multi walled carbon nanotubes
6.	Photoluminescence Spectra	CNT chirality or Asymmetry determination
7.	X-ray photoelectron spectroscopy	Electronic state of the element

Silent features/Properties of Nanomaterials:

a) Chemical properties: Reactivity; Catalysis.

b) Thermal property: Melting point.

c) Electronic properties: Electrical conduction.

d) Optical properties: Absorption and scattering of light.

e) Magnetic properties: Magnetization.

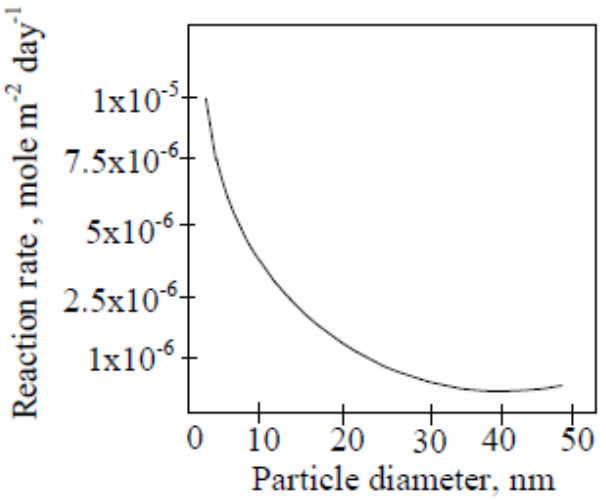
Silent features /properties of Nanomaterials

1) Chemical Properties based on Surface area

nanoscale materials have:

- ❑ **Increased total surface area, increases number of atoms accessible on the surface leading to enhanced catalytic activity.**
- ❑ **Different/tunable surface catalytic properties by the change in shape, size and composition.**
- ➢ **Hence, nanoscale catalysts can increase the rate, selectivity and efficiency of various chemical reactions.**

A good example is the catalytic activity of gold. Bulk gold is catalytically inactive. But, gold nano-particles are catalytically very active for selective redox reactions.



Effect of Particle Size on the Reaction Rate

Silent features / properties of Nanomaterials

2) Electrical properties:

- In bulk materials electronic bands are continuous due to overlapping of orbits of billions of atoms, hence conduction of electrons is delocalized, that is, electrons can move freely in all directions.

- When the scale is reduced to nanoscale, only very few atoms or molecules are present where the quantum effect dominates and electronic bands becomes separate. For zero dimensional nanomaterials, all the dimensions are at the nanoscale and hence the electrons are confined in 3-D space. Therefore no electron delocalization (freedom to move) occurs.

- For one dimensional nanomaterials, electrons confinement occurs in 2-D space and hence electron delocalization takes place along the axis of nanotubes/nanorods/nanowires.

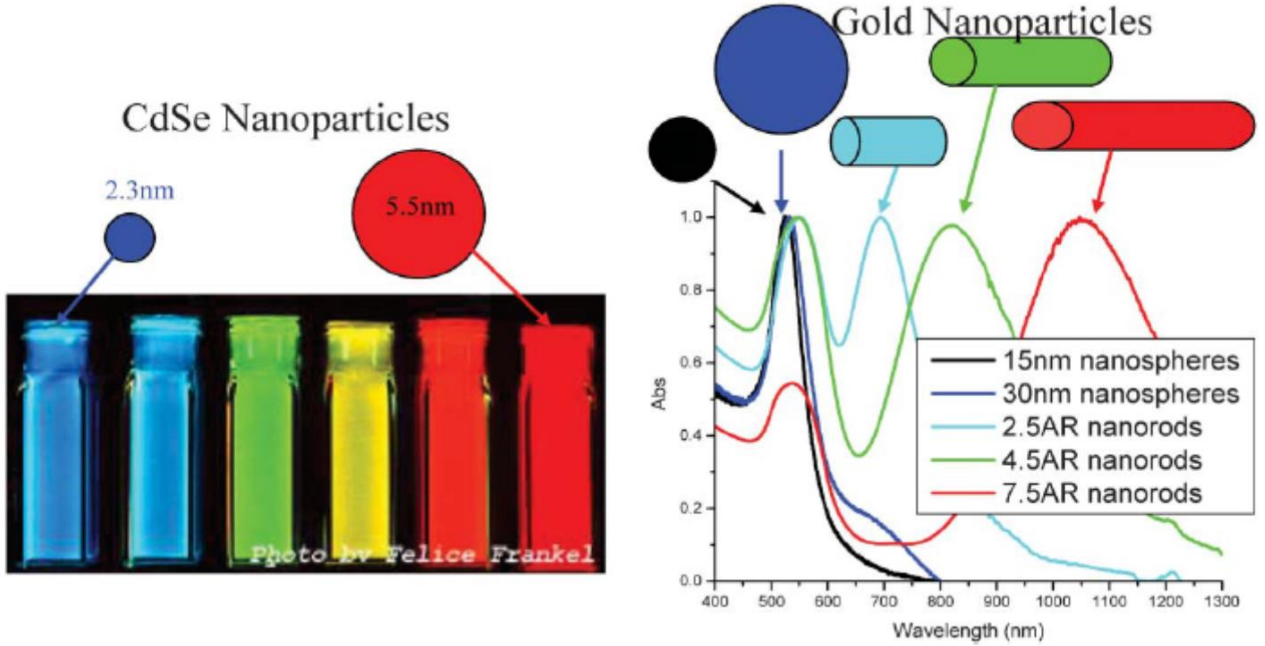
- Due to electron confinement, the energy bands are replaced by discrete energy states which make the conducting materials to behave like either semiconductors or insulators. Hence, some metals which are good conductors in bulk become semiconductors and insulator as their size is decreased to nano level.

Silent features / properties of Nanomaterials

3) Optical properties:

One of the most fascinating and useful aspects of nanomaterials is their optical properties. Applications based on optical properties of nanomaterials include optical detector, laser, sensor, imaging, phosphor, display, solar cell, photocatalysis, photo-electrochemistry and biomedicine.

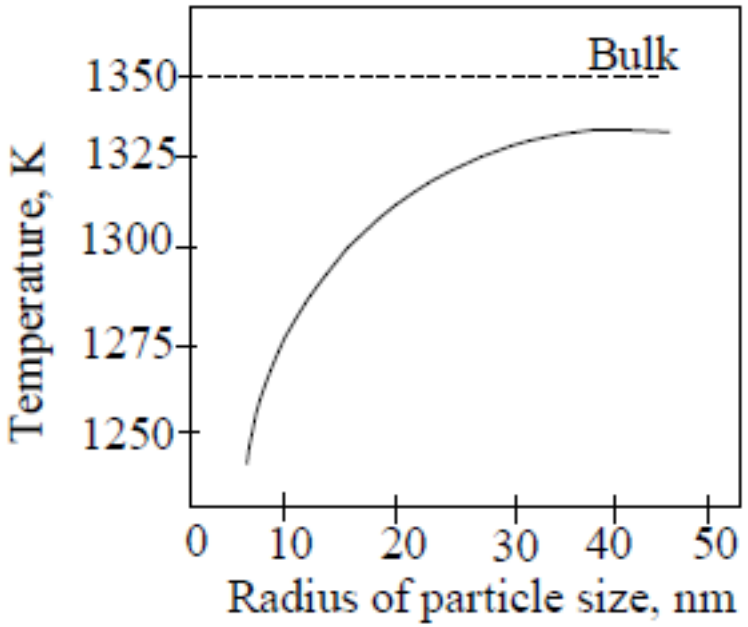
The optical properties of nanomaterials depend on parameters such as feature size, shape, surface characteristics of nanostructures. Likewise, shape can have dramatic influence on optical properties of metal nanostructures. In the CdSe semiconductor nanoparticles, a simple change in size alters the optical properties of the nanoparticles. When metal nanoparticles are enlarged, their optical properties change only slightly as observed for the different samples of gold nanospheres in fig. below .



Silent features / properties of Nanomaterials

4) Thermal Properties

- **The melting point of a material directly correlates with the bond strength. In bulk materials, the surface to volume ratio is small and hence the surface effects can be neglected. However, in nanomaterials the melting temperature is size dependent and it decreases with the decrease particle size diameters. The reason is that in nanoscale materials, surface atoms are not bonded in direction normal to the surface plane and hence the surface atoms will have more freedom to move.**



Effect of Particle Size on the Melting Point

Synthetic Methods

The particle size, chemical composition, crystallinity and shape of nanomaterials can be controlled by temperature, pH value, concentration, chemical composition and surface modifications.

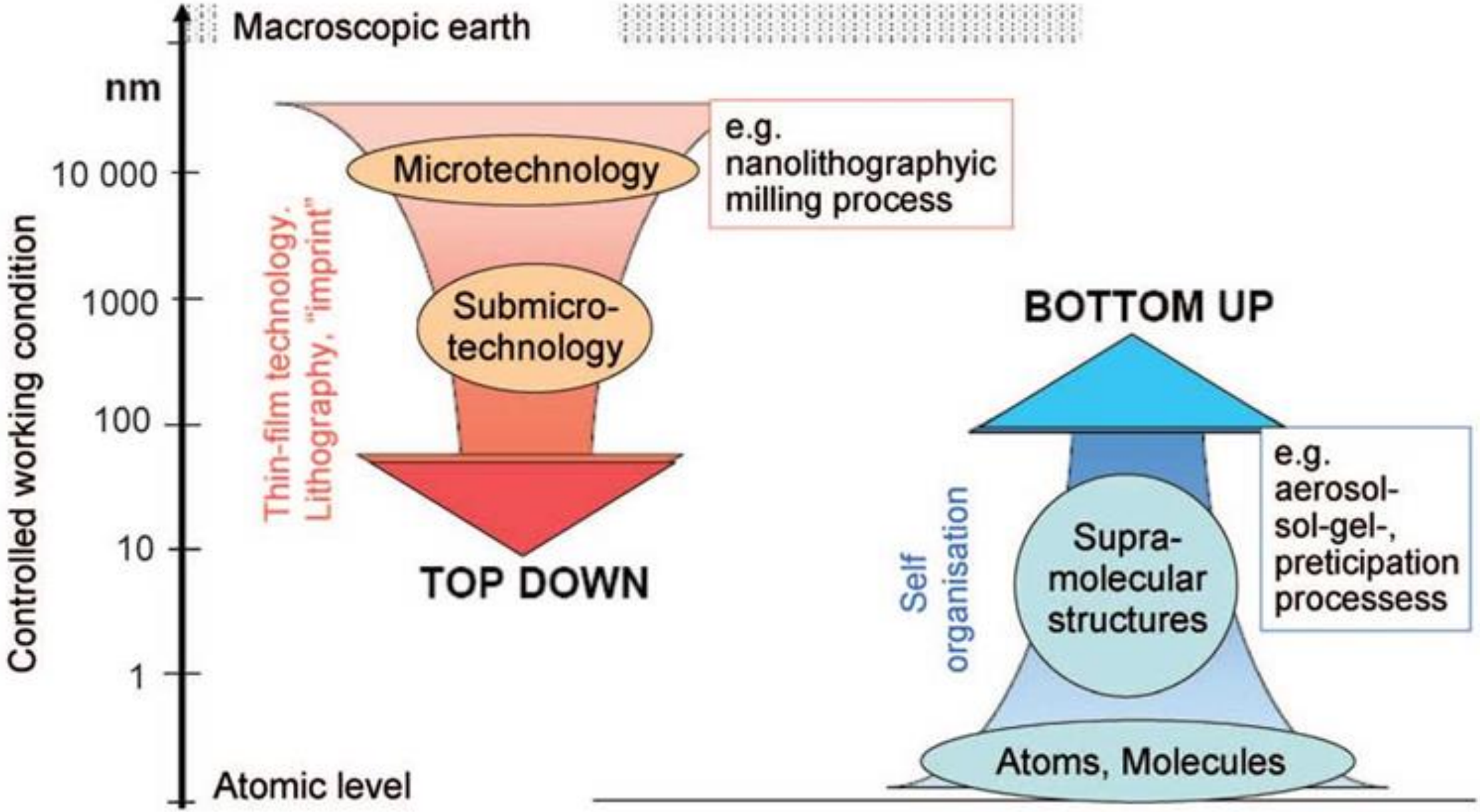
Two basic strategies of synthesis of nanoparticle are:

(i) Bottom-up approach: The building of nanostructures starting with small components such as atoms or molecules is called bottom-up approach.
Ex: Sol-Gel Process, precipitation, Chemical vapour deposition, Chemical Reduction methods, etc.

(ii) Top-down approach: The process of making nanostructures starting with larger structures and breaking away to nano size is called top-down approach.
Ex: Ball milling, Grinding, Lithography, Epitaxy, etc.

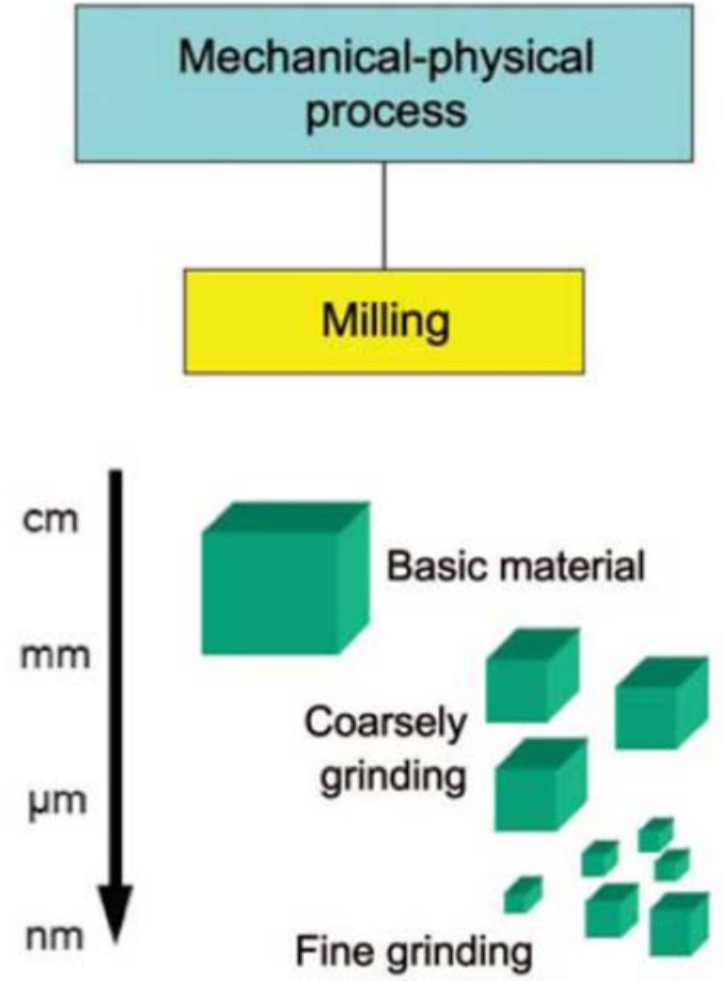
The selection of the respective process depends on the chemical composition and desired features specified for the nanoparticles.

Synthetic Methods



1) Top-down approach/ Mechanical-physical production process:

'Top-down' refers to mechanical-physical particle production processes based on principles of microsystem technology. The traditional mechanical-physical crushing methods for producing nanoparticles involve various milling techniques



1) Top-down approach/ Mechanical-physical production process:

a) Milling processes

- The mechanical production approach uses milling to crush microparticles.
- This approach is applied in producing metallic and ceramic nanomaterials.
- For metallic nanoparticles, for example, traditional source materials (such as metal oxides) are pulverized using high-energy ball mills. Such mills are equipped with grinding media composed of wolfram carbide or steel.
- Milling involves thermal stress and is energy intensive. Lengthier processing can potentially abrade the grinding media, contaminating the particles.
- Compared to the chemo-physical production processes (see below), using mills to crush particles yields product powders with a relatively broad particle-size ranges. This method does not allow full control of particle shape.

2) Bottom-up/Chemo-physical production processes

Bottom-up methods are based on physicochemical principles of molecular or atomic self-organization. This approach produces selected, more complex structures from atoms or molecules, better controlling sizes, shapes and size ranges. It includes aerosol processes, precipitation reactions and sol-gel processes.

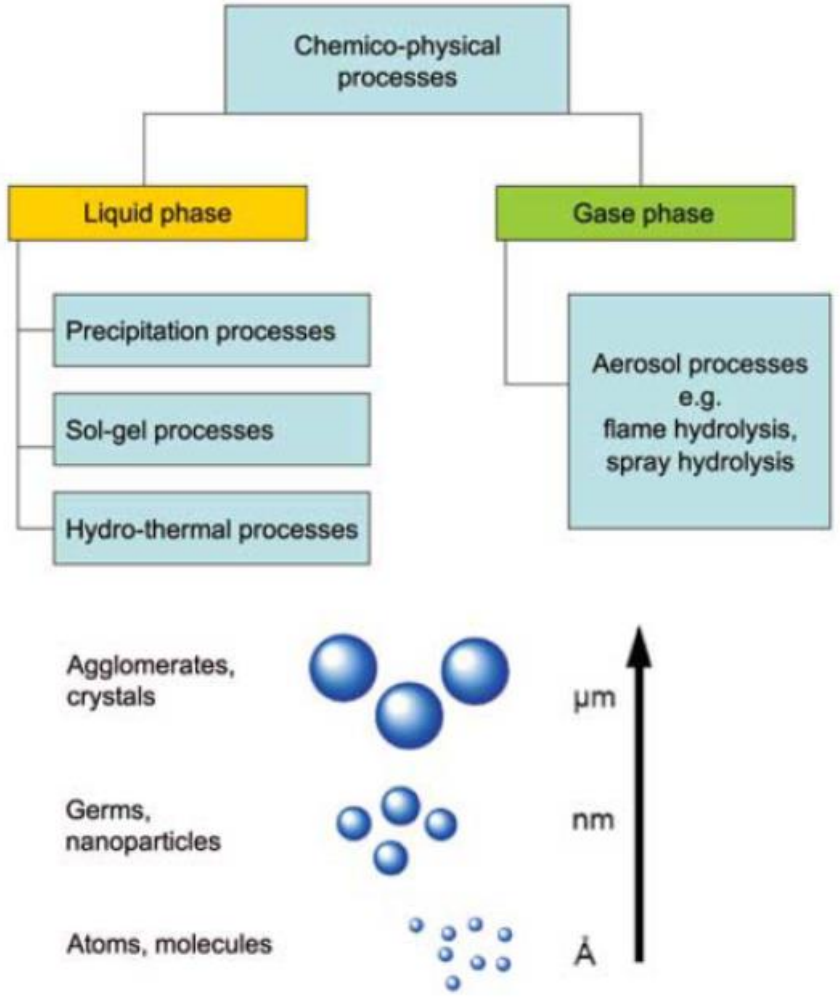


Figure: Chemo-physical process in nanoparticle production.

Liquid phase processes:

The wet-chemical synthesis of nanomaterials typically takes place at lower temperatures than gas phase synthesis. The most important liquid phase processes in nanomaterial production are precipitation, sol-gel-processes and hydrothermal.

a) Precipitation processes

- **The precipitation of solids from a metal ion containing solution is one of the most frequently employed production processes for nanomaterials.**
- **Metal oxides as well as metallic nanoparticles can be produced by this approach.**
- **The process is based on reactions of salts in solvents. A precipitating agent is added to yield the desired particle precipitation, and the precipitate is filtered out and thermally post-treated.**
- **In precipitation processes, particle size and size distribution, crystallinity and morphology (shape) are determined by reaction kinetics (reaction speed). The influencing factors include, beyond the concentration of the source material, the temperature, pH value of the solution, the sequence in which the source materials are added, and mixing processes.**
- **A good size control can be achieved by using self-assembled membranes, which in turn serve as nanoreactors for particle production. Such nanoreactors include microemulsions, bubbles, micelles and liposomes. They are composed of a polar group and a non-polar hydrocarbon chain.**

Precipitation Method:

In this method solid nano particles are obtained by careful precipitation from their solution. Precipitation method can be used to prepare nano particles of metal oxides, metal sulphides and metals.

a) In this method, an inorganic metal salt (such as nitrate, chloride or acetate of metal) is dissolved in water (precursor solution)

b) Metal cations exist in the form of metal hydrate species, for example, $(Al(H_2O)_6)^{3+}$ or $(Fe(H_2O)_6)^{3+}$.

c) These metal hydrates are added to precipitating agent like NaOH or NH_4OH, it changes the pH & causes condensation of precursor.

d) Thus concentration of solution increases and reaches a critical level called super saturation. At this concentration nucleus formation is initiated. The nucleus further grows into particles, which gets precipitate.

e) The precipitate obtained is filtrated, washed with water, air dried and finally calcined at high temperature to get nanomaterial.

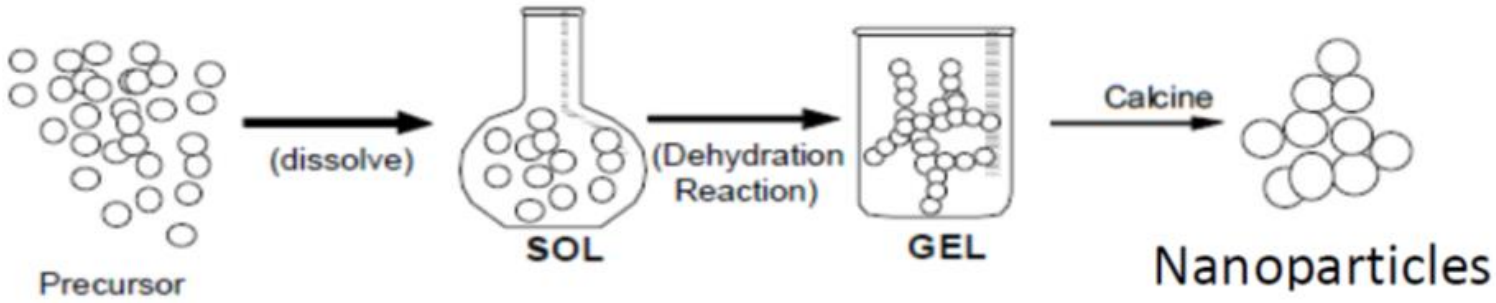
Advantages

1. The process is relatively economical.
2. Wide range of single and multicomponent of oxide nano powders can be synthesized.

b) Sol-Gel-Method

The sol-gel process has been mainly used in the synthesis of monodispersed nano particles of metal oxide and temperature sensitive organic- inorganic hybrid material.

Examples: Zinc oxide nano particles, TiO_2 nano particles can be synthesized by this method.



The following steps are involved in the synthesis of nano materials by sol-gel process.

a) Preparation of sol: In this method, metal alkoxide is used a precursor to synthesis nano particles of a metal oxide. Metal alkoxide is dissolved in alcohol and then water is added under acidic or neutral or basic conditions. Addition of water leads to hydrolysis in which alkoxide ligand is replaced with a hydroxyl ligand.

$$MOR + H_2O \text{—>} MOH + ROH \text{ (hydrolysis)}$$

b) Conversion of sol to gel: The polycondensation reaction between MOH and ROM results in the formation of an oxide —or alcohol —bridged network(gel).

$$MOH + ROM \text{ —>} M—O—M + R—OH \text{ (Polycondensation)}$$

b) Sol-Gel-Method cont……

c) Aging of the gel: The reaction mixture is allowed to continue polycondensation reactions until the gel transforms into a solid mass, accompanied by contraction of the gel network and expulsion of solvent from gel pores.

d) Removal of a solvent: The water and other volatile liquids are removed from the gel network. If isolated by thermal evaporation, the resulting product is termed a xerogel. If the solvent is extracted under supercritical conditions, resulting product is termed an aerogel.

e) Heat treatment: The sample obtained is calcined at high temperature (800°C) to obtain nano particles. Nano particles formed by sol-gel process commonly have a size ranging from 1 to 100 nm.

Advantages :

1. Nano materials of high purity with good homogeneity can be obtained.
2. Samples can be prepared at lower temperature.
3. Easy to control synthesis parameters to control physical characteristics like shape and size of the resulting materials.
4. Simple and inexpensive equipment

Applications of Sol-gel process :

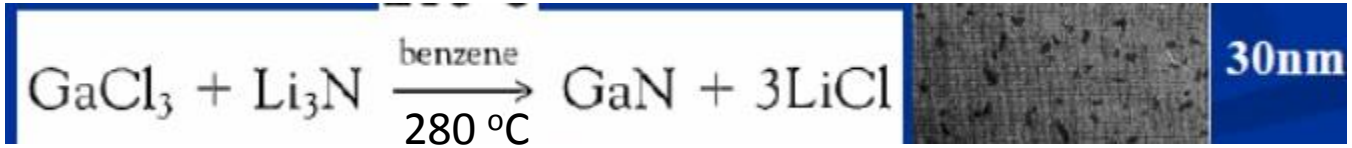
- **It can be used in ceramics manufacturing processes or as a means of producing very thin films of metal oxides for various purposes.**

- **Sol-gel derived materials have diverse applications in optics, electronics, energy, space, (bio) sensors, medicine (e.g. controlled drug release) and separation (e.g. chromatography) technology.**

- **One of the more important applications of sol-gel processing is to carry out zeolite synthesis.**

Hydrothermal/solvothermal Synthesis

- **Hydrothermal synthesis refers to the synthesis by chemical reactions of precursors reactants in a sealed heated aqueous solution above ambient temperature and pressure.**
- **Solvothermal synthesis route was first proposed by Yi-Tai Quian in 1996 (University of Science and Technology of China) and similar to the hydrothermal route, only difference is precursor solution is usually non-aqueous.**



- **"A solvothermal reaction can be defined as a chemical reaction (or a transformation) between precursor(S) in a solvent (in a closed system) at a temperature higher than boiling temperature of that solvent and under higher pressure (autogenous or imposed pressure).**

Apparatus Hydrothermal Synthesis

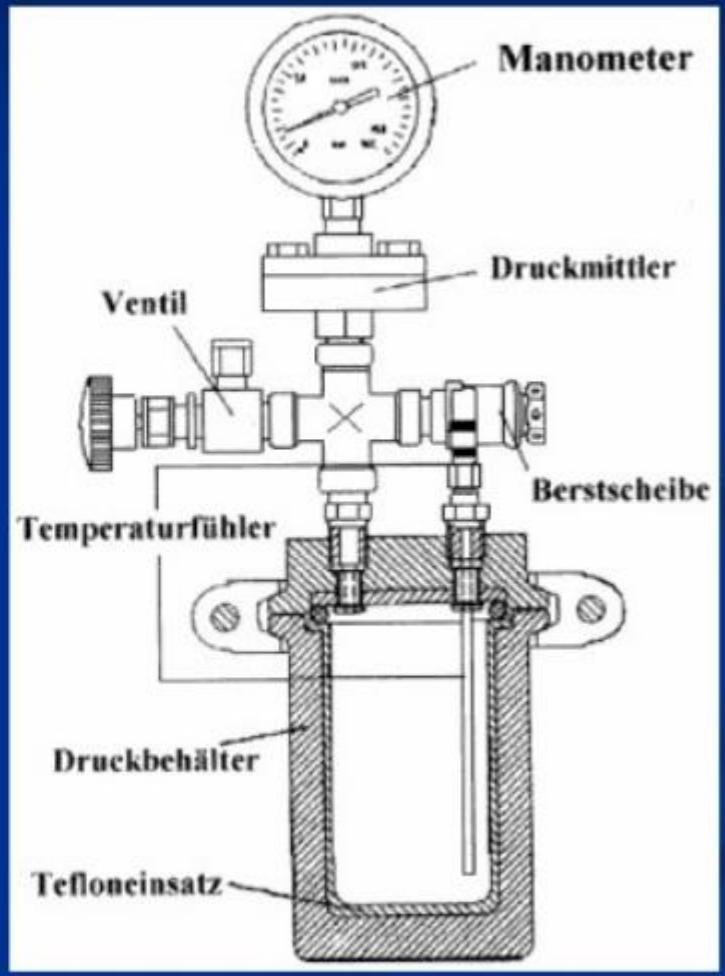
- Usually autoclaves are used in hydrothermal/solvothermal synthesis are usually thick walled steel cylinders with a hermetic seal (makes a given object airtight) which must withstand high temperatures and pressures for prolonged periods of time.

- Further, the autoclaves material must be inert with respect to the solvent.

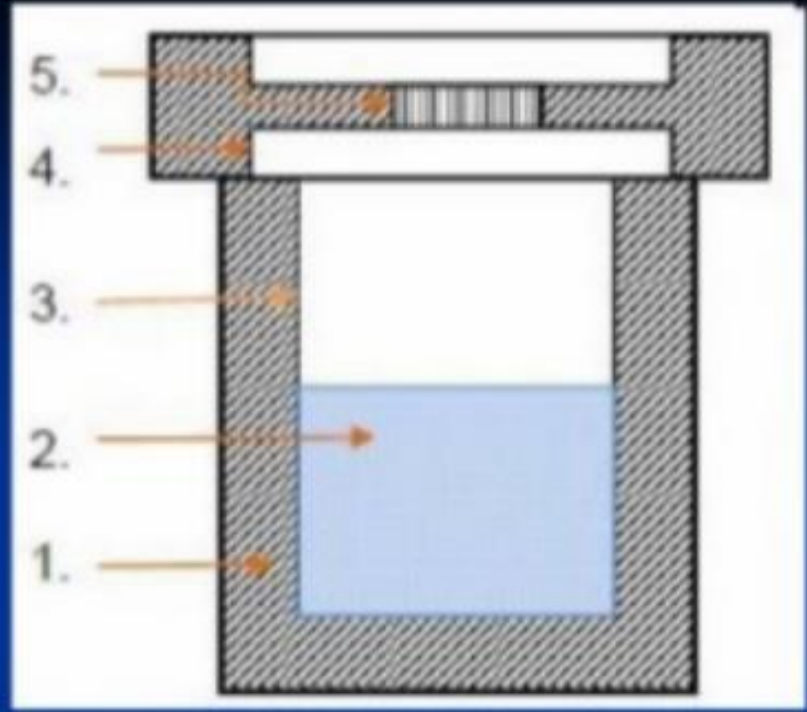
- In most of the cases steel-corroding solutions are used in hydrothermal experiments. To prevent corrosion of internal cavity of the autoclave, protective inserts are generally used. These may have the same shape as the autoclave fit in the internal cavity (contact type insert) or be a floating type insert which occupy only part of the autoclave interior. Insert may be made up of copper, silver, gold platinum, titanium, glass or Teflon depending on temperature and solution used.

Apparatus in hydrothemal synthesis

Commercially available autoclaves. *(Photo courtesy of Parr Instruments Co., Illinois, USA.)*



Commercially available autoclaves. *(Courtesy of M/S/ Toshin Kogyo Co. Ltd., Japan.)*

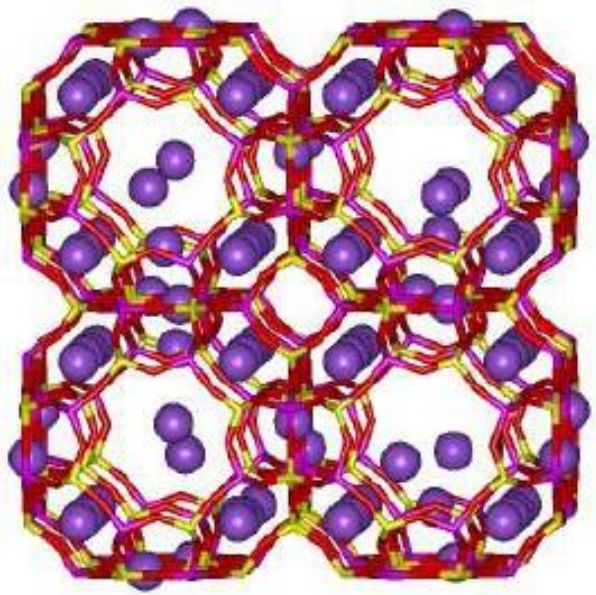


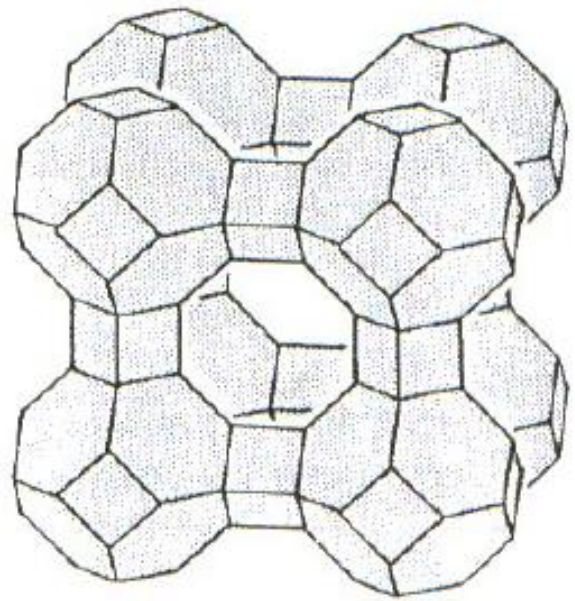
Schematic diagram of the autoclave used in hydrothermal / solvothermal synthesis (1) stainless steel autoclave (2) precursor solution (3) Teflon liner (4) stainless steel lid (5) spring

autoclave used in my group

Hydrothermal synthesis of zeolite A, $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$.

- Hydrated alumina, $Al_2O_3\cdot 3H_2O$ is dissolved in concentrated NaOH.
- The cooled solution is mixed with sodium metasilicate, $Na_2SiO_3\cdot 9H_2O$ and a thick white gel forms.
- The gel is placed in a closed teflon bottle and heated to 363 K over 6 hours.
- Changes in the form of alumina, pH of the solution, type of base used and proportions of alkali, aluminum compound, and silica lead to the production of different zeolites.





zeolite A

CHEMICAL VAPOUR DEPOSITION (CVD)

Principle:

Chemical vapour deposition (CVD) method involves a transport of reactant gases towards the substrate kept at some temperature (300-1200 °C) where reactants diffuse on the surface and undergo certain chemical reactions at appropriate site they nucleate and grow to form desired films, coatings, nnowires and nnotubes.

Precursors :

The common precursors used in CVD reactions are

o Metal hydrides – SiH_4 , GeH_4

o Metal halides-$TiCl_4$, $TaCl_5$, WF_6

o Metal organics- $AlMe_3$, $AlBu_3$, $Fe(CO)_5$, $Ni(CO)_4$

CVD Reactions

(i) Thermal Decomposition (Pyrolysis):

Silicon deposition from SiH_4 at 650ºC

$SiH_4\ (g) \rightarrow Si\ (s) + 2H_2\ (g)$

(ii) Reduction: W-deposition at 300ºC

$WF_6\ (g) + 3H_2 \rightarrow W\ (s) + 6HF\ (g)$

(iii) Oxidation:

SiO_2 deposition at 450ºC

$SiH_4\ (g) + O_2 \rightarrow SiO_2\ (s) + 2H_2\ (g)$

CHEMICAL VAPOUR DEPOSITION (CVD)

Types of CVD

In CVD, the temperature of 300-1200^{o}C is usually used. The heat input can be in the form of thermal, light, plasma and so on. This give rise to number of CVD techniques.

S. No.	Name of the CVD	Source of thermal energy
1.	Thermal activated CVD	IR radiation, RF heating
2.	Photo assisted CVD	Arc lamps, CO laser, Nd:YAG laser, Argon ion laser
3.	Plasma assisted CVD	RF diode, microwave
4.	Metal organic CVD	It uses organo metallic as precursors

Steps involved in synthesis:

The system follows a five step for any type of CVD.

a) Transport of precursors into the reactors

b) Absorption and diffusion of precursors on the substrate

c) Chemical reactions at the substrate

d) Deposition and growth of film

e) Transport of unreacted precursors and by-products

CHEMICAL VAPOUR DEPOSITION (CVD)

Advantages :

- Versatile method- CVD can deposit any element or compound.
- CVD produces high dense films.
- Economical in production since many products can be coated at a time.
- Used for coatings
- extremely high purity deposits (>99.995% purity)
- Controllable thickness and morphology

CHEMICAL VAPOUR DEPOSITION (CVD)

Applications

- CVD can be used for the synthesis of nanotubes and nanowires.
- CVD can be used for hard coatings and metal films which are used in microelectronics.
- CVD can also be used for preparing semiconducting devices, dielectrics, energy conversion devices etc.
- CVD processes are used on a wide range of industrial components such as aircraft and land gas turbine blades.

PHYSICAL VAPOUR DEPOSITION

Nanomaterials in the form of thin films, multilayer films, nanoparticles and nanotubes can be produced by physical vapour deposition methods.

- **Physical vapour deposition (PVD) is a technique by which a metal, ceramic or a compound can be converted into gaseous form and then deposited on the surface of a substrate.**

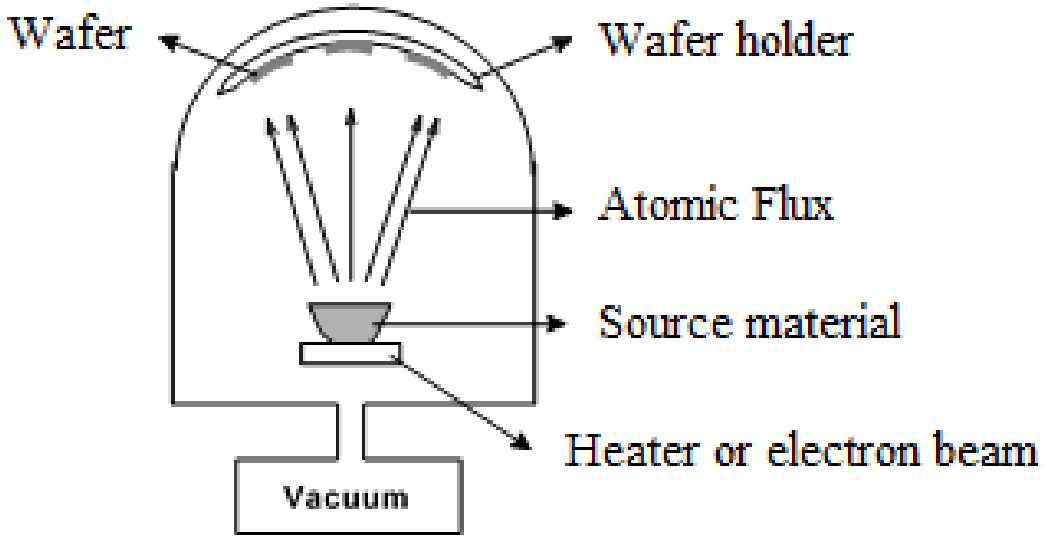
In general, PVD methods are subdivided into:

1. **Evaporation**
2. **Pulsed Laser Deposition**

PHYSICAL VAPOUR DEPOSITION

EVAPORATION

- The source materials used in this process are generally refractory metals such as W, Ta, Mo etc.
- In evaporation technique, both substrate and source materials (to be deposited) are placed inside the vacuum chamber (10^{-6} to 10^{-7} torr).
- The vacuum is required to allow the molecules to evaporate and to move freely in the chamber. An electron gun (e-gun) is used to produce electron beam of 10 keV. This beam is directed at the source material in order to develop sufficient vapour so as to produce deposits on wafer or substrates. Figure below shows the schematic diagram of evaporation equipment.

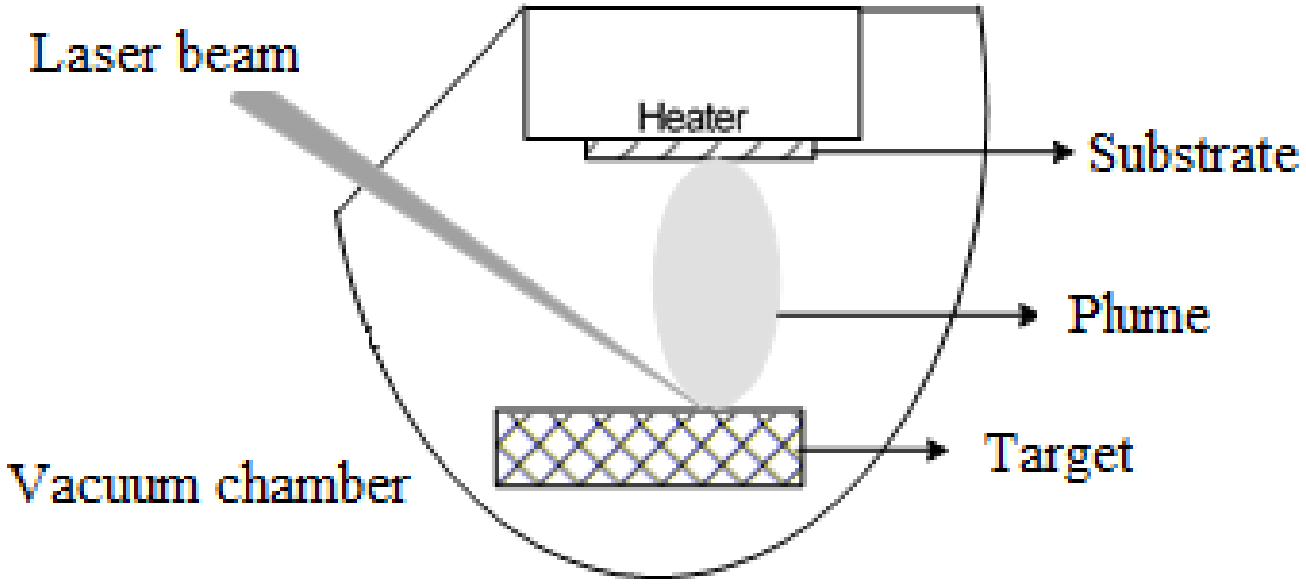


Schematic diagram of evaporation equipment

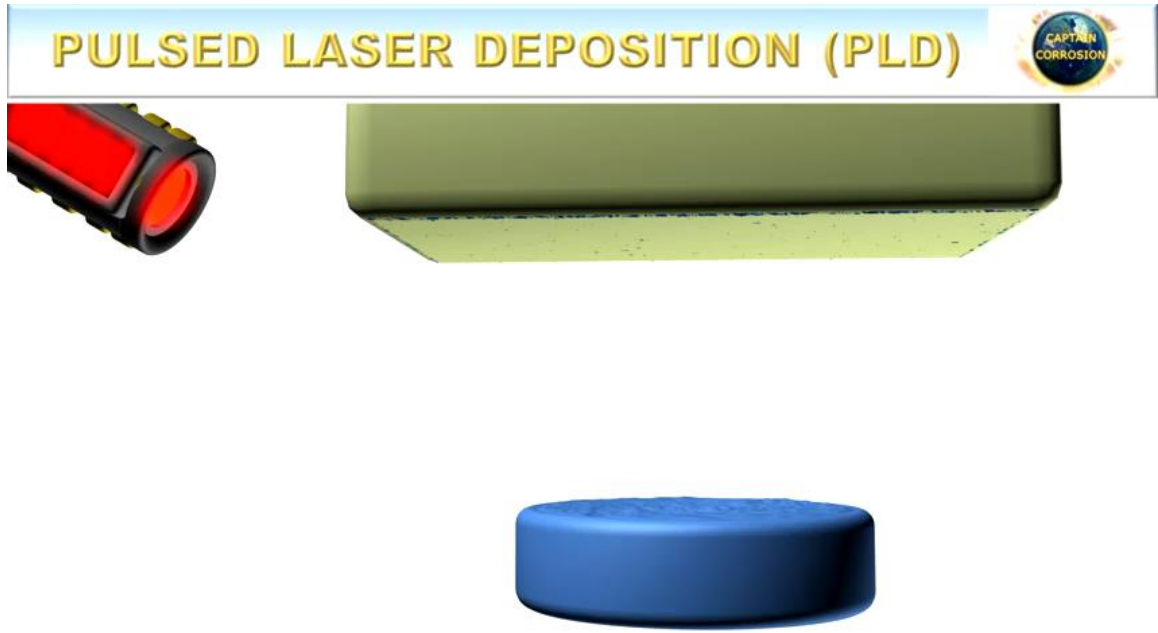
PHYSICAL VAPOUR DEPOSITION cont….

Pulsed Laser Deposition

Pulsed Laser Deposition (PLD) is a thin film deposition technique that is used to deposit materials on substrates. A base system consists of a target, substrate carrier which is mounted in a vacuum chamber. An excimer laser is used to energize the surface of a target to produce a deposition cloud. The cloud is typically directed towards the substrate where a thin-film is deposited. Since each shot of the laser is directly related to the amount of material deposited, the deposition rate can be calibrated and controlled very precisely. Figure shows the schematic diagram of pulsed laser deposition.



Schematic diagram of Pulsed Laser Deposition



PHYSICAL VAPOUR DEPOSITION cont….

Advantages

- Ultrapure films or particles can be produced by PVD since it uses a vacuum environment.
- PVD can provide good structural control by careful monitoring of the processing conditions.
- Almost any type of inorganic material can be used as well as some kinds of organic materials.
- The process is more environmentally friendly than processes such as electroplating.

Disadvantages

- Since PVD operates in a low pressure range, it increases the complexity of deposition and cost of production.
- High capital cost.
- Some processes operate at high vacuums and temperatures requiring skilled operators.
- Processes requiring large amounts of heat.
- The rate of coating deposition is usually quite slow.

PHYSICAL VAPOUR DEPOSITION cont….

Applications

- **PVD is used to produce the deposit of various metals, alloys or compounds in the form of coatings or films for:**

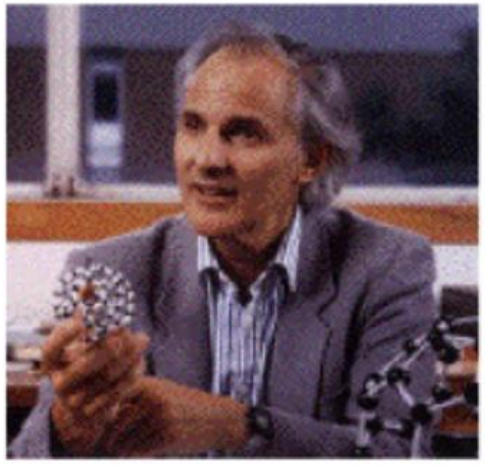
Optics (Ex: Antireflection coatings)
Electronics (Ex: Metal contacts)
Mechanics (Ex: hard coatings on tools) etc.
PVD coatings are generally used to improve hardness, wear resistance and oxidation resistance.
PVD coatings use in a wide range of applications such as:

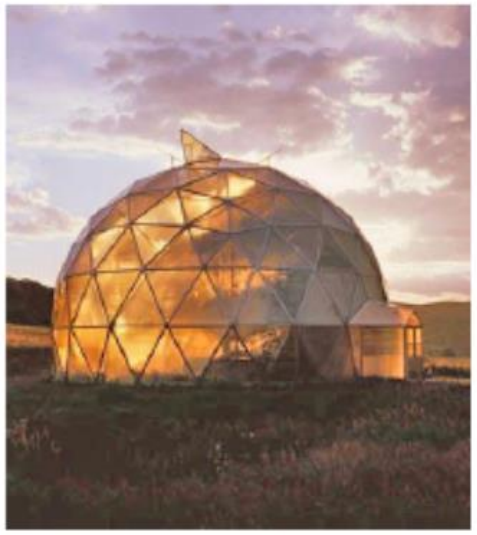
- **Aerospace**
- **Automotive**
- **Surgical/Medical**
- **Dies and moulds for all manner of material processing**
- **Cutting tools**
- **Fire arms**

Fullerenes

- **Fullerenes were discovered by Harry Kroto, Robert Curl and Richard Smalley in 1985. This nanometer scale structure was named fullerene due to its resemblance to the highly symmetric domes designed by the architect Richard Buckminster Fuller.**
- **Buckminster fullerenes or fullerenes are the third allotrope of carbon and consist of a family of spheroidal or cylindrical molecules with all the carbon atoms sp^2 hybridized. C_{60} was the first fullerene to be discovered. 60 carbon atoms bonded together in pentagons and hexagons. The carbon atoms are sp^2 hybridized, but unlike graphite, they are not arranged in a plane and is made up of 12 pentagons and 20 hexagons arranged in a spherical shape.**

Professor Sir Harold W. Kroto

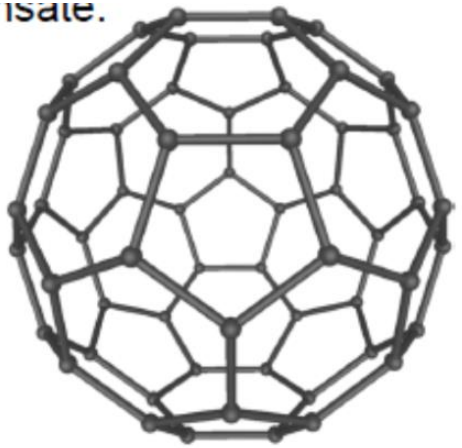




Geodesic dome

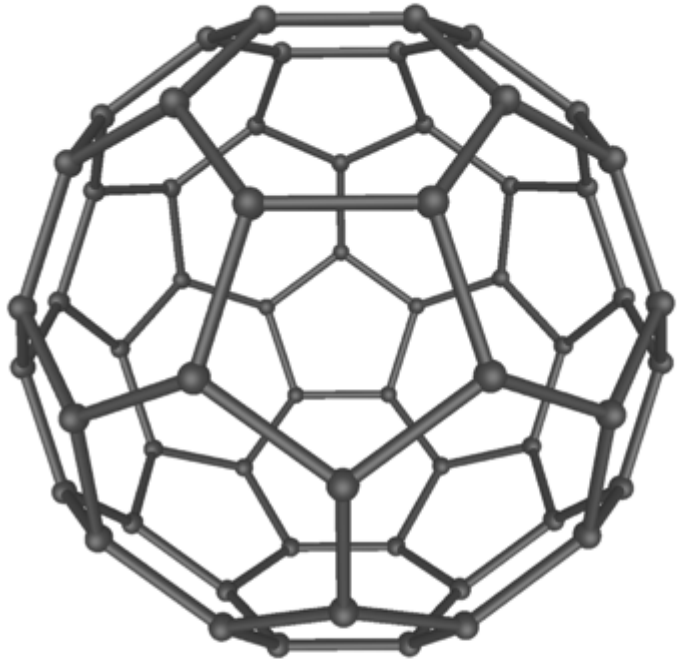
on condensate.

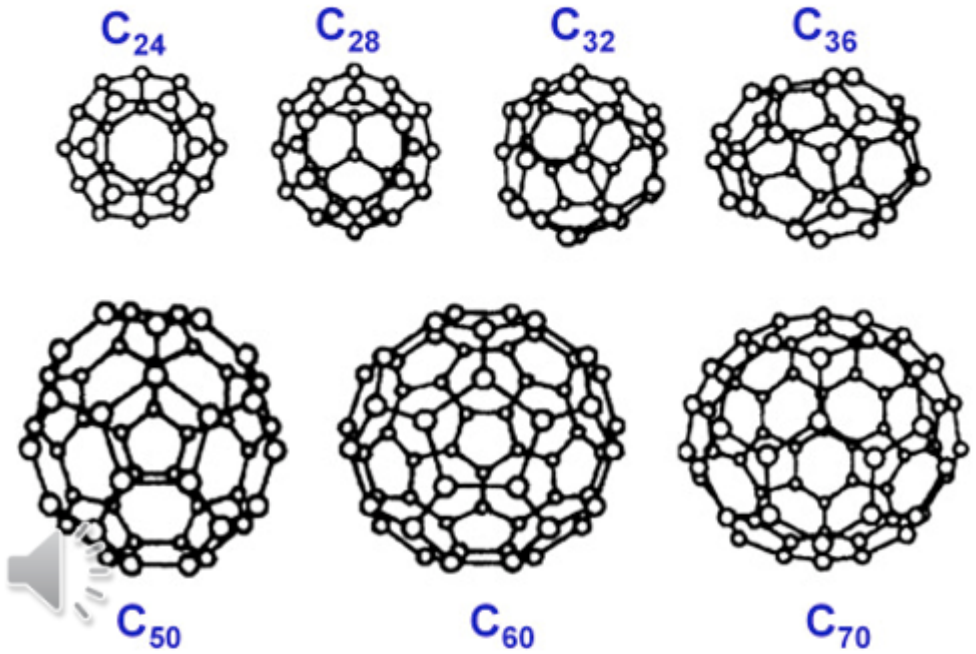
C 60



Football like structure
20 hexagones
12 pentagones

fullerenes





C_{60}

- Hollow
- Spherical fullerenes are called ‘Buckyballs’
- Can be used as lubricants.
- Lower melting point than graphite or diamond

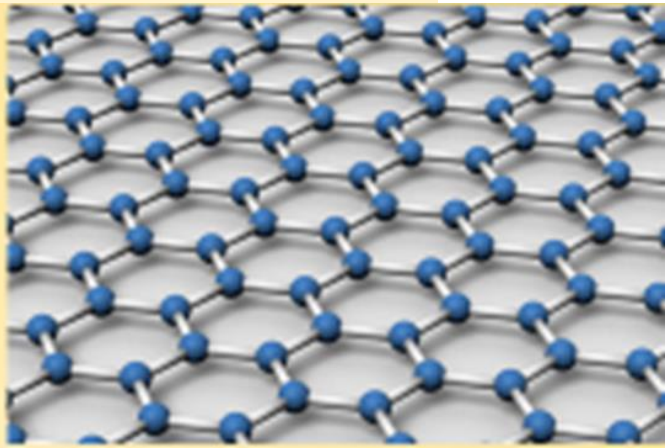
Fullerenes

Applications

1. Fullerenes are extremely flexible and strong nature, therefore are being considered for use in combat armor.
2. Researchers have found that water-soluble derivatives of fullerenes inhibit the HIV-1 protease (enzyme responsible for the development of the virus) and are therefore useful in fighting the HIV virus that leads to AIDS.
3. Elements can be bonded with C_{60} or other fullerenes to create more diverse materials, including superconductors and insulators.
4. Fullerenes and their derivatives are also applied to coat materials on some chemical sensors, such as quartz crystal microbalance (QCM) and surface acoustic wave sensors (SAW)

Graphene

- Graphene is an individual layer in graphite – the material pencil 'leads' are made from - so the chances are that you have some of this amazing nanomaterial lying around you right now.
- Despite being just **one atom thick** and looking somewhat like chicken-wire, graphene is **stiffer than diamond** and **more than 100 times stronger than steel** but it **can be stretched like rubber**. Despite its extreme thinness, it is **very dense** and impermeable to gases or liquids (they can't pass through it). These properties mean that it has a future in the development of body armour, aircraft fuselages and crack-proof television screens.
- Uses being trialled in screens, batteries and electronics.



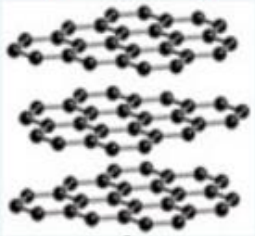
Allotropes of Carbon → Element exist in different form/physical state

Diamond

Electrical conductivity → Poor → - No free moving electron

Special property → - Hardest substance - Jewellery

Graphite



Electrical conductivity → Good → - Within layer - ONE free delocalized π electron

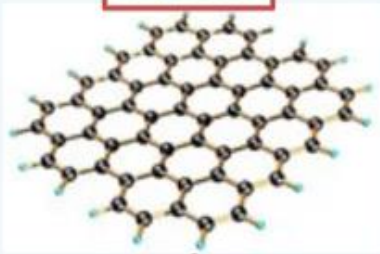
Special property → - Soft, layer slide across each other


graphite

lubricant


electrode

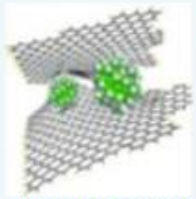
Graphene



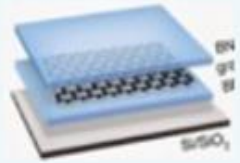
Electrical conductivity → Very Good → - Within layer - ONE free delocalized π electron moving across the layer easily

Special property → Lightest/strongest material replacing silicon in photovoltaic cell

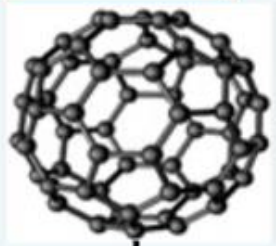
Drug delivery


Drug in graphene

Transistor/Electronic Transparent conducting electrode

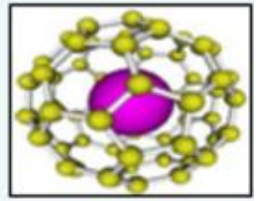


Fullerene, C60



Electrical conductivity → Semiconductor → - Surface sphere, not planar - Some conductivity. - Lower electron mobility

Special property → Potential medicinal use
- Drug delivery
- Target cancer cells



Application of nano-materials :

Nanomaterials having wide range of applications in the field of electronics, fuel cells, batteries, agriculture, food industry, and medicines, etc... These applications include, but are not limited to the following:

1) Silver nanoparticles have good antibacterial properties and are used in surgical instruments, refrigerators, air-conditioners, water-purifiers etc.

2) Gold nano-particles are used in catalytic synthesis of silicon nano-wires, sensors carrying drugs and in detection of tumors.

3) Zinc oxide nano-particles are used in electronics, ultra-violet light emitters and chemical sensors.

4) TiO_2 nano-particles are used as photocatalyst and sunscreen cosmetics (UV blocking pigment)

5) As Catalysis : Higher surface area available with the nanomaterial counterparts, nano-catalysts tend to have exceptional surface activity. For example, reaction rate at nano-aluminum can go so high, that it is utilized as a solid-fuel in rocket propulsion, whereas the bulk aluminum is widely used in utensils. Nano-aluminum becomes highly reactive and supplies the required thrust to send off pay loads in space. Similarly, catalysts assisting or retarding the reaction rates are dependent on the surface activity, and can very well be utilized in manipulating the rate-controlling step.

Application of nano-materials cont….:

6. In Phosphors for High-Definition TV: The resolution of a television, or a monitor, depends greatly on the size of the pixel. These pixels are essentially made of materials called "phosphors," which glow when struck by a stream of electrons inside the cathode ray tube (CRT). The resolution improves with a reduction in the size of the pixel, or the phosphors. Nanocrystalline zinc selenide, zinc sulfide, cadmium sulfide, and lead telluride synthesized by the sol-gel techniques are candidates for improving the resolution of monitors. The use of nanophosphors is envisioned to reduce the cost of these displays so as to render highdefinition televisions (HDTVs) and personal computers affordable to be purchase.

7. Sun-screen lotion : Prolonged UV exposure causes skin-burns and cancer. Sun-screen lotions containing nano-TiO_2 provide enhanced sun protection factor (SPF) while eliminating stickiness. The added advantage of nano skin blocks (ZnO and TiO_2) arises as they protect the skin by sitting onto it rather than penetrating into the skin. Thus they block UV radiation effectively for prolonged duration. Additionally, they are transparent, thus retain natural skin color while working better than conventional skin-lotions.

8. Sensors : Sensors rely on the highly active surface to initiate a response with minute change in the concentration of the species to be detected. Engineered monolayers (few Angstroms thick) on the sensor surface are exposed to the environment and the peculiar functionality (such as change in potential is detected) is utilized in sensing.

Application of nano-materials cont….:

9. Biomedical and Pharmaceutical Applications: Nanomaterials have a wide range of applications in Antimicrobials, Bio-detection and labeling, Bio-magnetic separations, Drug delivery, MRI contrast agents, Orthopedics/implants, Sunscreens and thermal spray coatings.

10. Photovoltaic Applications (Solar Cells) : Solar cells are generally constructed using two electrodes with a semiconductor TiO_2 nano-particle layer between them. TiO_2 nanoparticles can be transparent and function in solar cells as the electrons acceptor.

11. Automotive Industry: Nanomaterials have a wide range of applications in the automotive industry. Nanomaterials are used for lightweight construction, painting (fillers, basecoat, and clear coat), catalysts, tires (fillers), and sensors, coatings for windscreen and car bodies in the automotive industry.

12. Electronic Industry: Nanomaterials are used for data memory (MRAM, GMR-HD), displays (OLED, FED), laser diodes, glass fibers, optical switches, filters (IR-blocking), conductive and antistatic coatings in the electronic industry.

13. Medicine Industry: Nanomaterials are used for drug delivery systems, active agents, contrast medium, medical rapid tests, prostheses and implants, antimicrobial agents, coatings and agents in cancer therapy in the medicine industry.

14. Cosmetics: Nanomaterials are used for sun protection, lipsticks, skin creams and tooth paste in the cosmetics industry.

15. Tougher and Harder Cutting Tools: The cutting tools made by Nanocrystalline materials, such as tungsten carbide, tantalum carbide, and titanium carbide, are much harder, much more wear resistant, erosion resistant, and last longer than their conventional counterparts.

Nanotechnology or Nanoparticles in Medicine

The use of nanotechnology in medicine offers some exciting possibilities. Some techniques are only imagined, while others are at various stages of testing, or actually being used today.

1) Nanotechnology in drug delivery: One application of nanotechnology in medicine currently being developed involves employing nanoparticles to deliver drugs, heat, light or other substances to specific types of cells (such as cancer cells). Particles are engineered so that they are attracted to diseased cells, which allows direct treatment of those cells. This technique reduces damage to healthy cells in the body and allows for earlier detection of disease.

2) Nanotechnology in Diagnostic Techniques: The antibodies attached to carbon nanotubes in chips used to detect cancer cells in the blood stream. The researchers believe this method could be used in simple lab tests that could provide early detection of cancer cells in the bloodstream.

Methods for early detection of kidney damage is being developed. This method uses gold nanorods functionalized to attach to the type of protein generated by damaged kidneys. When protein accumulates on the nanorod the colour of the nanorod shifts. The test is designed to be done quickly and inexpensively for early detection of a problem.

3) Nanotechnology in Antibacterial Treatments: The gold nanoparticles and infrared light used to kill bacteria. This method is under clinical trials. Researchers are also investigating the use of quantum dots to treat antibiotic resistant infections.

Disadvantages of Nanomaterials

(i) Instability of the particles - Retaining the active metal nanoparticles is highly challenging, as the kinetics associated with nanomaterials is rapid. In order to retain nanosize of particles, they are encapsulated in some other matrix. Nanomaterials are thermodynamically metastable and lie in the region of high-energy local-minima. Hence they are prone to attack and undergo transformation. These include poor corrosion resistance, high solubility, and phase change of nanomaterials. This leads to deterioration in properties and retaining the structure becomes challenging.

(ii) Fine metal particles act as strong explosives owing to their high surface area coming in direct contact with oxygen. Their exothermic combustion can easily cause explosion.

(iii) Biologically harmful - Nanomaterials are usually considered harmful as they become transparent to the cell-dermis. Toxicity of nanomaterials also appears predominant owing to their high surface area and enhanced surface activity. Nanomaterials have shown to cause irritation, and have indicated to be carcinogenic. If inhaled, their low mass entraps them inside lungs, and in no way they can be expelled out of body. Their interaction with liver/blood could also prove to be harmful (though this aspect is still being debated on).

(iv) Difficulty in synthesis, isolation and application - It is extremely hard to retain the size of nanoparticles once they are synthesized in a solution. Hence, the nanomaterials have to be encapsulated in a bigger and stable molecule/material. Hence free nanoparticles are hard to be utilized in isolation, and they have to be interacted for intended use via secondary means of exposure. Grain growth is inherently present in nanomateirals during their processing. The finer grains tend to merge and become bigger and stable grains at high temperatures and times of processing.

Disadvantages of Nanomaterials cont….

(v) Recycling and disposal - There are no hard-and-fast safe disposal policies evolved for nanomaterials. Issues of their toxicity are still under question, and results of exposure experiments are not available. Hence the uncertainty associated with effects of nanomaterials is yet to be assessed in order to develop their disposal policies.

Electron Microscopy

Why use electrons instead of light in a microscope?

- **Given sufficient light, the human eye can distinguish two points 0.2 mm apart, without the aid of any additional lenses. This distance is called the resolving power or resolution of the eye.**

- **A lens or an assembly of lenses (a microscope) can be used to magnify this distance and enable the eye to see points even closer together than 0.2 mm.**

- **A modern light microscope has a maximum magnification of about 1000x.**

- **The resolving power of the microscope was not only limited by the number and quality of the lenses but also by the wavelength of the light used for illumination.**

- **visible light has wavelengths from 400 to 700 nanometers (nm). The average wavelength is 550 nm which results in a theoretical limit of resolution of the light microscope in white light of about 200 – 250 nm.**

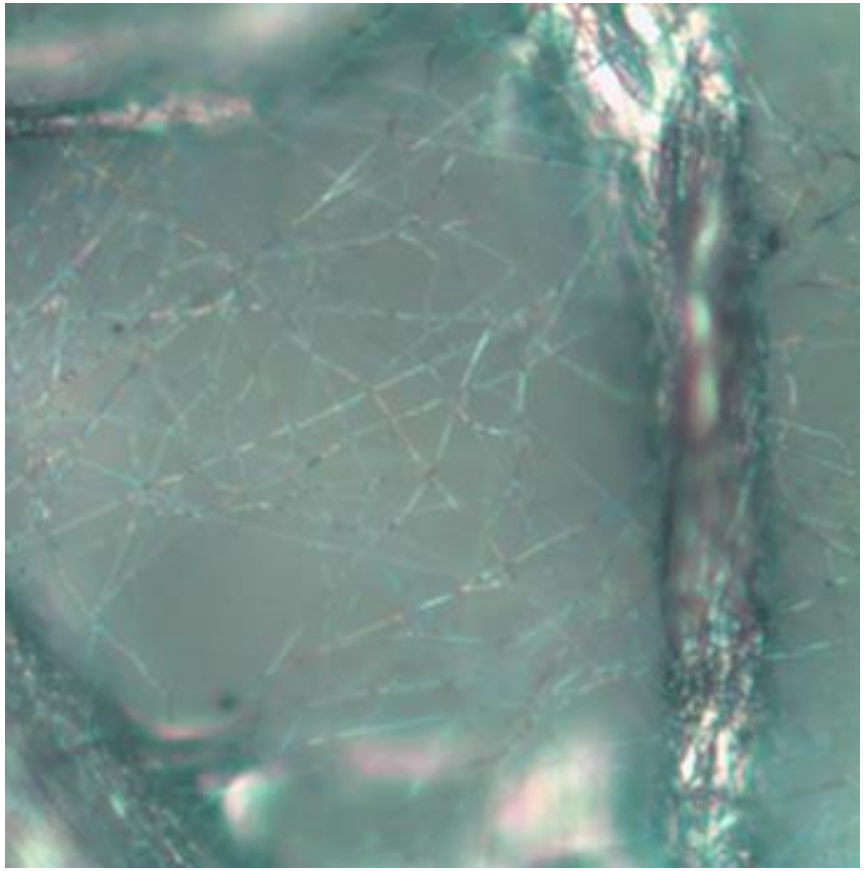
Electron Microscopy

The figure below shows two points at the limits of detection and the two individual spots can still be distinguished. The right image shows the two points so close together that the central spots overlap.

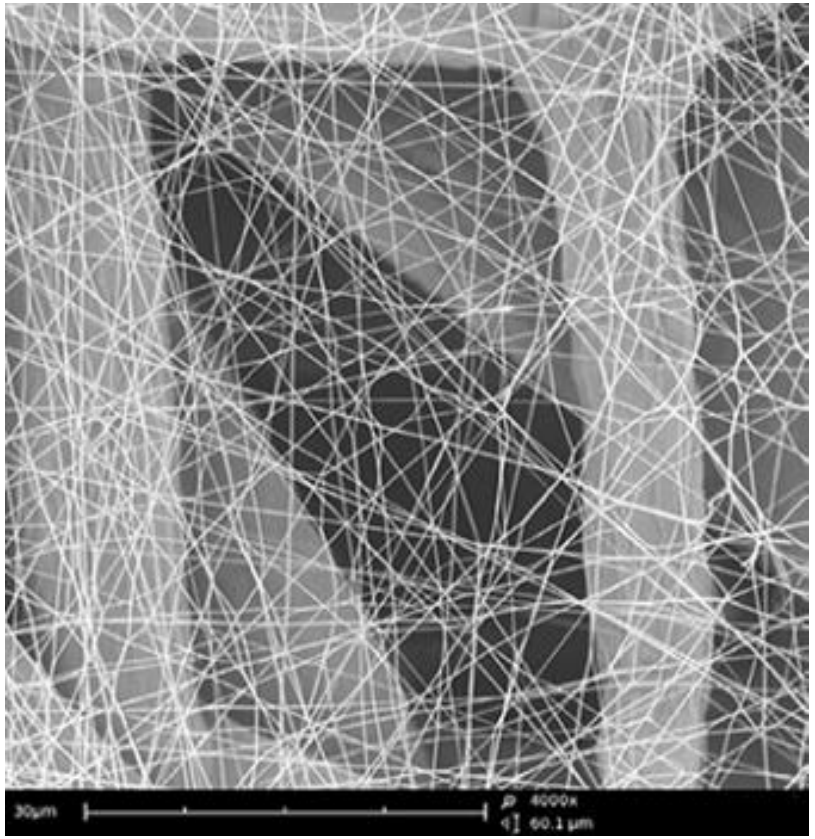
two points showing the limits of detection

- **The electron microscope was developed when the wavelength became the limiting factor in light microscopes. Electrons have much shorter wavelengths, enabling better resolution.**

Compare an Optical Microscope vs a Scanning Electron Microscope



Optical microscope image of nanofibers



Scanning electron microscope image at 4000x magnification of the same nanofibers

Electron Microscope

The *resolving power* of optical (and electron) microscopes is the smallest separation of two objects which may be reproduced clearly in the image and is given by the equation

$$\text{resolving power} = \frac{0.61\lambda}{n \sin \alpha}$$

where n is the refractive index of the medium in which the object is immersed.

α is the maximum half angle subtended at the objective lens by the object. The product $n\sin\alpha$ is the *numerical aperture* of the objective lens.

- **The main variable in equation is the wavelength of the radiation used, λ, which shows why electron microscopes, with electron wavelengths 1 A° , have resolving powers that are orders of magnitude greater than those of optical microscopes.**

Electron Microscope

- **An electron microscope is a microscope that uses a beam of accelerated electrons as a source of illumination.**

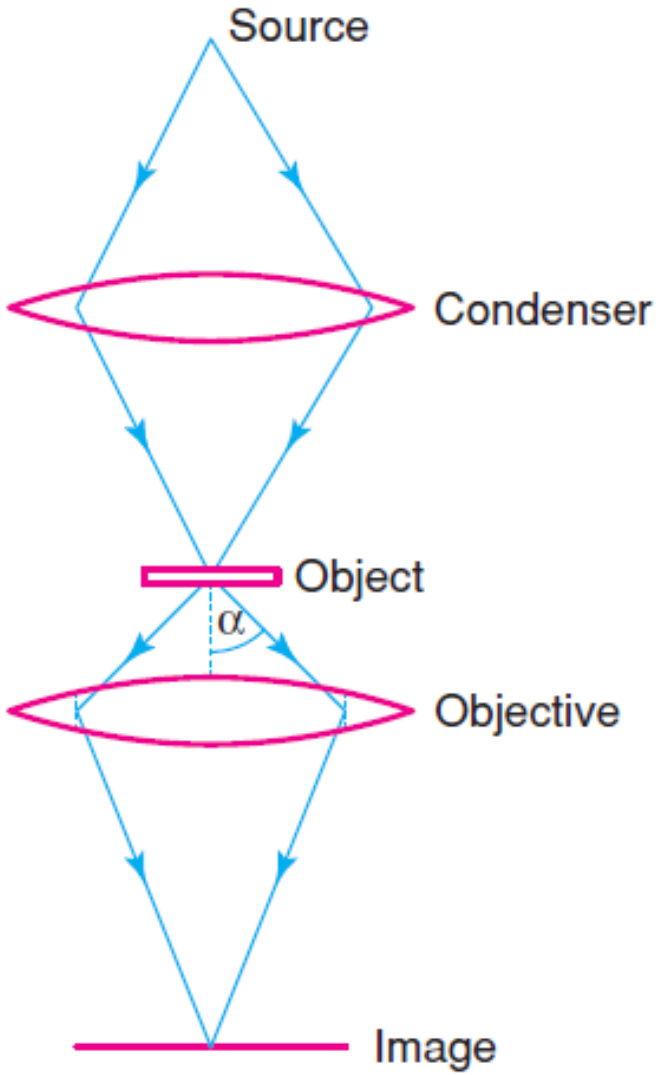
- **As the wavelength of an electron can be up to 1,00,000 times shorter than that of visible light photons, so electron microscopes have a higher resolving power than light microscopes and can reveal the structure of smaller objects.**

- **A scanning transmission electron microscope has achieved better than 50 pm resolution in annular dark-field imaging mode whereas most light microscopes are limited by diffraction to about 200 nm resolution and useful magnifications below 2000×.**

Timeline of the electron microscope history

- **In 1926, Hans Busch invented the first electromagnetic lens and, although he allegedly filed a patent for an electron microscope in 1928, he did not construct the microscope.**
- **In 1931, Ernst Ruska and Max Knoll, a physicist and an electrical engineer, respectively, from the University of Berlin, who created the first electron microscope. This prototype was able to produce a magnification of four-hundred-power and was the first device to show what was possible with electron microscopy**
- **In the same year, Reinhold Rudenberg, who was the scientific director of Siemens-Schuckertwerke acquired the electron microscope patent.**
- **Siemens-Schuckertwerke released the first commercial electron microscope to the public in 1938.**
- **In 1986, Ernst Ruska was awarded the Nobel Prize in Physics for the invention of the electron microscope**

Electron Microscope



Simplified ray diagram for an optical microscope

Scanning Electron Microscope

- A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the surface topography and composition of the sample.

- Light microscope has a magnification of about 1000x and enables the eye to resolve objects separated by 200 nm. Electron Microscopes were developed due to the limitations of light microscopes, which are limited by the physics of light.

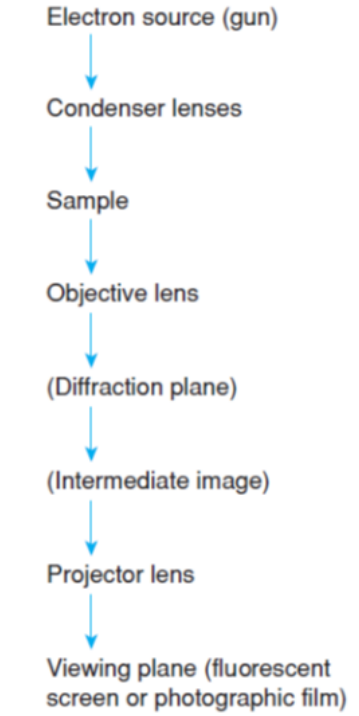
- Electron Microscopes are capable of much higher magnifications and have a greater resolving power than a light microscope, allowing it to see much smaller objects at sub cellular, molecular and atomic level.

- The smallest the wavelength of the illuminating sources is the best resolution of the microscope.

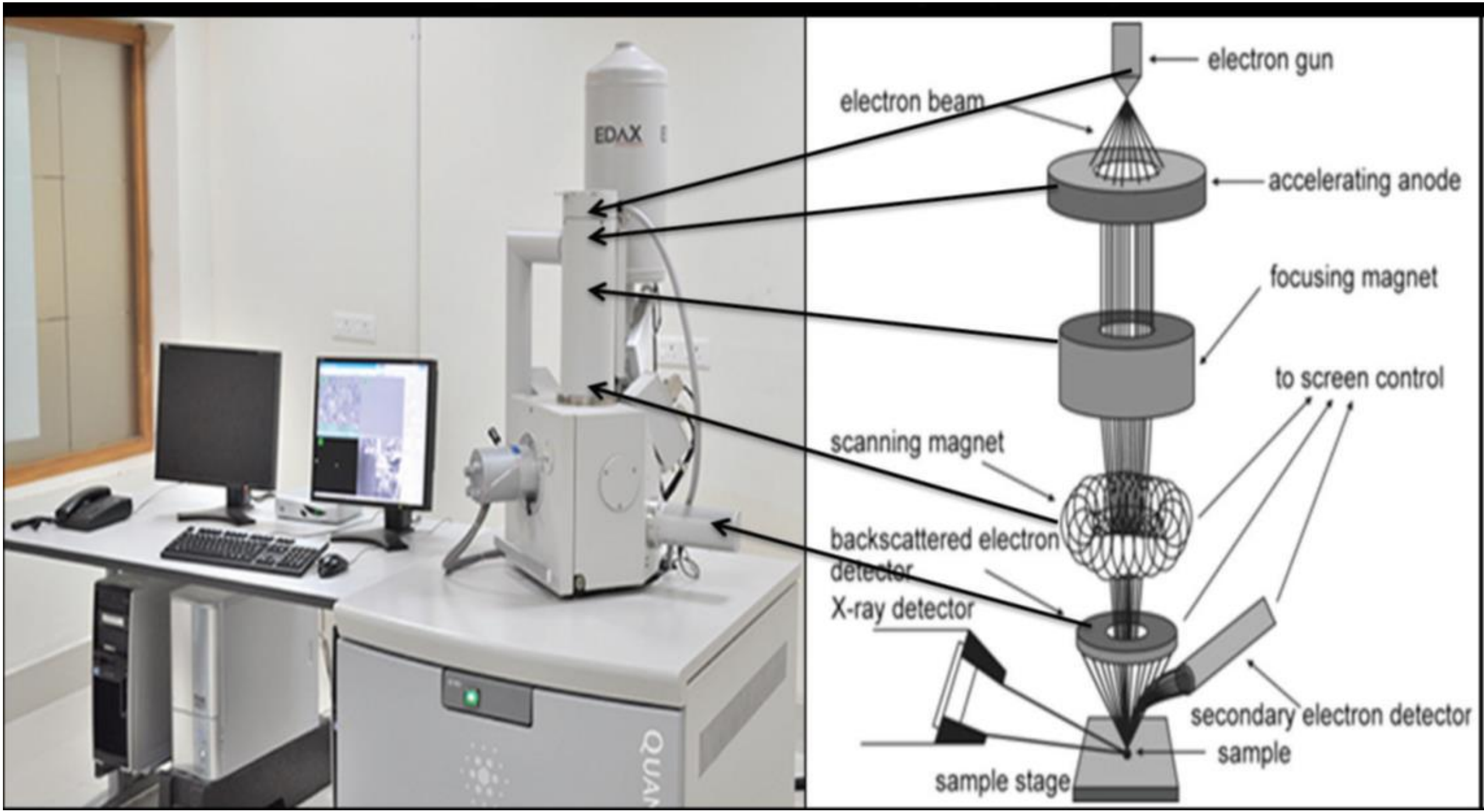
Scanning Electron Microscope

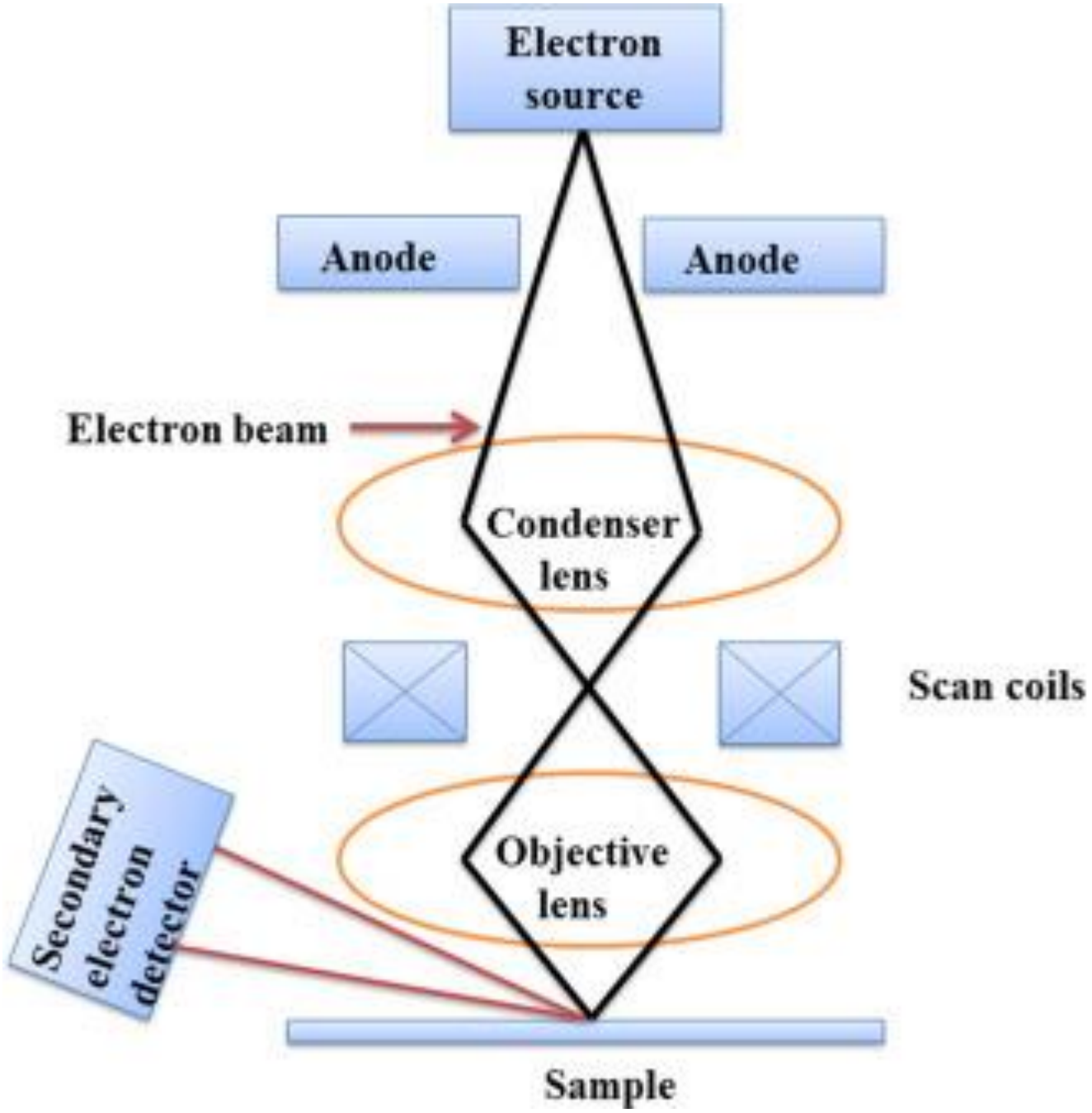
Working principles of SEM

- A beam of electrons from the Electron Source are accelerated toward the specimen using a positive electrical potential.
- The electron beam is confined and focused using metal apertures and magnetic lenses into a thin, focused, monochromatic beam.
- The Electrons in the beam interact with the atoms of the specimen, producing signals that contain information about its surface topography, and composition. These interactions and effects are detected and transformed into an image.



Basic components of an electron microscope.


EDAX
electron gun
electron beam
accelerating anode
focusing magnet
to screen control
scanning magnet
backscattered electron detector
X-ray detector
secondary electron detector
sample
sample stage



Block diagram of SEM

Components of SEM

Electron Column or Electron Beam:

- **The electron beam is generated at electron column under vacuum, then focused to a small diameter, and scanned across the surface of a specimen by electromagnetic deflection coils.**

- **The lower portion of the column is called the specimen chamber.**

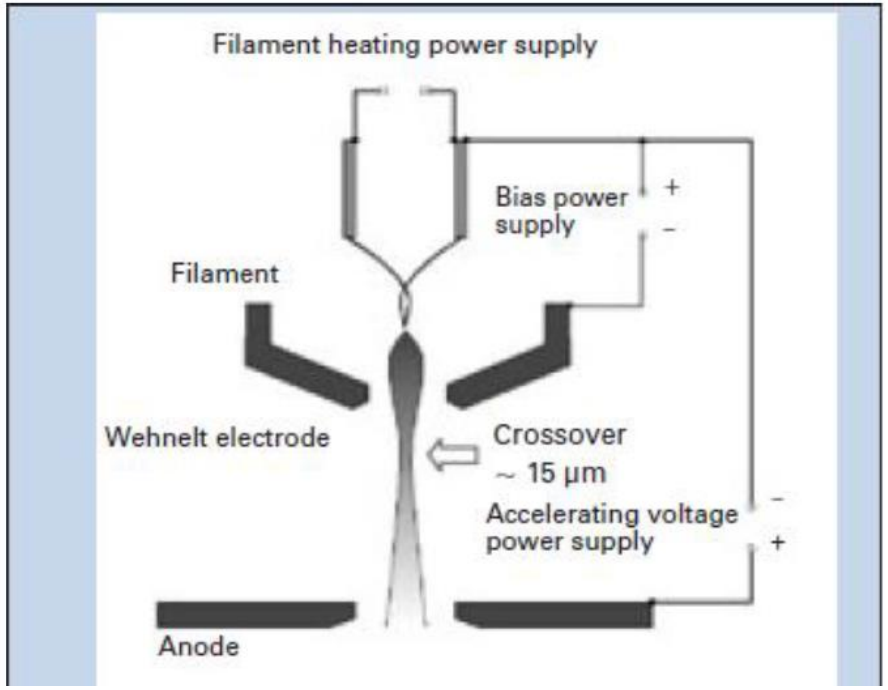
- **The voltage is variable from about 1 - 60keV. These values are specific to the instrument model**

Electron gun: **It is used to produce fine electron beam (and is also called as electron probe). Several different types of electron guns used are:**

a) TE (Thermionic- Emission) gun
b) FE (Field- Emission) gun
c) SE (Schottky- Emission) gun

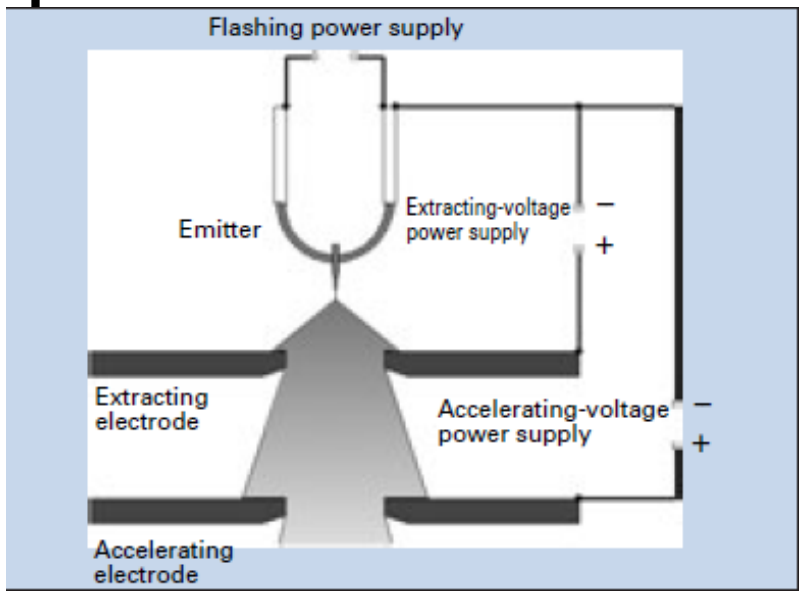
a) TE (Thermionic- Emission) gun

- **A thin tungsten wire filament acts as cathode to generate thermo electrons by heating the filament at 2800K.**
- **A positive voltage of about 1 to 30 KV is applied to the metal plate acting as anode, in order to collect these thermo electrons.**
- **By applying negative voltage to the Wehnelt electrode placed between the anode and the cathode, current of the electron beam is adjusted. This electrode also helps in focussing the electron beam.**
- **Thinnest point of beam known as cross-over (15-20µm Diameter), regarded as actual electron source.**
- **LaB_6 crystal is used as a cathode. It used to reduce the spot size. It requires high vacuum due to its higher activity.**



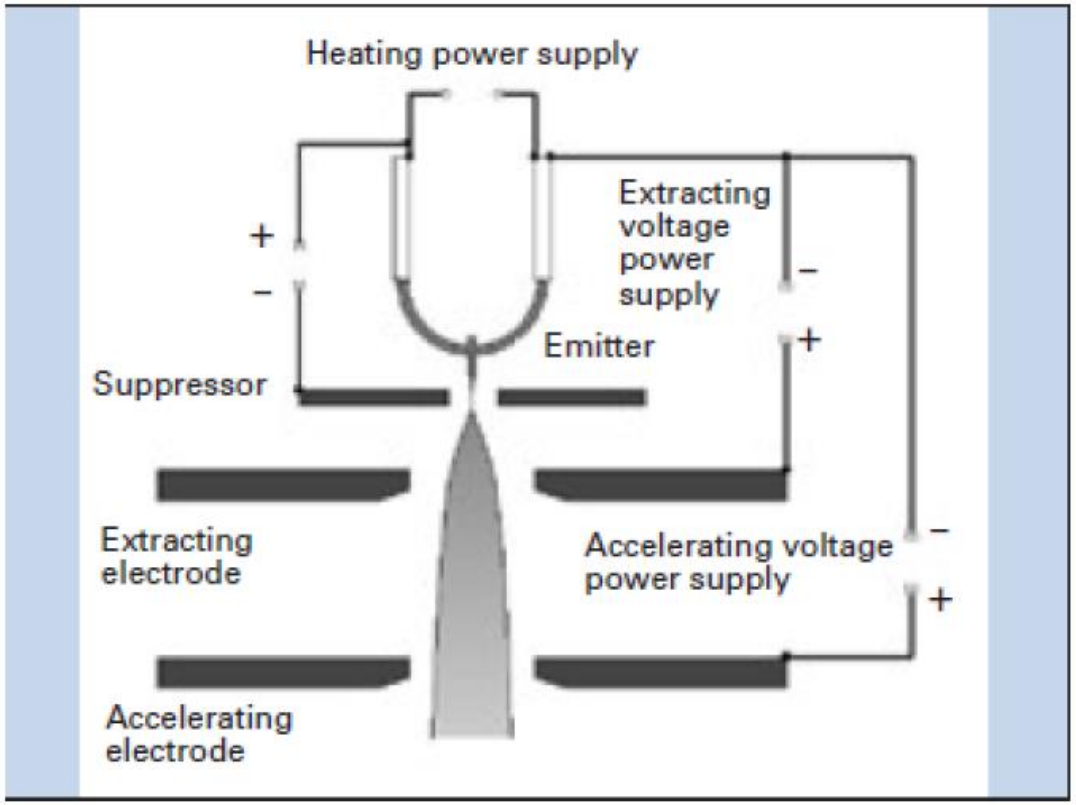
FE (Field- Emission) gun

- Provides high resolution. Field-emission is discharge of electrons from the surface of a material subjected to a strong electric field.
- Works on field-emission effect when high electric field is applied to the metal surface.
- A thin tungsten wire act as cathode wielded to the tungsten single crystal whose tip is curved with the radius of about 100nm, and is known as emitter.
- Electrons are emitted from emitter through tunnelling effect when positive voltage is applied to the extracting electrode.
- Hole is created in the extracting electrode to allow emitted electrons to flow through it. Then electron beam containing some energy is obtained by applying voltage to the accelerating electrode present beneath the extracting electrode.
- In FE gun energy spread is less because no heating is required and also electron beam diameter is 5-10nm.
- Requires ultra-high vacuum of the order of 10^{-8}Pa.



SE (Schottky- Emission) gun

- Works on Schottky emission effect when high electric field is applied to heated metal surface.
- A tungsten single crystal (tip radius – few hundred nm) coated with ZrO acts as cathode.
- ZrO coating reduces the work function to enhance the emission current at low cathode temperature.
- Thermo electrons are shielded from emitter by applying negative voltage to the suppressor electrode.
- Advantage: electron beam current is highly stable because emitter is placed in ultra high vacuum of the order of 10^{-7} Pa.
- Produces larger probe current.



Condenser and objective Lenses

- To produce finest beam of electron with desired crossover diameter, two- level lens system, i.e., condenser and objective lens, made of metal cylinders with cylindrical hole, operating in vacuum is used. These lenses are located beneath the electron gun.
- Magnetic field is generated in the inner part of the lenses to focus or de-focus the beam.

Role of condenser lens:

- Condenser lens affects the probe size.

- If it is strengthened then probe size is narrowed, if it is weakened then probe size is broadened. C1 and C2 lenses control the beam current by varying size and intensity of beam spot.

Role of objective lens:

- It is used for focusing and determines the final diameter of probe.

Scanning Coils-

- These coils deflect the beam in X or Y directions in order to scan the sample surface in a raster pattern

Specimen Chamber

- **It is a motorized plate which has movement in three directions X, Y and Z controlled by feeding value in the software.**

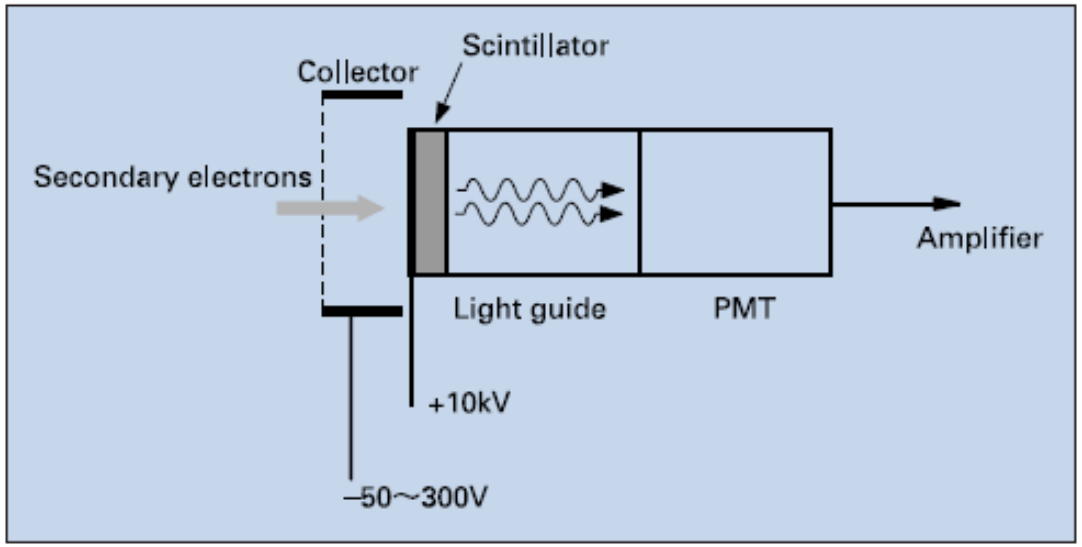
- **The samples are supported on it and move smoothly in the required direction. X and Y, the two horizontal movement are used to change the field of view whereas Z, the vertical movement is required for image resolution as well as depth of focus. Along with these movements rotation and tilting are also possible. Also, stage movement can be controlled manually through mouse in the user interface of the software.**

Components of SEM

Electron Detectors: **Secondary electrons emitted from the sample are measured using secondary electron detector.**

Secondary Electron Detector:

- **It includes a Scintillator coating at the detector tip and high positive voltage of 10 KV is applied to it.**
- **The secondary electrons emitted from the specimen get magnetized towards this positive voltage, also this secondary electron collection is supported by supplementary electrode (the collector) placed before scintillator by applying few volts to this collector.**
- **When they hit the scintillator, light is produced which is guided to PMT (Photo multiplier tube) through light guide.**
- **Then light is converted to electrons which are amplified as electric signal.**



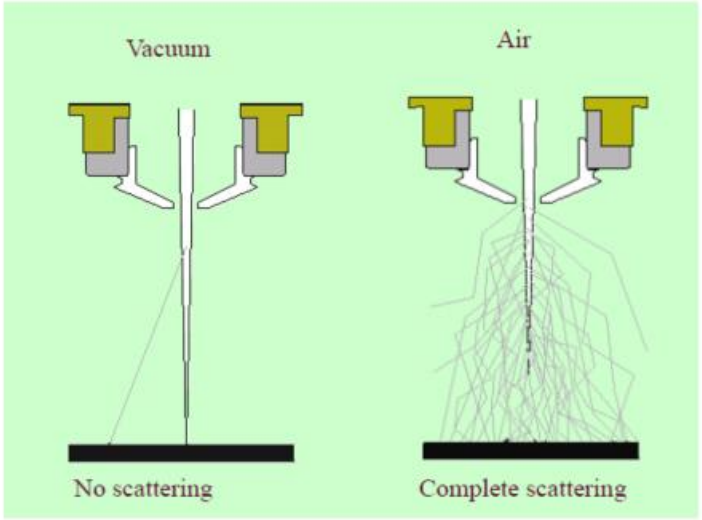
Display Unit and Recording system:

- **The output in the form of amplified electronic signal is send to the display unit. To form SEM image, scanning is synchronized with electron beam scan and brightness (which depends upon number of secondary electrons emitted) on the display unit. Originally, CRT (Cathode Ray Tube) was used as a display unit but these days it is replaced by LCD (Liquid - Crystal Display). Usually, very fast scan speed is used while focusing for observation, whereas slow speed is used for capturing or saving the image.**

Components of SEM

Vacuum System:

- Vacuum is produced by an oil diffusion pump backed by a mechanical pump.
- A mechanical pump and valve system are used to pre-evacuate the system because a diffusion pump only operates after a vacuum is created.
- If the column is gas filled environment, electrons will be scattered by colliding with air molecules which would lead to reduction of the beam intensity and stability. This would lower the contrast and obscure detail in the image.
- The field emission gun, LaB_6 and tungsten filament requires ~ 10^{-10}, ~ 10^{-6} and 10^{-4} Torr, respectively. Hence, gun column of electron microscope require vacuum to facilitate the electrons signals from the sample to the detector for better imaging.



How Scanning Electron Microscope (SEM) works

Ernst Ruska and Max Knoll developed first electron microscope during 1931with resolution of 100nm and later by addition of electromagnetic lenses, brought the resolution to 0.05nm. SEM is similar to the optical stereo-binocular microscope to observe the morphology and shape of the specimen.

- **The electron gun produces an electron beam when tungsten wire is heated by current and accelerated by the anode.**
- **The beam travels in the vacuum column through electromagnetic fields and lenses, which focus the beam down toward the sample.**
- **A mechanism of deflection coils enables to guide the beam so that it scans the surface of the sample in a raster pattern.**
- **When the incident beam touches the surface of the sample and produces signals *viz.,***

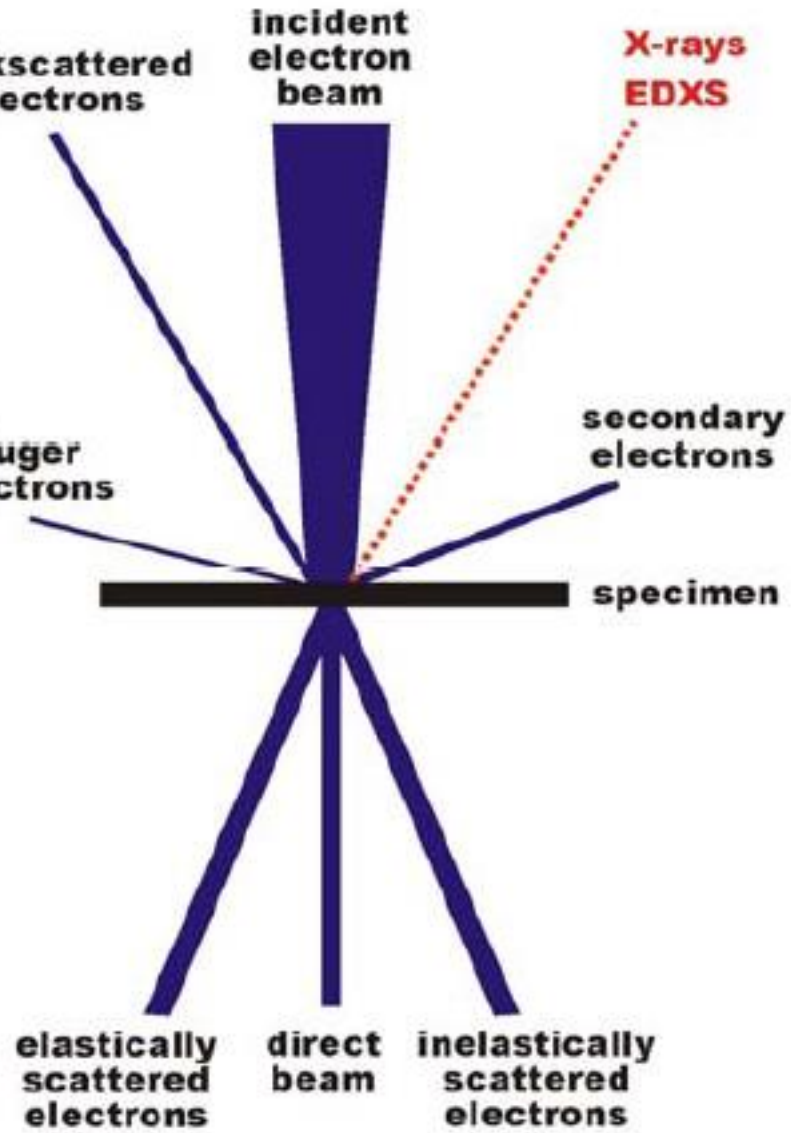
- **Secondary electrons (SE)**
- **Auger electrons**
- **Back scattered electrons (BSE)**
- **Characteristic X – Rays • Cathodoluminescence**

- **The emitted signals are trapped by electrical detectors, convert into digital images and displayed on a screen as digital image.**
- **Provides information sample's elemental composition, structural variation and morphology.**
- **In the SEM, use much lower accelerating voltages to prevent beam penetration into the sample since the requirement is generation of the secondary electrons from the true surface structure of a sample. Therefore, it is common to use low KV, in the range 1-5kV for biological samples, even though the SEMs are capable of up to 30 kV.**

Interaction of Electron Beam with Specimen:

- When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop-shaped volume of the specimen known as the interaction volume, which extends from less than 100 nm to approximately 10 µm into the surface.
- The size of the interaction volume depends on the electron's landing energy, the atomic number of the specimen and the specimen's density.
- The energy exchange between the electron beam and the sample results in the reflection of high-energy back scattered electrons by elastic scattering, emission of low energy secondary, auger electrons by inelastic scattering and the emission of electromagnetic radiation (X-rays and cathodoluminescence), each of which can be detected by respective detectors.
- The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current.
- Electronic amplifiers of various types are used to amplify the signals, electronic detectors convert the signals into digital images and displayed on a computer monitor.

Interactions of Electrons with Matter

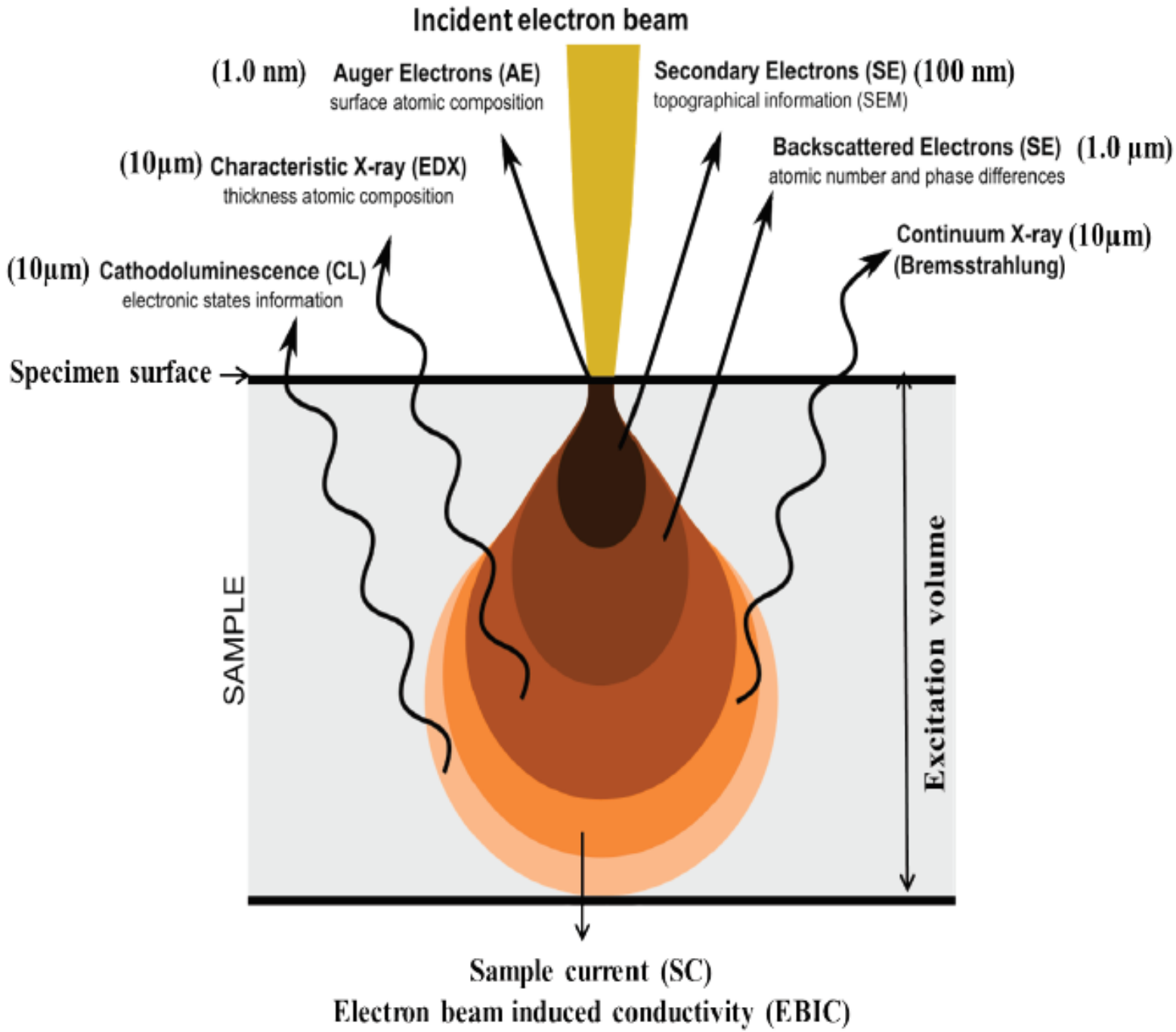


EDXS (EDX, EDS), WDS, EPMA

SEM

elastic scattering:
TEM, HRTEM, STEM, SAED, CBED

inelastic scattering:
EELS, ESI


Incident electron beam
(1.0 nm) Auger Electrons (AE)
surface atomic composition
Secondary Electrons (SE) (100 nm)
topographical information (SEM)
(10µm) Characteristic X-ray (EDX)
thickness atomic composition
Backscattered Electrons (SE) (1.0 µm)
atomic number and phase differences
Continuum X-ray (10µm)
(Bremsstrahlung)
(10µm) Cathodoluminescence (CL)
electronic states information
Specimen surface
SAMPLE
Excitation volume
Sample current (SC)
Electron beam induced conductivity (EBIC)

Scanning Electron Microscope

As an electron travels through the interaction volume, it is said to *scatter*; that is, lose energy and change direction with each atomic interaction. *Scattering events* can be divided into two general classes:

Elastic scattering occurs when the energy of the scattered electron is the same as the energy of the incident electron, i.e. there is no energy transferred from the beam into the specimen. Elastic scattering causes the beam to diffuse through the sample.

Inelastic scattering results when the incident electron loses energy in its interaction with the sample. There are a number of different processes that cause this. They include: plasmon excitation, excitation of conduction electrons leading to secondary electron emission, ionization of inner shells, Bremsstrahlung or Continuum x-Rays, and excitation of phonons. Inelastic scattering then, slows the electrons as they penetrate into the sample.

Backscattered electron:

- Those electrons, which are deflected, back in the direction of the beam.
- The special detector in scanning and transmission electron microscope traps these signals.
- These are used to discriminate areas of different atomic numbered elements. Higher atomic numbered elements gives off more backscattered electrons and appear brighter than lower numbered elements.

Secondary Electrons:

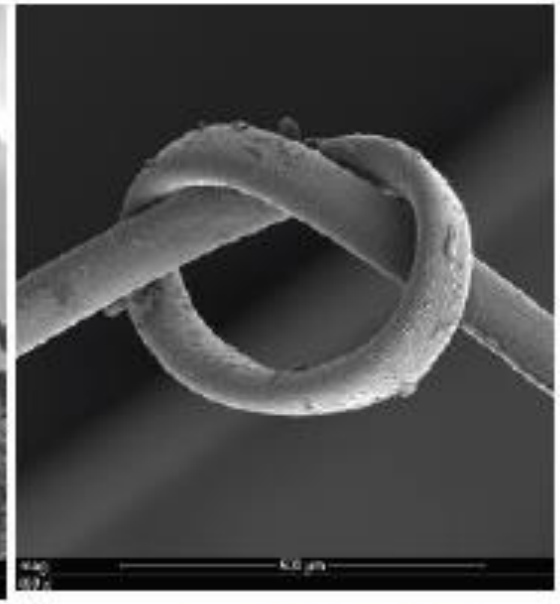
- These electrons are also collected with a special type of detector used in SEM and TEM. They are used primarily to reveal topographical feature of a specimen. It has the resolving power <10 nm.

Auger Electrons:

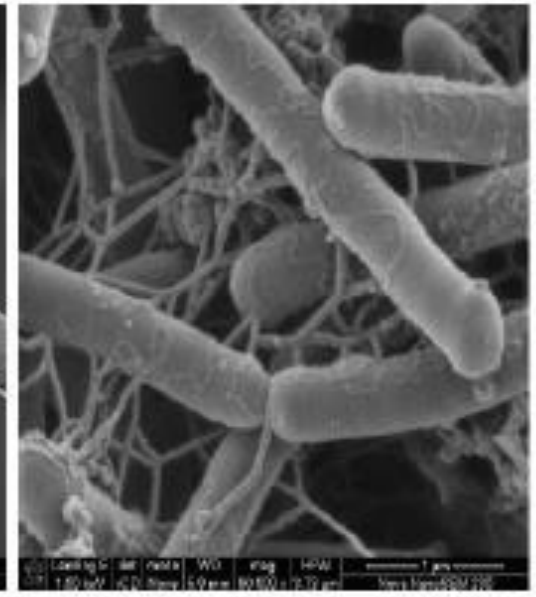
- These are special types of low energy electrons that carry the information about the chemical nature (atomic composition) of the specimen.
- These are generated from the upper layer of specimen.
- It is a powerful tool in the material sciences for studying the distribution of the lighter numbered atomic elements on the surface of the specimen.
- It has limited application in biological sciences. It is specialized equipment known as scanning auger electron spectrometer.

SEM micrographs

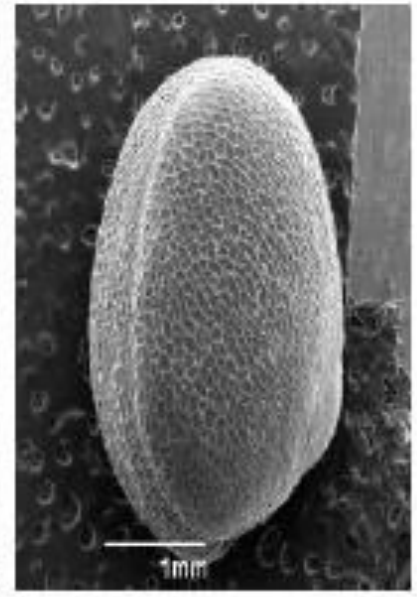
Pollen of Hibiscus



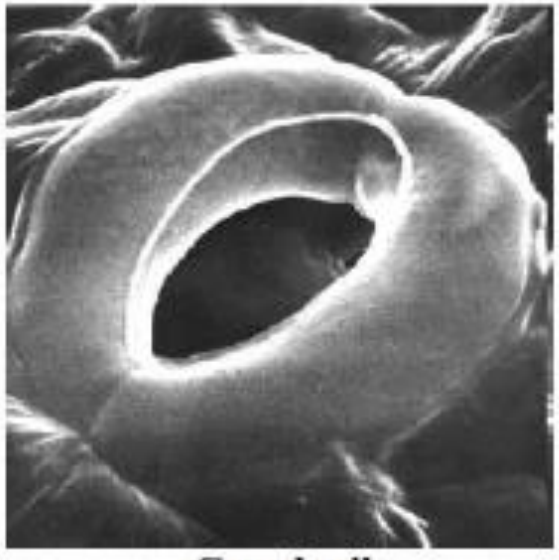
Knot Human Hair



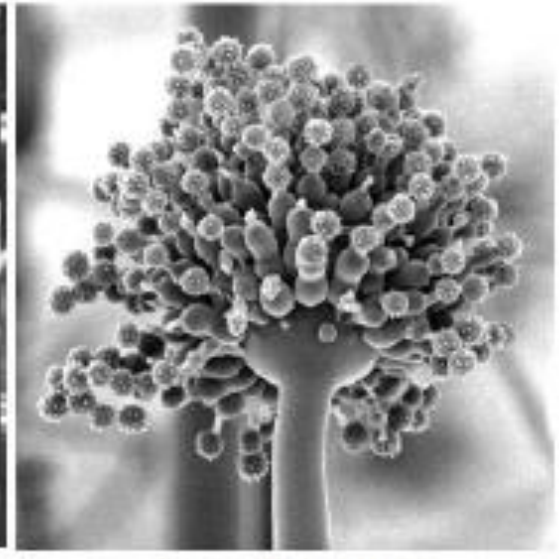
Salmonella Bacteria



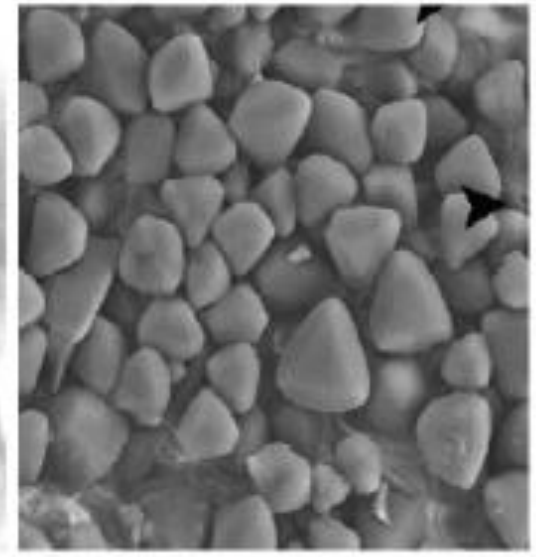
Radish seed



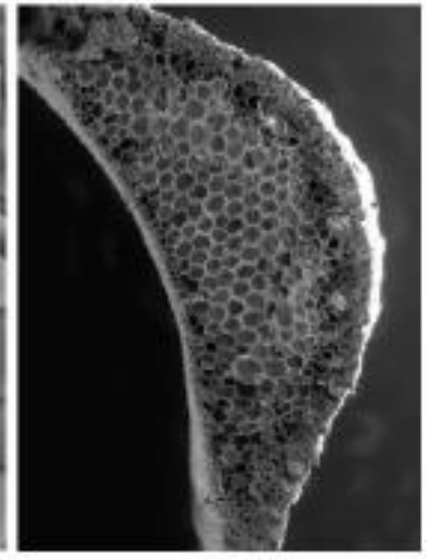
Guard cells



Aspergillus niger

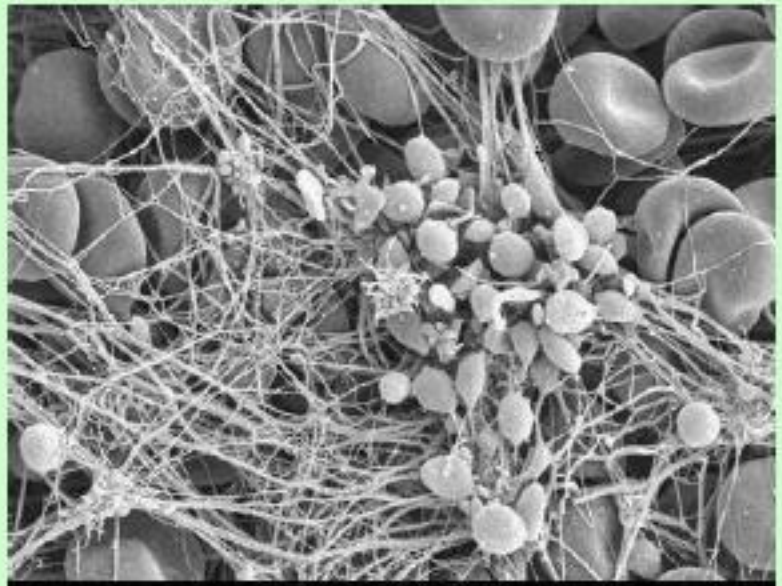


Nuclear Polyhedrosis Virus

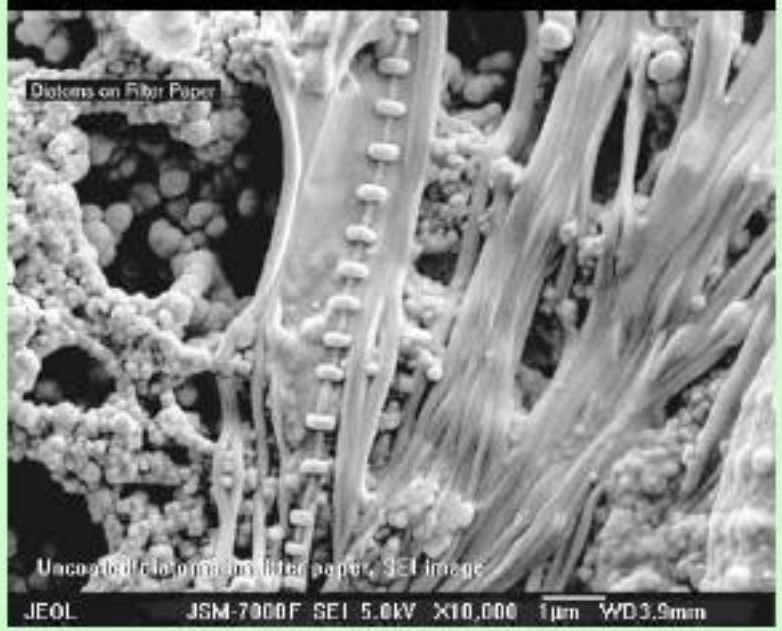


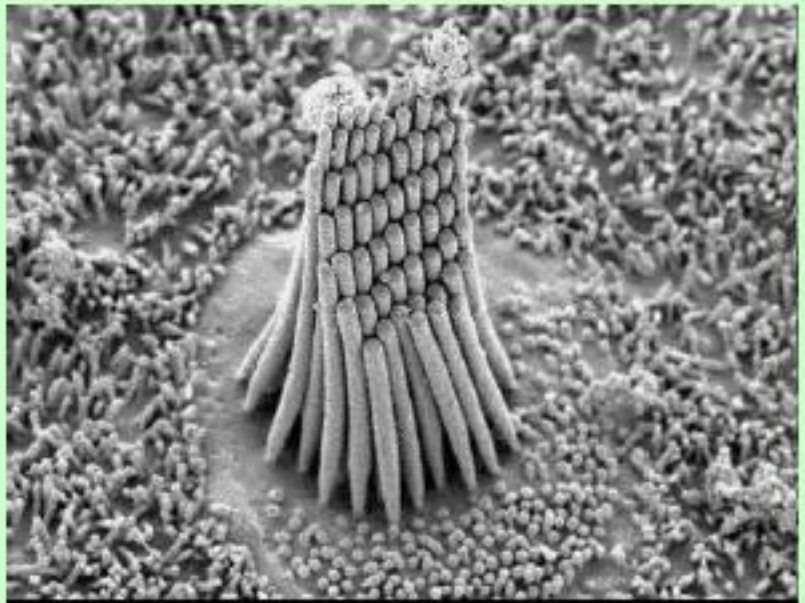
Cross section of leaf

Secondary Electron Images

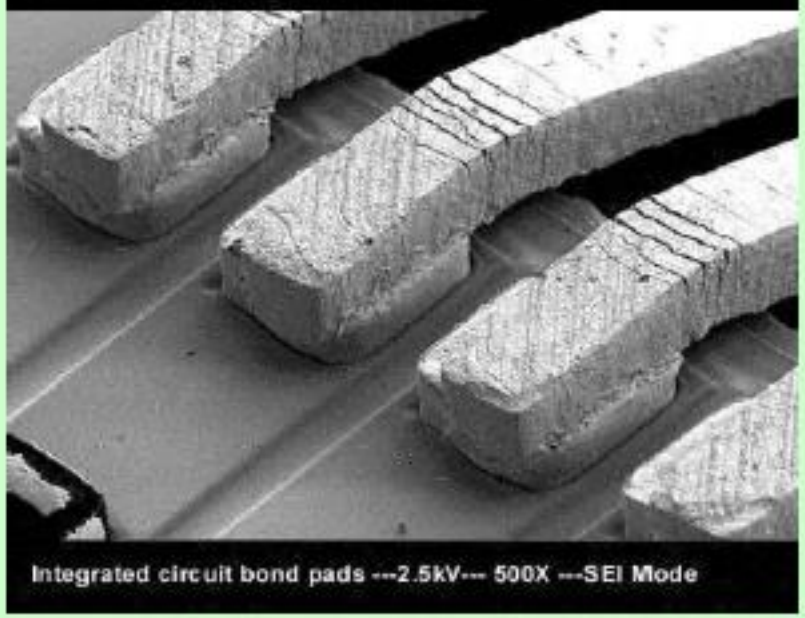


Blood Clot--- 5kV--- 3,700X--- SEI Mode





Mouse Inner Ear--- 2KV--- 12,000X--- SEI Mode



Integrated circuit bond pads ---2.5kV--- 500X ---SEI Mode

Applications of Scanning Electron Microscopy

Topography: **The surface features of an object or "how it looks", its texture; direct relation between these features and materials properties (hardness, reflectivity...etc.)**

Morphology: **The shape and size of the particles making up the object; direct relation between these structures and materials properties (ductility, strength, reactivity...etc.)**

Composition: **The elements and compounds that the object is composed of and the relative amounts of them; direct relationship between composition and materials properties (melting point, reactivity, hardness...etc.)**

Crystallographic Information: **How the atoms are arranged in the object; direct relation between these arrangements and materials properties (conductivity, electrical properties, strength.etc.)**

Advantages of SEM

- It gives detailed 3D and topographical imaging and the versatile information garnered from different detectors.
- This instrument works very fast.
- Modern SEMs allow for the generation of data in digital form.
- Most SEM samples require minimal preparation actions.

Disadvantages of SEM

- SEMs are expensive and large.
- Special training is required to operate an SEM.
- SEMs are limited to solid samples.
- SEMs carry a small risk of radiation exposure associated with the electrons that scatter from beneath the sample surface.

SEM Sample:

Conducting samples provide a path to ground for the beam electrons, and therefore require no special preparation. Insulating materials, however, require a thin coating of a conductor (often carbon or gold) in order to prevent charging.

Sample Preparation

It is done in order to eliminate the sample charging few steps are followed:

1. Charging: A thin metal coating of about 10nm is done on the sample because metal film is highly stable and its secondary electron yield is higher. Too thin coating is not preferred because continuity is lost.

2. Low accelerating voltage: Low KV value of about 1KV can be used to scan insulating samples because the number of incident electrons becomes equal to the number of emitted secondary electrons, implying that the sample is not charged.

3. Tilt Observation: In this case secondary electrons yield is higher as electron beam is entering at an angle.

4. Low Vacuum SEM observation: On decreasing the vacuum, the gas molecules within the sample chamber increases, which get ionized due to electrons and thus, on reaching the specimen as positive ions neutralize the charging.

Transmission Electron Microscope (TEM)

➢The **transmission electron microscope** (TEM) was the first type of Electron Microscope to be developed and is patterned exactly on the light transmission microscope except that a focused beam of electrons is used instead of light to "see through" the specimen. It was developed by Max Knoll and Ernst Ruska in Germany in 1931.

MICROSCOPE	RESOLUTION	MAGNIFICATION
OPTICAL	200 nm	1000X
TEM	0.2 nm	5,00000X

Introduction

- **Transmission electron microscopy** (**TEM**, also sometimes **conventional transmission electron microscopy** or **CTEM**) is a microscopy technique in which a beam of electrons is transmitted through a specimen to form an image.
- The specimen is most often an ultrathin section less than 100 nm thick or a suspension on a grid.
- An image is formed from the interaction of the electrons with the sample as the beam is transmitted through the specimen.
- The image is then magnified and focused onto an imaging device, such as a fluorescent screen, a layer of photographic film, or a sensor such as a charge-coupled device.

Introduction

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- The image is then magnified and focused onto an imaging device, such as a fluorescent screen, a layer of photographic film, or a sensor such as a charge-coupled device.

- Transmission electron microscopes are capable of imaging at a significantly higher resolution than light microscopes, owing to the smaller de Broglie wavelength of electrons.

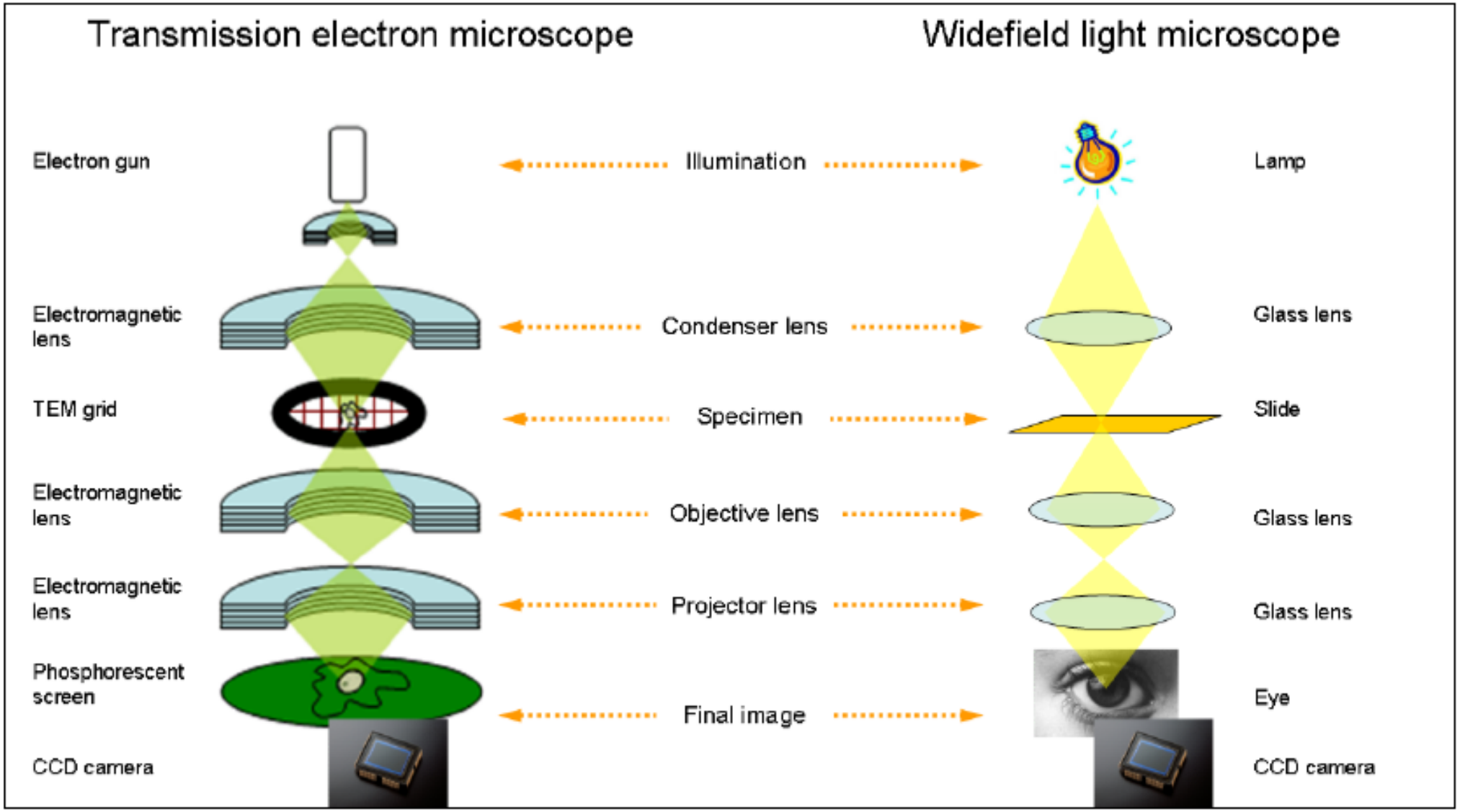
- This enables the instrument to capture fine detail—even as small as a single column of atoms, which is thousands of times smaller than a resolvable object seen in a light microscope.

- Transmission electron microscopy is a major analytical method in the physical, chemical and biological sciences.

- TEMs find application in cancer research, virology, and materials science as well as polluton, nanotechnology and semiconductor research.

Transmission electron microscopy (TEM)

Design of TEM similar to a light microscope-



DIFFERENCES BETWEEN OM AND EM

OPTICAL MICROSCOPE	ELECTRON MICROSCOPE
1. The source of light. Visible light 2. The specimen On glass slide 3. The lenses that makes the specimen seem bigger. 4. The magnified image of the specimen that you see.	1. The light source is replaced by a beam of very fast moving **electrons**. 2. The specimen usually has to be specially prepared and held inside a **vacuum chamber** from which the air has been pumped out (because electrons do not travel very far in air). 3. The lenses are replaced by a series of coil-shaped **electromagnets** through which the electron beam travels. 4. The image is formed as a photograph (called an electron micrograph) or as an image on a **TV screen**.

Transmission electron microscopy (TEM)

- **Recent Transmission electron microscopy commonly contains a beam column which is around 2.5m tall and has a 30cm diameter, and its ability to attain a 2Å resolution.**

- **The transmission electron microscope is a very powerful tool for material science.**

- **In TEM high energy beam of electrons is passes through a very thin sample, and the interactions between the electrons and the atoms can be used to observe features such as the topographical, morphological, compositional and crystalline information and features in the structure like dislocations and grain boundaries. Chemical analysis can also be performed. High resolution can be used to analyze the quality, shape, size and density of quantum wells, wires and dots.**

- **The TEM operates on the same basic principles as the light microscope but uses electrons instead of light. Because the wavelength of electrons is much smaller than that of light, the optimal resolution attainable for TEM images is many orders of magnitude better than that from a light microscope. Thus, the so formed image can be magnified and focused on the device used for an imaging, like a fluorescent screen, on a photographic film layer, or to be identified by a sensor like a CCD camera. Thus, TEMs can reveal the finest details of internal structure - in some cases as small as individual atoms.**

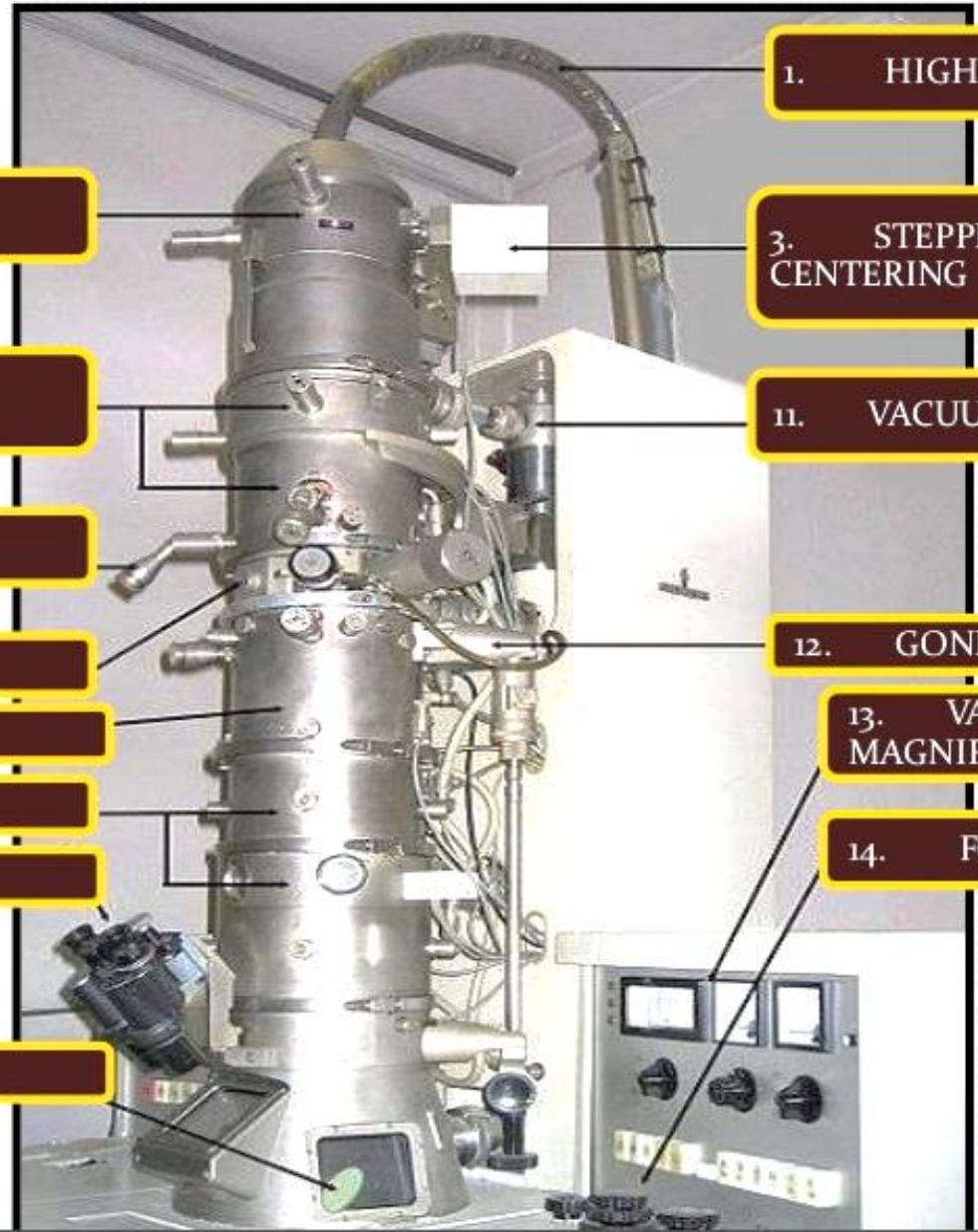
The principles of TEM

- Transmission electron microscopy uses high energy electrons (up to 300 kV accelerating voltage) which are accelerated to nearly the speed of light.
- The electron beam behaves like a wavefront with wavelength about a million times shorter than lightwaves.
- When an electron beam passes through a thin-section specimen of a material, electrons are scattered.
- A sophisticated system of electromagnetic lenses focuses the scattered electrons into an image or a diffraction pattern, or a nano-analytical spectrum, depending on the mode of operation.

- Each of these modes offers a different insight about the specimen. The imaging mode provides a highly magnified view of the micro- and nanostructure and ultimately, in the high resolution imaging mode a direct map of atomic arrangements can be obtained (high resolution EM = HREM).

- The diffraction mode (electron diffraction) displays accurate information about the local crystal structure. The nanoanalytical modes (x-ray and electron spectrometry) tell researchers which elements are present in the tiny volume of material.
- These modes of operation provide valuable information for scientists and engineers in search of stronger materials, faster microchips, or smaller nanocrystals.

DIFFERENT COMPONENTS OF TEM



1. HIGH TENSION CABLE
2. ELECTRON EMITTER
3. STEPPER MOTORS FOR CENTERING THE ELECTRON BEAM
4. CONDENSER
5. APERTURE CONTROLS
6. SPECIMEN HOLDER
7. OBJECTIVE LENS
8. PROJECTOR LENS
9. OPTICAL LENS
10. FLUORESCENT SCREEN
11. VACUUM PUMP LEADS
12. GONIOMETER
13. VACUUM AND MAGNIFICATION CONTROL
14. FOCUSING CONTROL

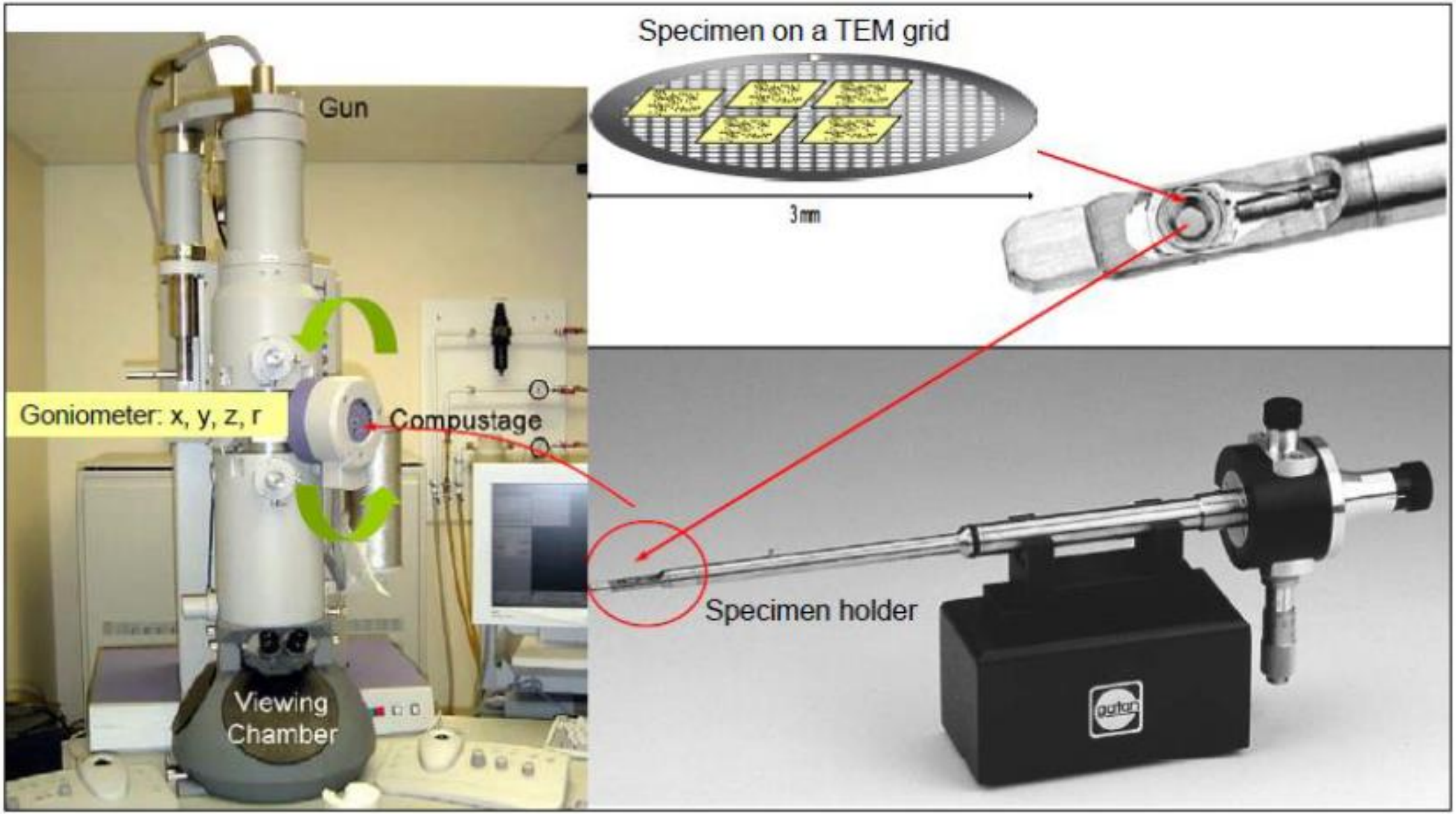
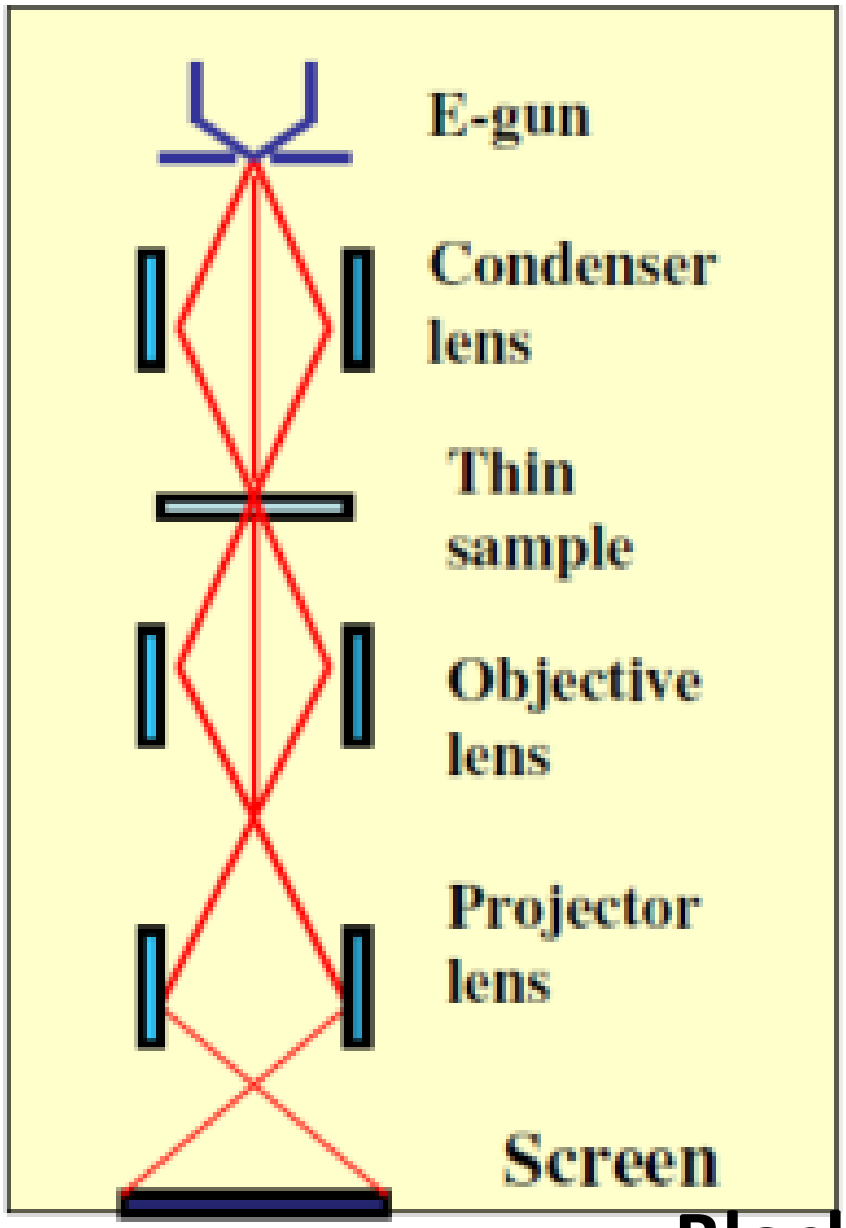
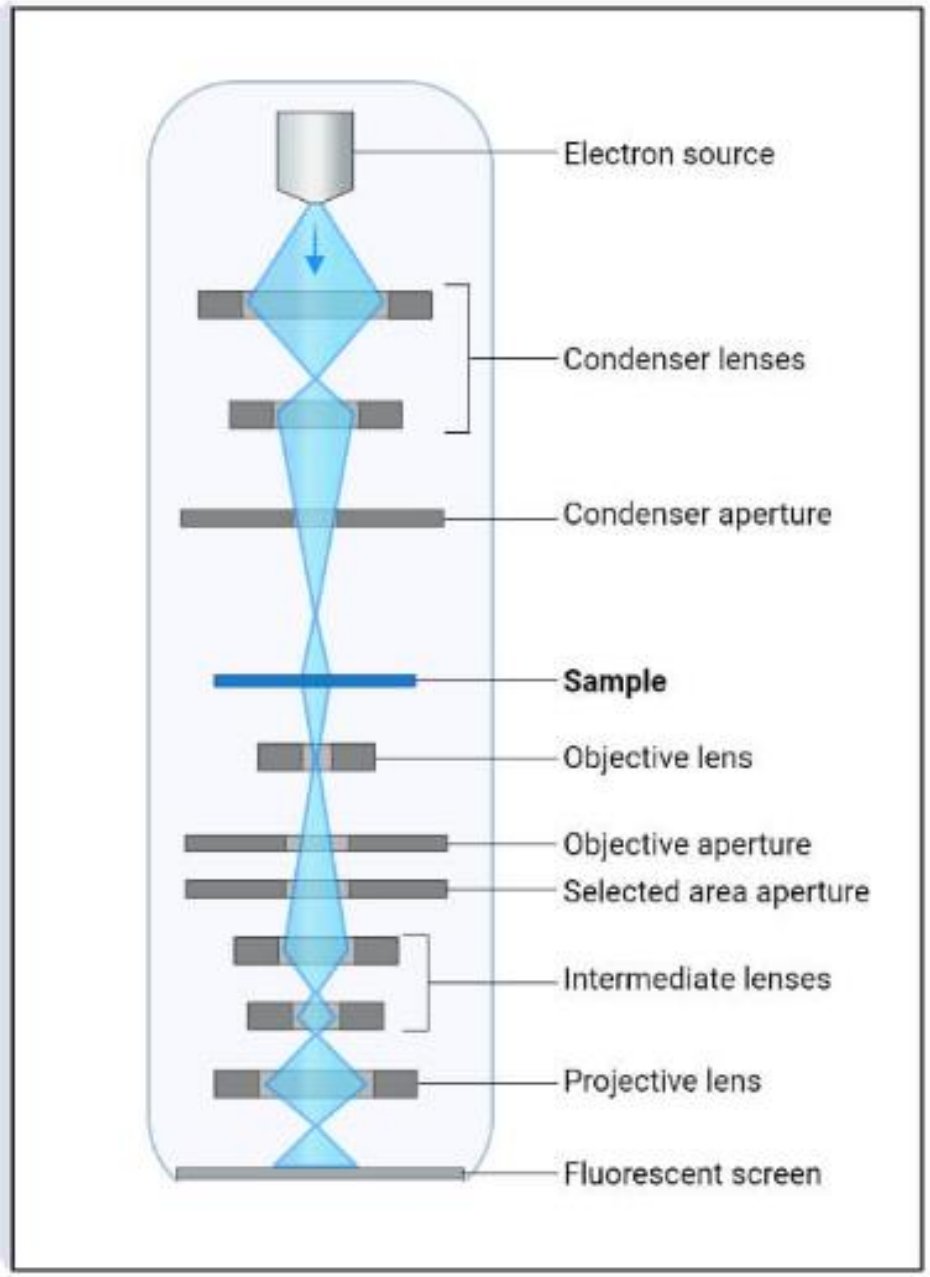


Fig 4: Thin sections of a specimen on a TEM grid, holder tip and complete specimen holder, which is introduced into the goniometer of the TEM through a vacuum lock.

Instrumentation of TEM





Block diagram of TEM

- The "Virtual Source" at the top represents the electron gun, producing a stream of monochromatic electrons.
- This stream is focused to a small, thin, coherent beam by the use of condenser lenses 1 and 2. The first lens (usually controlled by the "spot size knob") largely determines the "spot size"; the general size range of the final spot that strikes the sample.
- The second lens (usually controlled by the "intensity or brightness knob" actually changes the size of the spot on the sample; changing it from a wide dispersed spot to a pinpoint beam.
- The beam is restricted by the condenser aperture (usually user selectable), knocking out high angle electrons (those far from the optic axis, the dotted line down the center)

- The beam strikes the specimen and parts of it are transmitted.
- This transmitted portion is focused by the objective lens into an image
- The image is passed down the column through the projector lenses, being enlarged all the way.
- The image strikes the phosphor image screen and light is generated, allowing the user to see the image

How does a Transmission Electron Microscope (TEM) work?

From the instrumentation described, the working mechanism is a sequential process of the parts of the TEM mentioned above. To mean:

- **A heated tungsten filament in the electron gun produces electrons that get focus on the specimen by the condenser lenses.**
- **Magnetic lenses are used to focus the beam of electrons of the specimen. By the assistance offered by the column tube of the condenser lens into the vacuum creating a clear image, the vacuum allows electrons to produce a clear image without collision with any air molecules which may deflect them.**
- **On reaching the specimen, the specimen scatters the electrons focusing them on the magnetic lenses forming a large clear image, and if it passes through a fluorescent screen it forms a polychromatic image.**
- **The denser the specimen, the more the electrons are scattered forming a darker image because fewer electron reaches the screen for visualization while thinner, more transparent specimens appear brighter.**

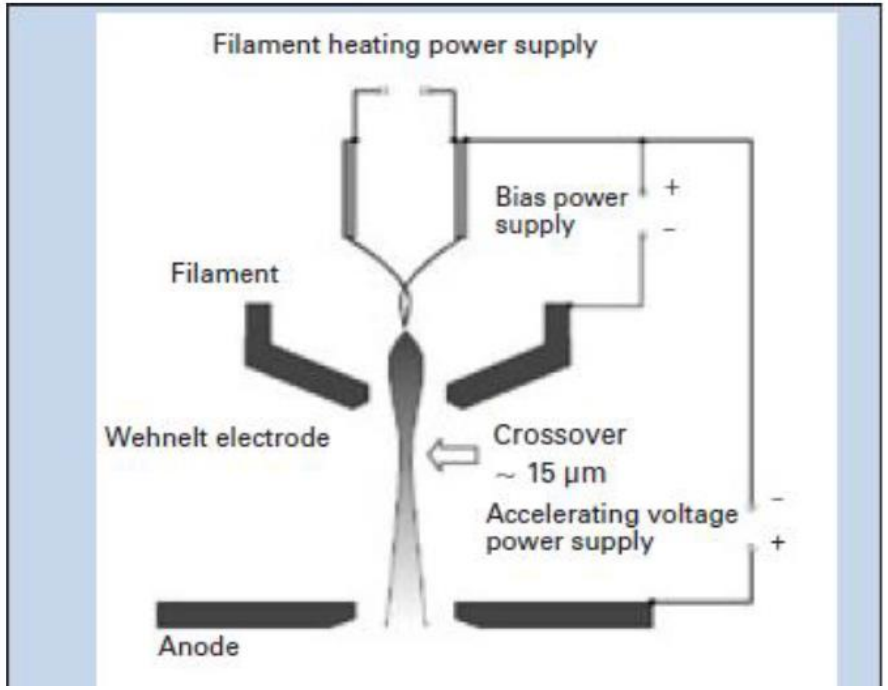
Parts of the machine

- The typical transmission electron microscope laboratory contains a machine with these components:

I. Electron gun
II. Electron column
III. Electro-magnetic lens system
IV. Detectors
V. Water chilling system
VI. Specimen/sample chamber
VII. Main control panel and operational controls
VIII. Image capture

TE (Thermionic- Emission) gun

- **A thin tungsten wire filament acts as cathode to generate thermo electrons by heating the filament at 2800K.**
- **A positive voltage of about 1 to 30 KV is applied to the metal plate acting as anode, in order to collect these thermo electrons.**
- **By applying negative voltage to the Wehnelt electrode placed between the anode and the cathode, current of the electron beam is adjusted. This electrode also helps in focussing the electron beam.**
- **Thinnest point of beam known as cross-over (15-20µm Diameter), regarded as actual electron source.**

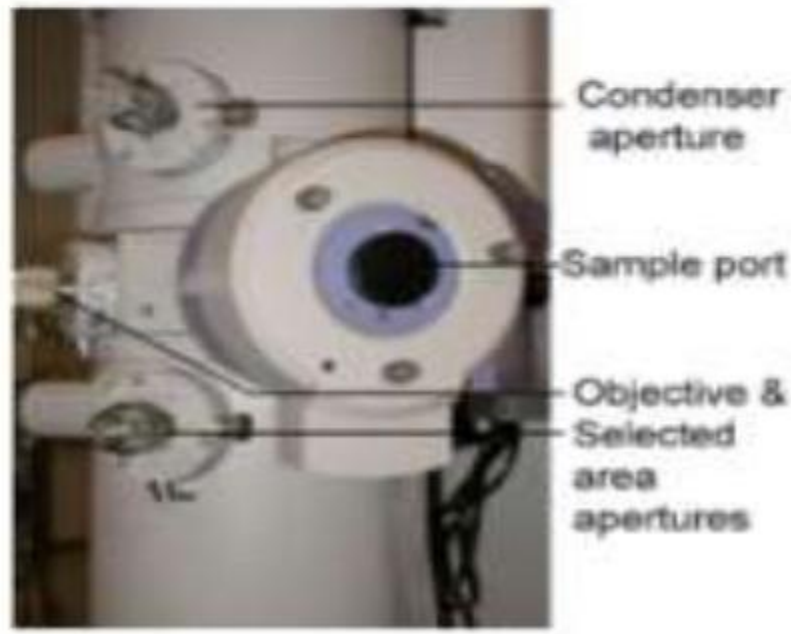


Accelerating voltage

- **Electrons emitted by the filament are accelerated by a series of anodes.**
- **For transmission electron microscopy, accelerating voltages typically range from 60 kV to 200 kV.**
- **Higher accelerating voltages give higher resolution, but less contrast.**
- **High accelerating voltages can also result in greater specimen damage. For these reasons, studies of biological samples tend to employ low accelerating voltages (60 kV to 100 kV), while studies of inorganic materials, which often require higher resolution, usually employ an accelerating voltage of 200 kV.**

Electron column

- The electron column is made up of the gun assembly at the top, a column filled with a set of electromagnetic lenses, the sample port and airlock, and a set of apertures that can be moved in and out of the path of the beam. The contents of the column are under vacuum.



Apertures

- **The condenser aperture controls the fraction of the beam which is allowed to hit the specimen. It therefore helps to control the intensity of illumination.**
- **The objective aperture is used to select which beams in the diffraction pattern contribute to the image, thus producing diffraction contrast.**
- **The selected area aperture is used to selected a region of the specimen from which a diffraction pattern or image to be obtained.**

Objective lenses:

- **Objective lens is used primarily to focus the transmitted electrons and initially magnify the image.**

- **The projector lenses are used to expand the beam onto the phosphor screen or other imaging device, such as film. The magnification of the TEM is due to the ratio of the distances between the specimen and the objective lens' image plane**

Specimen holders and stages:

- In TEM, the electron column does not offer a lot of space for the sample. Additionally, the sample should be fine (thin around 100nm) so that the electrons can penetrate the specimen and form an image.
- The average thickness of a biological specimen should be around 70 nm for a TEM with an acceleration voltage for the electrons of ~100 kV (the higher the voltage, the thicker specimens can be examined).
- Thin sections of the specimen are mounted on copper grids of 3 mm diameter, which are available in a wide variety of materials and mesh sizes.
- The grids with the sections on top are attached in a holder and introduced into the goniometer of the TEM through a vacuum lock, since the system always stays under high vacuum.
- The goniometer is the mechanical setup which enables highly precise and stable control of the specimen holder during imaging. Any drift or instability results in an un-sharp image, in particular at high magnifications.

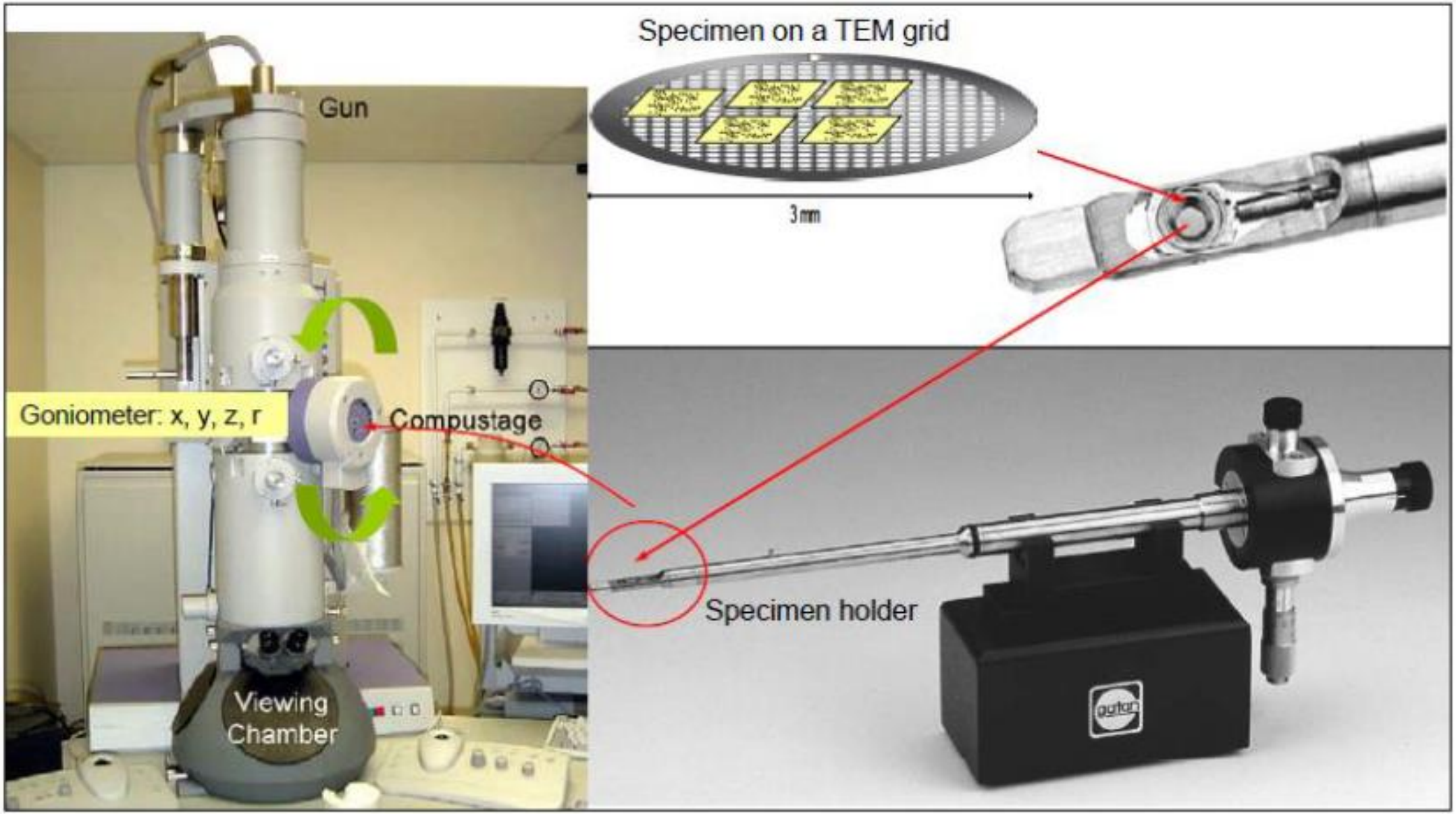
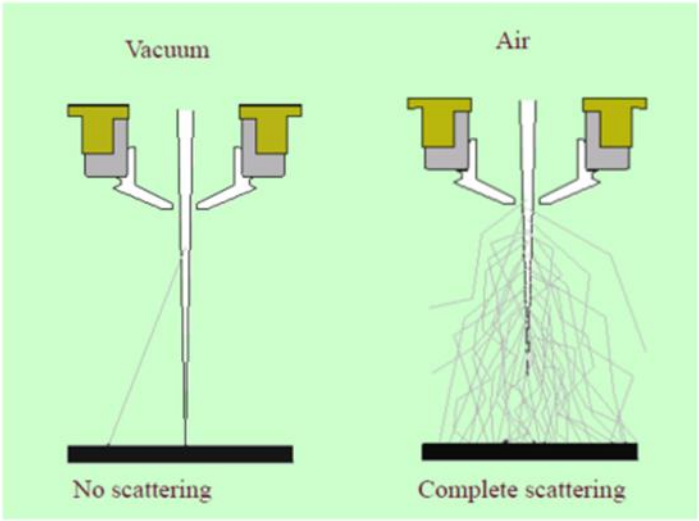


Fig 4: Thin sections of a specimen on a TEM grid, holder tip and complete specimen holder, which is introduced into the goniometer of the TEM through a vacuum lock.

Vacuum System:

Vacuum system is employed in electron microscopes for 4 reasons:

- **To avoid scattering of electrons.**
- **The purpose of the vacuum system is to provide insulation amongst the filament of both anode and cathode as well as in the region around the field emitters, thus avoiding the undesirable electron gun electrical discharge.**
- **In order to inhibit the oxidation and 'burning out' of the filament, so oxygen is eliminated around the filament.**
- **To decrease Samples contamination by reducing the interaction amongst beam of the electron and molecules of the gas.**



Phosphor or fluorescent screen (Imaging Device):

There are 2 modes for specimen observation in TEM.

1. **Image mode .**
2. **Diffraction mode**

- **In case of image mode, the electron beam hitting the sample is controlled by condenser lens and aperture, the beam which is transmitted will be focused and enlarged by objective and projector lens thus the image is formed on the screen, providing the microstructure of the sample.**

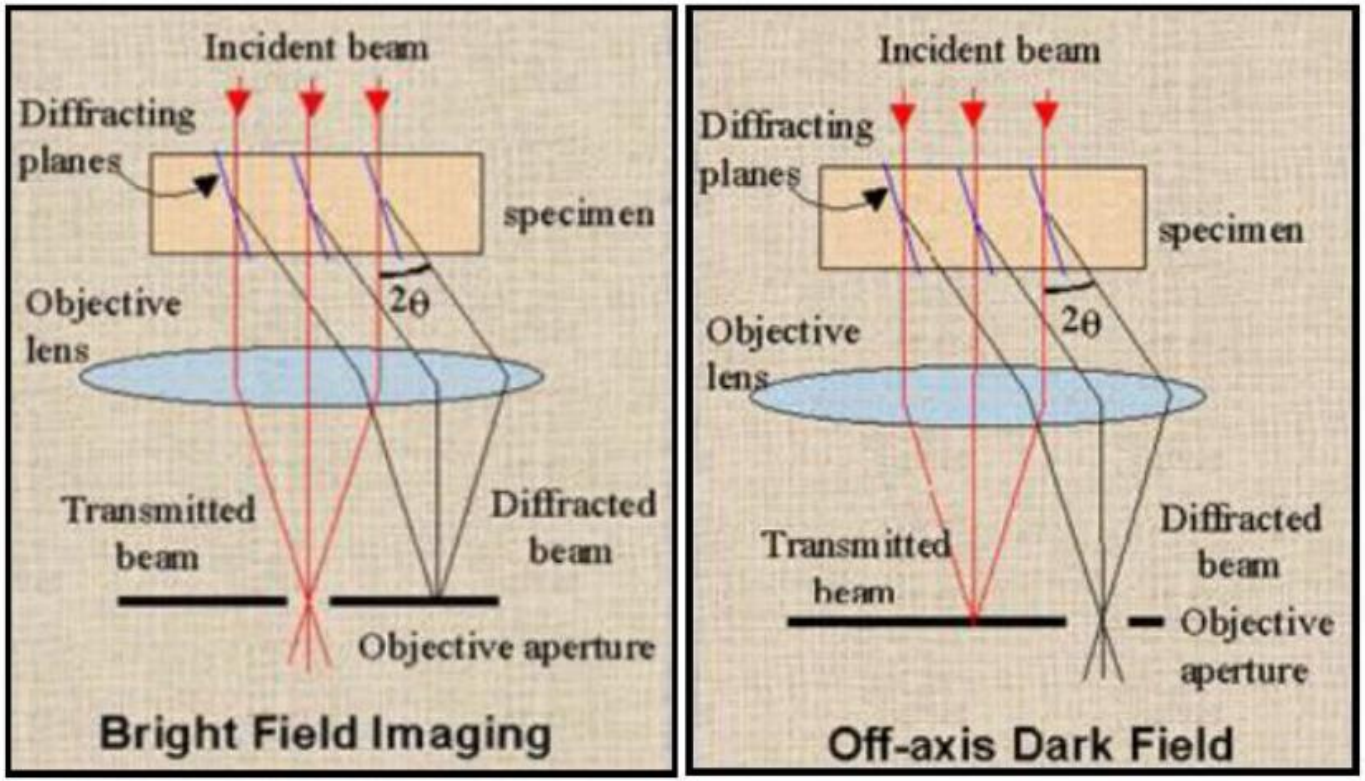
- **In case of diffraction mode, at the fluorescent screen a diffraction pattern (of electron) is attained which has originated from the electron beam illuminated sample region. The pattern of diffraction is completely equal to that of a pattern of X−ray diffraction. The spot pattern is produced by a single crystal on the screen whereas poly-crystal produces a pattern of powder or ring. The purpose of the image mode is to analyse microstructure, e.g. the grain size, and lattice defects, whereas the use of diffraction mode is to examine crystalline structure.**

Image Modes of TEM-

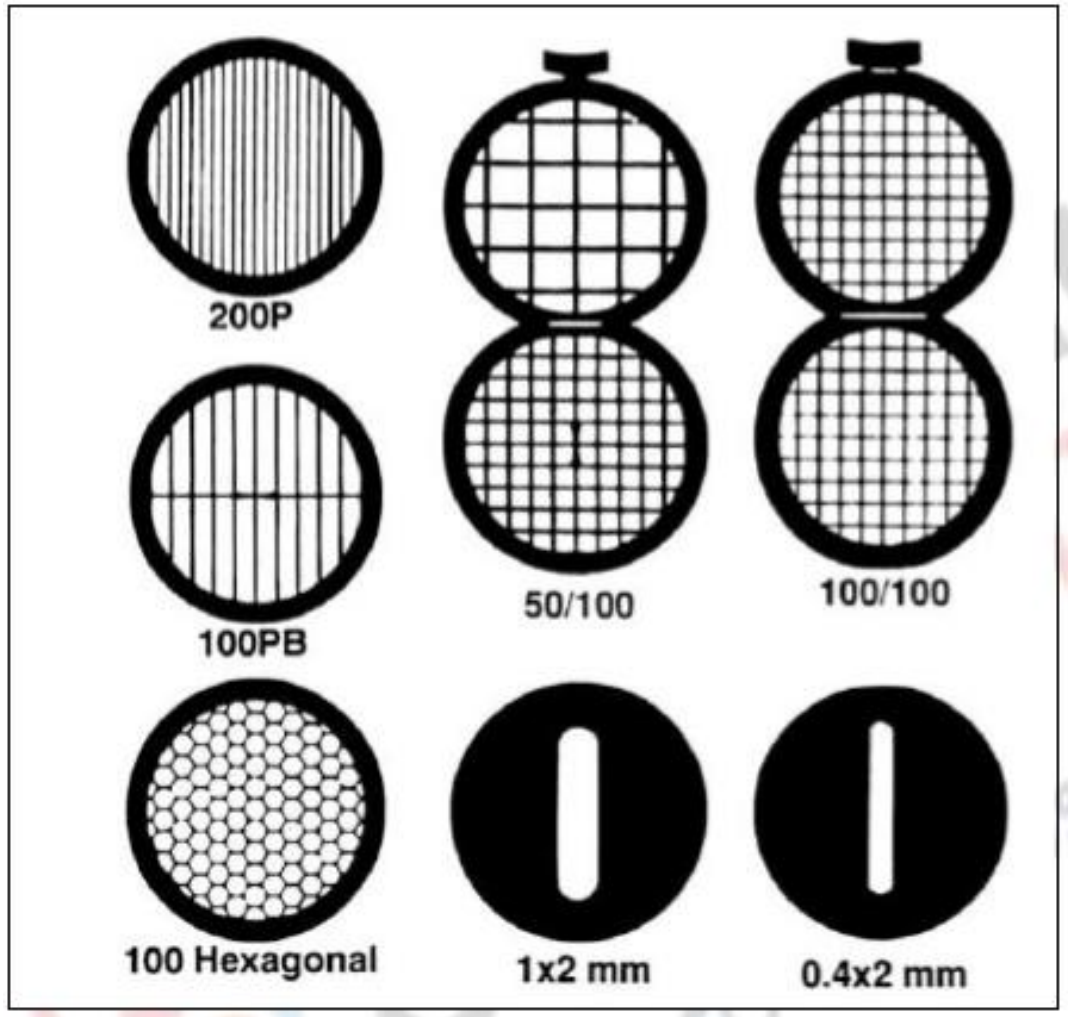
In TEM, the primary image modes are

1. **Bright field microscopy**
2. **Dark field microscopy**

In bright field imaging, the image formed of a thin sample is by the transmitted electrons that permit through the film deprived of diffraction, the diaphragm is used to stop the diffracted electrons. In the corresponding dark field imaging mode, the image is formed by a diffracted beam.

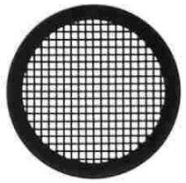


TEM samples are either self-supported or mounted on a grid for analysis. Copper grids are the most commonly used, though for high temperature work Mo grids are used. For nanoparticles and thin films a-C (amorphous carbon) film is used as support. a-C has low contrast in the TEM and will not affect the contrast arising from the specimen. Some typical TEM grids are shown below

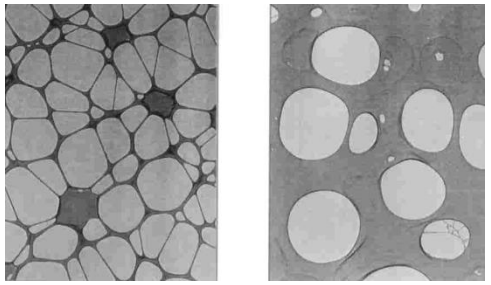


Specimen preparation for TEM

- **Specimens for TEM are typically supported on 3 mm diameter grids, usually made of copper. These grids may have thin carbon films suspended across them, which may be continuous or holey.**
- Specimens for TEM need to be less than ~ 100 nm in thickness, in order for the electrons to pass through and form an image. For some materials, e.g. inorganic powders, specimen preparation is extremely straightforward and simply involves grinding the material to a fine powder, dispersing in a liquid, pipetting onto a grid and allowing to dry. For organic or biological materials more specialised techniques are needed.



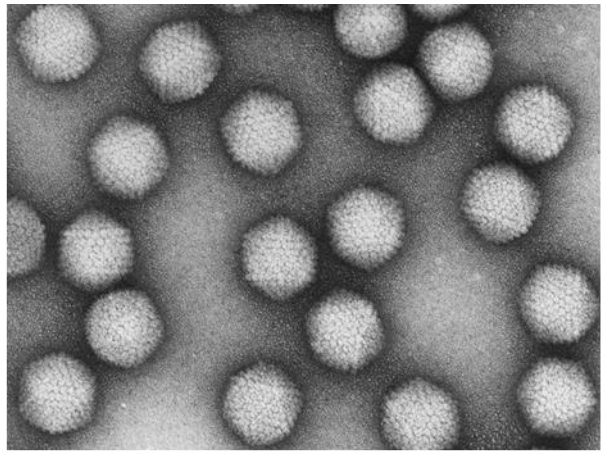
3 mm TEM grid



Carbon films

Specimen preparation for TEM -

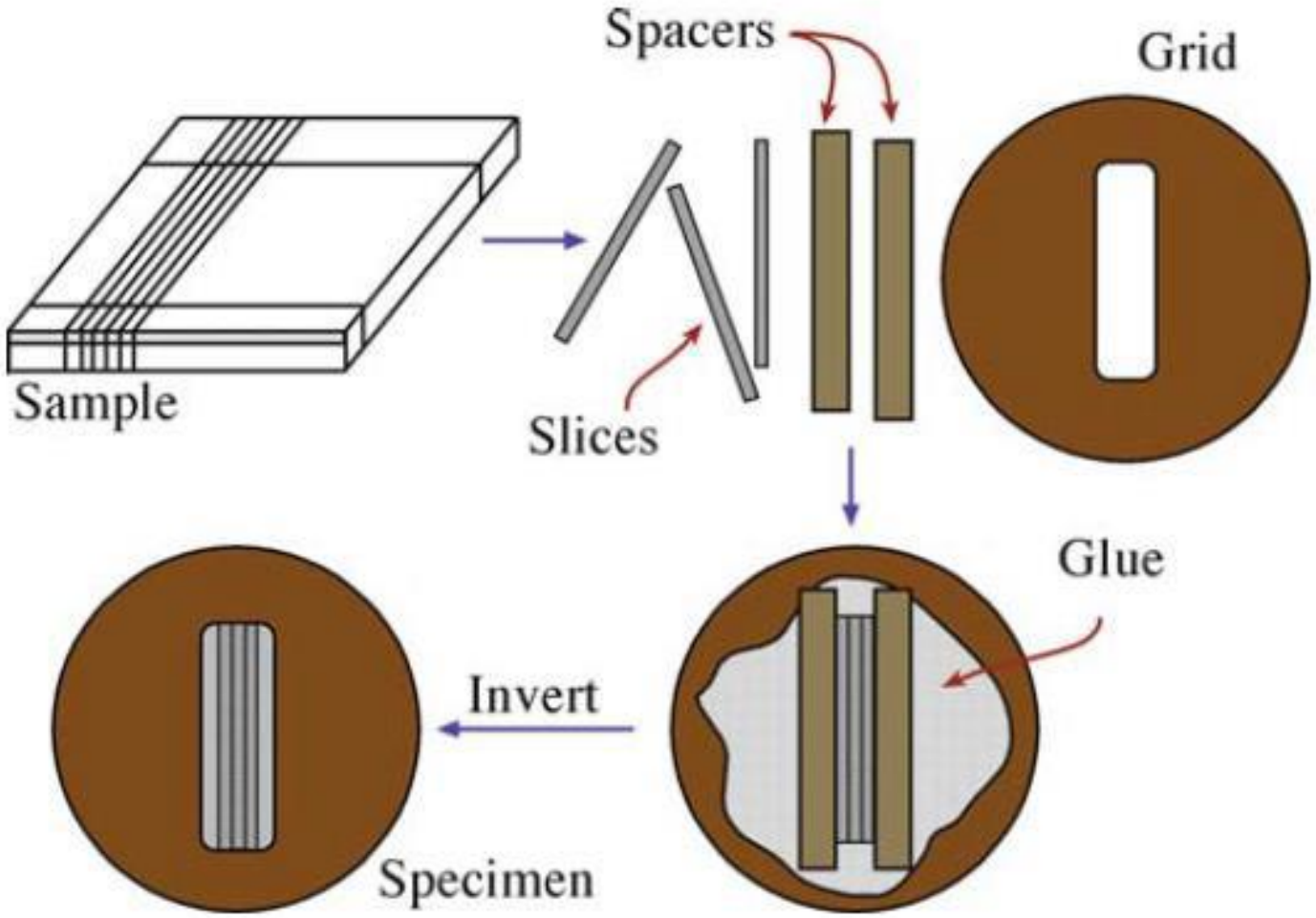
- **Small biological structures such as viruses and bacteria can be deposited onto carbon films from solution, but would give very little contrast in their untreated state. In such cases the technique of negative staining is often used to reveal structure.**
- Negative staining involves surrounding the biomolecules with thin amorphous layer of heavy metal salt. This reveals the structure, and reduces the structural flattening that occurs in the absence of stain.
- Commonly used stains: uranyl acetate, uranyl formate, sodium/potassium phosphotungstate, ammonium molybdate.



Adenovirus negatively stained with uranyl acetate

Cross section sample preparation:

Slices of the sample are cut using a diamond slicer. These slices are placed between spacer layers and then glued on to a grid. The slices are glued in such a way that the interface is parallel to the slot in the grid. This sample is then thinned by standard tripod polishing until it is a few µm thick. The finally sample is thinned using a ion beam miller to create an electron transparent sample.



TEM sample Preparation

- ***Cleaning the surface of the specimen***

  The proper cleaning of the surface of the sample is important because the surface can contain a variety of unwanted deposits, such as dust, silt, and detritus, media components, or other contaminants.

  The best way to clean the surface of specimen from contaminants is to carefully rinse them three times for 10 min in 0.1 M cacodylic acid buffer (pH 7.3) at room temperature.

TEM sample Preparation

- ***Primary fixation of the specimen***

  Fixation can be achieved by perfusion and microinjection, immersions, or with vapours using various fixatives including aldehydes(glutaraldehyde), osmium tetroxide,, tannic acid, or thiocarbohydrazide.

  ➢ **FIXATIVES**- are chemicals that denature and precipitate cellular macromolecules.

Some common fixatives:

1. GLUTARALDEHYDE- is a 5-carbon with an aldehyde group at each end of the molecule. An aldehyde groups reacts with amino groups and cross link with the proteins into an insoluble network.
2. OSMIUM- heavy metal that reacts primarily with fatty acids leading to the preservation of cellular membranes.

TEM sample Preparation

- ***Rinsing of the specimen***

  After the fixation step, samples must be rinsed in order to remove the excess fixative. To remove excess glutaraldehyde from the samples, the specimen should be subjected to a thorough but carefully conducted rinsing procedure. Specimens can be washed in 0.1 M cacodylic acid buffer (pH 7.3), starting with one time for 10 min, and then three times for 20 min at 4 0C.

TEM SAMPLE PREPARATION

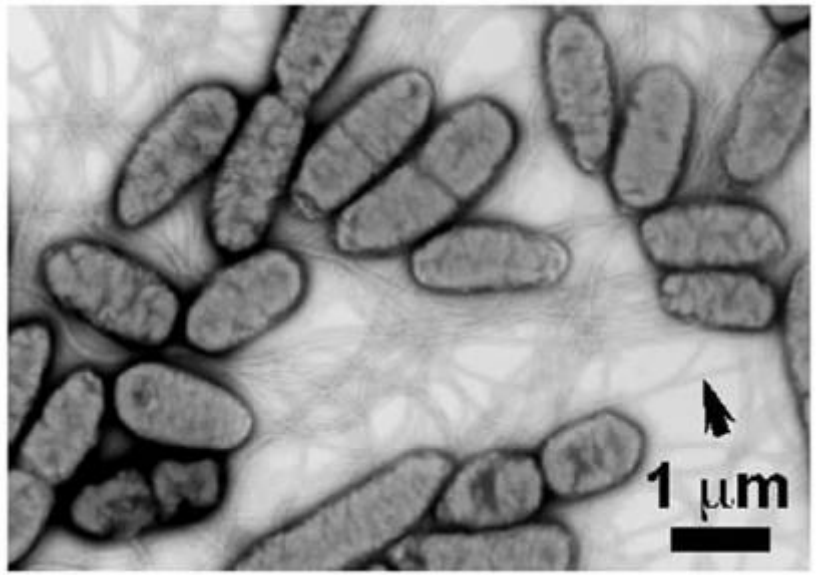
- ***Secondary fixation of the specimen***

  Specimen can be successfully stabilized for TEM investigation by post fixation with 1% osmium tetroxide prepared in 0.1 M cacodylic acid buffer (pH 7.3) for 1.5 hrs at room temperature (immersion fixation).

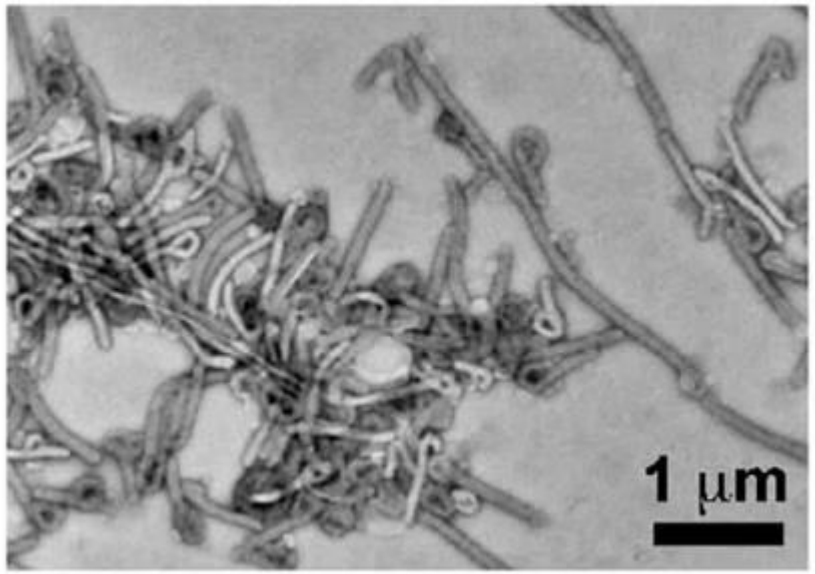
TEM sample Preparation

- ***Dehydrating the specimen***

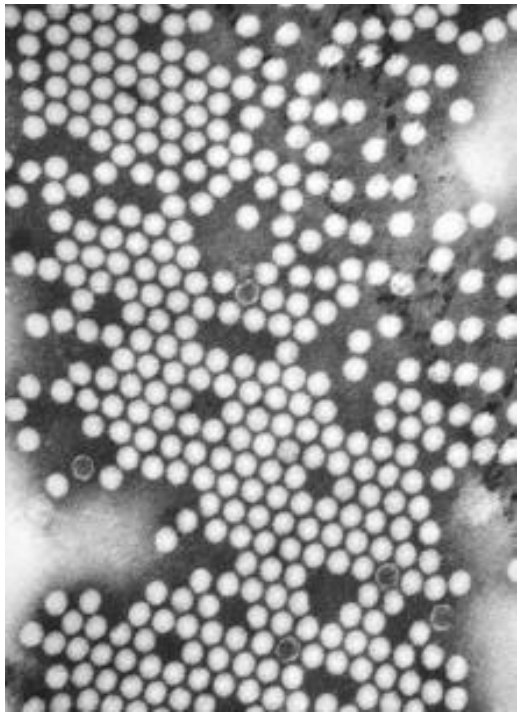
  For TEM investigation, specimen can be dehydrated in a graded series of ethanol. More specifically, the following protocol is useful: Dehydration of specimen in 50% ethanol for 5 min, 70% ethanol for 10 min, 80% ethanol for 10 min, 90% ethanol for 15 min, and 99.9% ethanol (dried with a 4-mesh molecular sieve) twice for 20 min at room temperature. This process allows the water in the samples to be slowly exchanged through liquids with lower surface tensions.



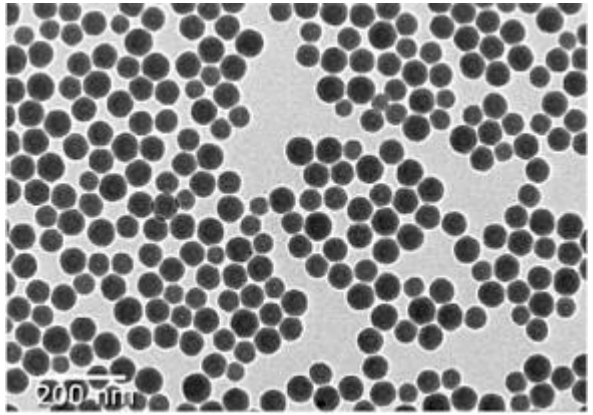
***Salmonella* Senftenberg virus**



Ebola virus



Polio virus



Silica nanoparticles

Applications of Transmission Electron Microscope (TEM) :

TEM is used in a wide variety of fields From Biology, Microbiology, Nanotechnology, forensic studies, etc. Some of these applications include:

1. **To visualize and study cell structures of bacteria, viruses, and fungi**
2. **To view plasmids**
3. **To view the shapes and sizes of microbial cell organelles**
4. **To study and differentiate between plant and animal cells.**
5. **Its also used in nanotechnology to study nanoparticles such as ZnO nanoparticles**
6. **It is used to detect and identify fractures, damaged microparticles which further enable repair mechanisms of the particles.**

Advantages of TEM

- **TEMs offer the most powerful magnification, potentially over one million times or more**
- **TEMs have a wide-range of applications and can be utilized in a variety of different scientific, educational and industrial fields**
- **TEMs provide information on elements and compound structure**
- **Provides Images of high-quality**
- **TEMs are able to yield information of surface features, shape, size and structure**
- **They are easy to operate with proper training**

Disadvantages of TEM

- **The instruments are very large and expensive.**
- **TEMs require special housing and maintenance because they are sensitive to mechanical vibration, fluctuation of electromagnetic fields, and variation of cooling water.**
- **Sample preparations from bulk materials are normally very time-consuming.**
- **Potential artifacts can be generated by sample preparation.**
- **Special training is needed for tool operation and data analysis.**
- **TEM samples are limited to those that tolerate the vacuum chamber and are small enough to fit in the chamber.**

Comparison b/w SEM and TEM

- SEM is based on scattered electrons while TEM is based on transmitted electrons.
- The sample in TEM has to be cut thinner whereas there is no such need with SEM sample.
- SEM allows for large amount of sample to be analysed at a time whereas with TEM only small amount of sample can be analysed at a time.

Microscopy

Optical

- uses visible light and system of lenses to magnify
- oldest and simplest design
- new digital microscopes use CCD camera
- magnification up to 2000 times

Electron

- uses a particle beam of electrons to illuminate a specimen
- create a highly-magnified image
- uses electrostatic and electromagnetic lenses
- magnification up to 2 million times

Scanning Probe

- forms images of surfaces using a physical probe that scans the specimen
- surface image produced by mechanically moving probe in a raster scan of the specimen and recording probe-surface interaction as a function of position
- atomic resolution
- was founded in 1981

Scanning Probe Microscopy

What are scanning probe microscopes?

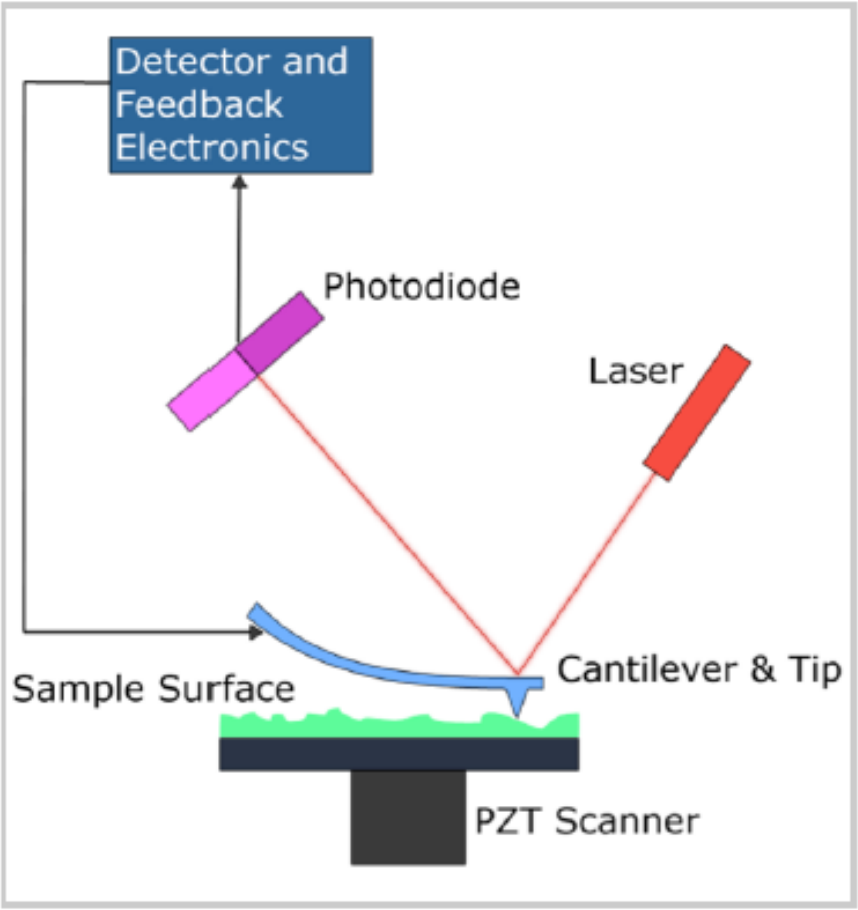
- Scanning probe microscopes (SPMs) are a family of tools used to record images of nanoscale surfaces and structures, including atoms. They use a physical probe to scan back and forth over the surface of a sample.
- During this scanning process, a computer gathers data that are used to generate an image 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?

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.

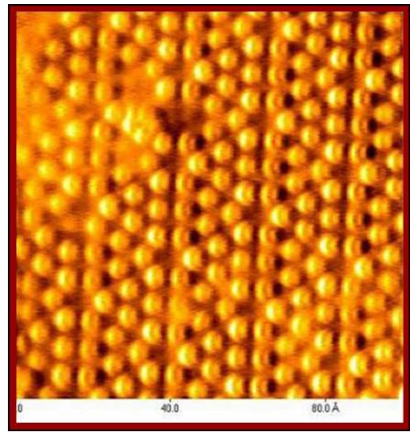
The distance of the deflection is measured by a laser that is reflected off the top of the cantilever and into an array of photodiodes (similar to the devices used in digital cameras). SPMs can detect differences in height that are a fraction of a nanometer, about the diameter of a single atom.



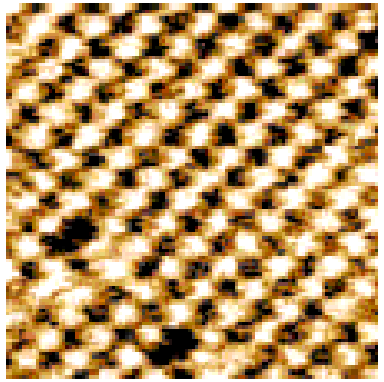
Scanning probe microscope

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 colourless 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 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.



Structure of silicon atoms


SPM Image of Sodium Chloride

SPM Types

- AFM, atomic force microscope
- BEEM, ballistic electron emission microscope
- EFM, electrostatic force microscope
- ESTM, electrochemical scanning tunneling microscope
- FMM, force modulation microscope
- KPFM, kelvin probe force microscope
- MFM, magnetic force microscope
- MRFM, magnetic resonance force microscope
- NSOM, Near-Field scanning optical microscope (or SNOM, scanning near-field optical microscopy)
- PFM, Piezo Force Microscopy
- PSTM, photon sanning tunneling microscope
- PTMS, photothermal microspectroscopy/microscope
- SAP, scanning atom probe
- SECM, scanning electrochemical microscope
- SCM, scanning capacitance microscope
- SGM, scanning gate microscope
- SICM, scanning ion-conductance microscope
- SPSM, spin polarized tunneling microscope
- SThM, scanning thermal microscope
- STM, scanning tunneling microscope
- SVM, scanning voltage microscope
- SHPM, scanning Hall probe microscope

1981: Dr. Binnig and Dr. Rohrer invent the scanning tunneling microscope (STM).

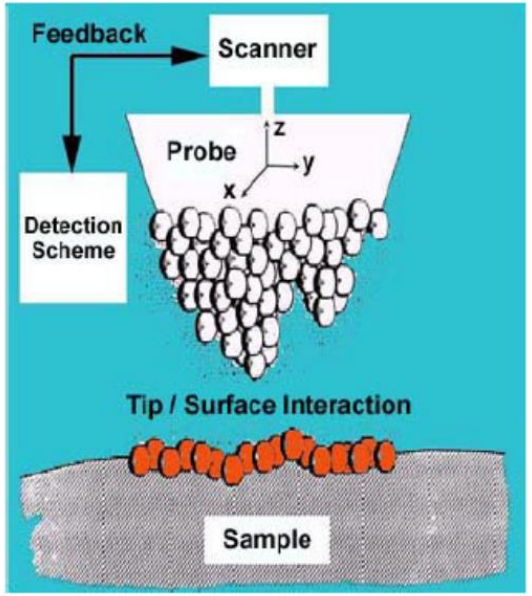
1985: Dr. Binnig, Dr. Christoph Gerber (IBM Zurich Research Center), and Dr. C. F. Quate (Stanford University) develop the atomic force microscope (AFM).

1986: Dr. Binnig and Dr. Rohrer are awarded the Nobel Prize in physics for the invention of the STM.

1988: AFM becomes available commercially.

- **Scanning probe microscopy was developed in the 1980s to enable scientists to investigate surfaces with atomic resolution.**
- **Scanning probe microscopes have a very sharp tip – so sharp that may be only one atom across at the tip. By dragging this tip around on different surfaces and recording the interaction between the tip and the sample, it is possible to image the surfaces at the atomic level.**
- **The invention of scanning probe microscopy was a great breakthrough in the field of nanotechnology. Now that scientists could see individual atoms, they could begin to manipulate these atoms to build different structures and study their properties.**

Scanning Probe Microscopy (SPM)

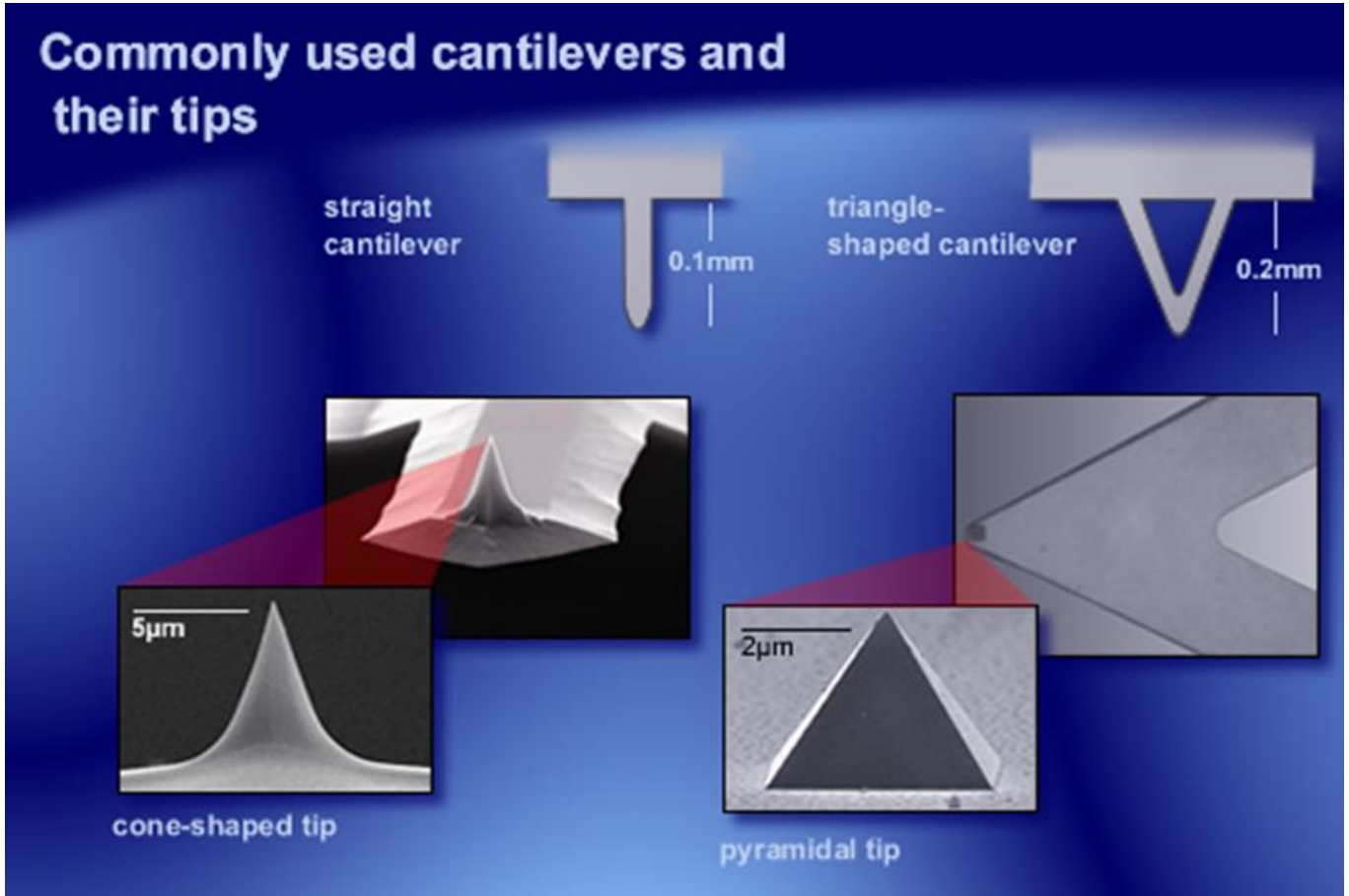


Atomic Force Microscope (AFM)

- Very high-resolution type of SPM
- Resolution in nanoscale, 1000 times better than the optical diffraction limit
- Binnig, Ouate and Gerber invented the first AFM in 1986
- One of the foremost tools for imaging, measuring and manipulating matter at the nanoscale
- Information is gathered by "feeling" the surface with a mechanical probe
- Piezoelectric material facilitate tiny but accurate and precise movements enable the very precise scanning

Cantilevers and their properties

- Typically made of Si_xN_y
- Spring constants in the range of 1 - 40 N/m (Forces from 0,1nN – 20 µN)
- Tips range from a pyramid to very sharp, high aspect ratio tips, to flat punches.



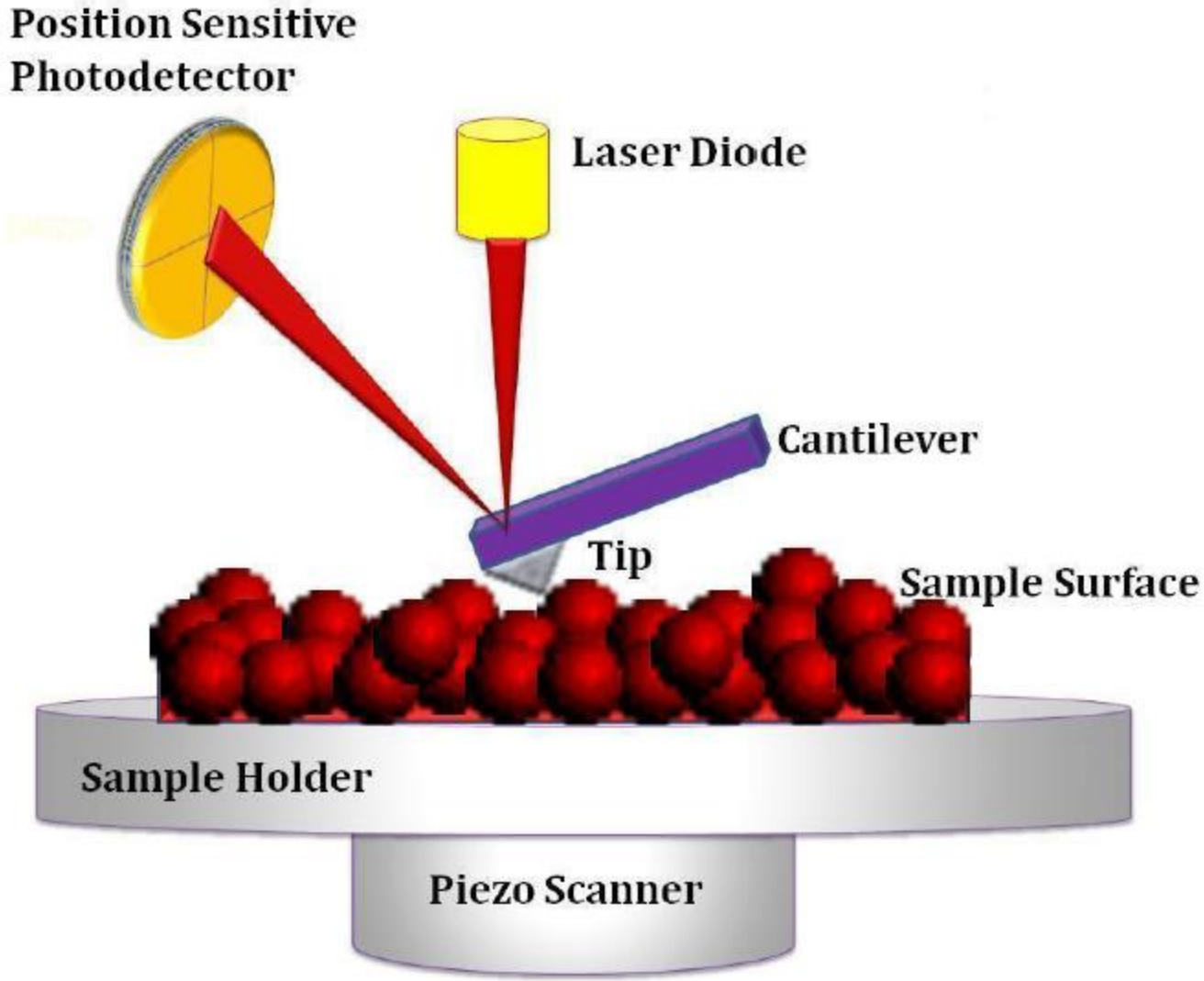
Basic principle

- Cantilever with a sharp tip (probe) is used to scan the specimen surface
- Tip is brought into proximity of a sample surface -> forces between tip and sample lead to a deflection of the cantilever according to Hooke's law

$$F=-k\cdot x$$

F = Force k = spring constant x = cantilever deflection

- Forces measured in AFM include mechanical contact force, Van der Waals forces, capillar forces, chemical bonding, electrostatic forces, solvation forces etc…
- Deflection is measured using a laser spot reflected from the top surface of the cantilever into an array of photodiodes
- If tip was scanned at a constant height -> risk that the tip collides with the surface -> damage -> feedback mechanism adjusts the tip-to-sample distance to maintain a constant force between tip and sample
- Sample is mounted on a piezoelectric tube which moves it *z* direction for maintaining a constant force, and *x* and *y* for scanning
- AFM can be operated in a number of modes, depending on the application
- Possible imaging modes are divided into static (also called Contact) modes and dynamic (or non-contact) modes where the cantilever vibrates
- AFM can be used to image and manipulate atoms and structures on surfaces


Position Sensitive
Photodetector
Laser Diode
Cantilever
Tip
Sample Surface
Sample Holder
Piezo Scanner

- **In AFM, a *tip* is used for imaging. It is generally made of silicon or silicon nitride (Si_3N_4). It approaches the sample in a range of interatomic distances (around 10 Å). The tip is commonly 3-15 microns in length. It is attached to the end of the spring cantilever. The cantilever is around 100-500 microns in length.**
- **When the tip, which is attached to the free end of the cantilever, come very close to the surface attractive and repulsive forces due to the interactions between the tip and the sample surface cause a negative or positive bending of the cantilever. This bending is detected by the help of a laser beam.**
- **The cantilever can be thought of as a spring. The quantity of the generated force between the tip and the surface depends on the spring constant (stiffness) of the cantilever and the distance between the tip and the surface. This force can be characterized with Hooke's Law.**

$$F=-k\cdot x$$

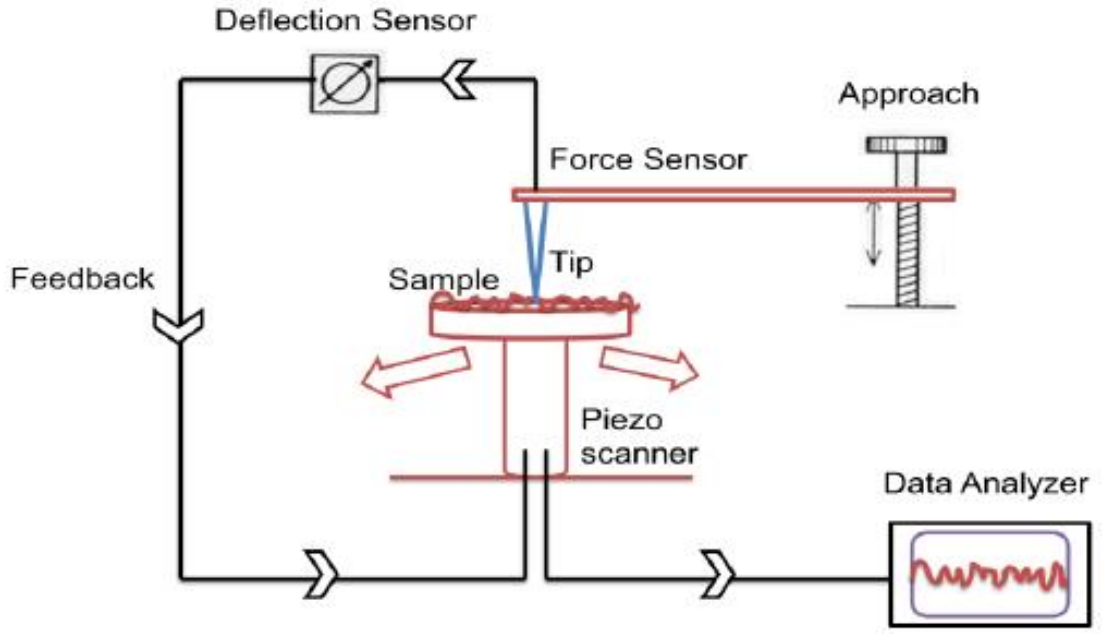
F = Force k = spring constant x = cantilever deflection

As the tip travels across the sample, it moves up and down according to the surface properties of the sample (eg. topography). These fluctuations are sourced by the interactions (electrostatic, magnetic, capillary, Van der Waals) between the tip and the sample. The displacement of the tip is measured and a topographical image is obtained.

Taking an Image

Generally the AFM probe does not move, instead of its motion, the sample is moved in the x,y,z direction by a piezoelectric material. Piezoelectric materials (piezocrystals) are ceramic materials that can enlarge or shrink when a voltage is applied. By this way, very precise movements in the x,y,z directions can be possible. (Position can be controlled in nanometer resolution) .

A laser beam is focused onto the back of the cantilever. It can be reflected back to a 4-quadrant photodiode detector. By the help of this position sensitive photodiode, the bending of the cantilever can be measured precisely. The cantilever deflects according to the atomic force variations between tip and the sample and thereby the detector measures the deflection. The created image is a topographical illustration of the sample surface.



Schematic diagram showing the operation principle of the AFM

Types of Imaging modes

1. Contact Mode (Static Mode)

- **In the contact mode, the cantilever's tip gently "moves" along the sample's surface, maintaining a constant "distance" between the tip and the surface.**

- **This distance is determined by the interaction of the attractive and deflective (repulsive) forces at the sample's surface.**

- **These force interactions provide feedback to the servo system that maintains a constant tip to surface distance of around 10 angstroms.**

- **As the sample moves in the x-y directions directly under the tip, the movement of the tip up or down in the z-direction is used to define the topography of the sample's surface and create an image.**

Intermittent Mode (Tapping):

This mode eliminates the frictional force by intermittently contacting the surface and oscillating with sufficient amplitude to prevent it from being trapped in by adhesive forces. This mode of operation is less destructive than contact mode. The cantilever oscillates nearby its resonance frequency. An electronic feedback loop provides the oscillation amplitude remaining constant so that a constant tip-sample interaction is conserved during the scan.

Advantages

- **AFM provides a true 3D surface profile**
- **samples viewed by AFM do not require special treatments**
- It can be used in vacuums, air, and liquids.
- Measurement of sample sizes is accurate
- It can be used to study living and nonliving elements
- It can be used to quantify the roughness of surfaces

Disadvantages

- The tip and the sample can be damaged during detection.
- It has a limited magnification..
- Incorrect choice of tip for required resolution can lead to image artifacts
- Relatively slow rate of scanning.

Application:

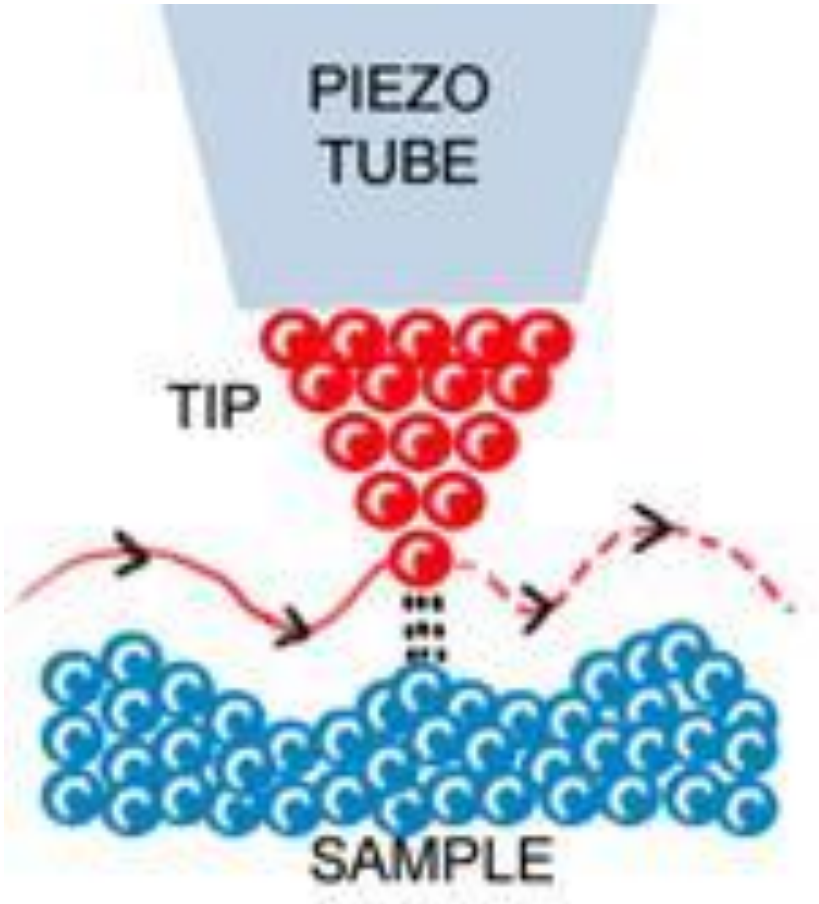
1. Evaluating force interactions between atoms

2.Studying the structural and mechanical properties of protein complexes and assembly, such as microtubules.

3. used to differentiate cancer cells and normal cells.

Scanning Tunneling Microscope

- The scanning tunneling microscope (STM) was developed by Gerd Binning and Heinrich Rohrer at IBM.
- When a metal tip is brought near a conducting surface, electrons can tunnel from the tip to the surface or vice-versa.
- For their work, Binning and Rohrer shared the 1986 Nobel Prize.



- During tunneling the current that results depends upon the distance between the probe tip and the sample surface. The tip is attached to a piezoelectric tube, and the voltage applied to the piezo rod is altered to maintain a constant distance of the tip from the surface. Changes in this voltage allow a three-dimensional picture of the material surface to be built up as the tip is scanned back and forth across the sample.

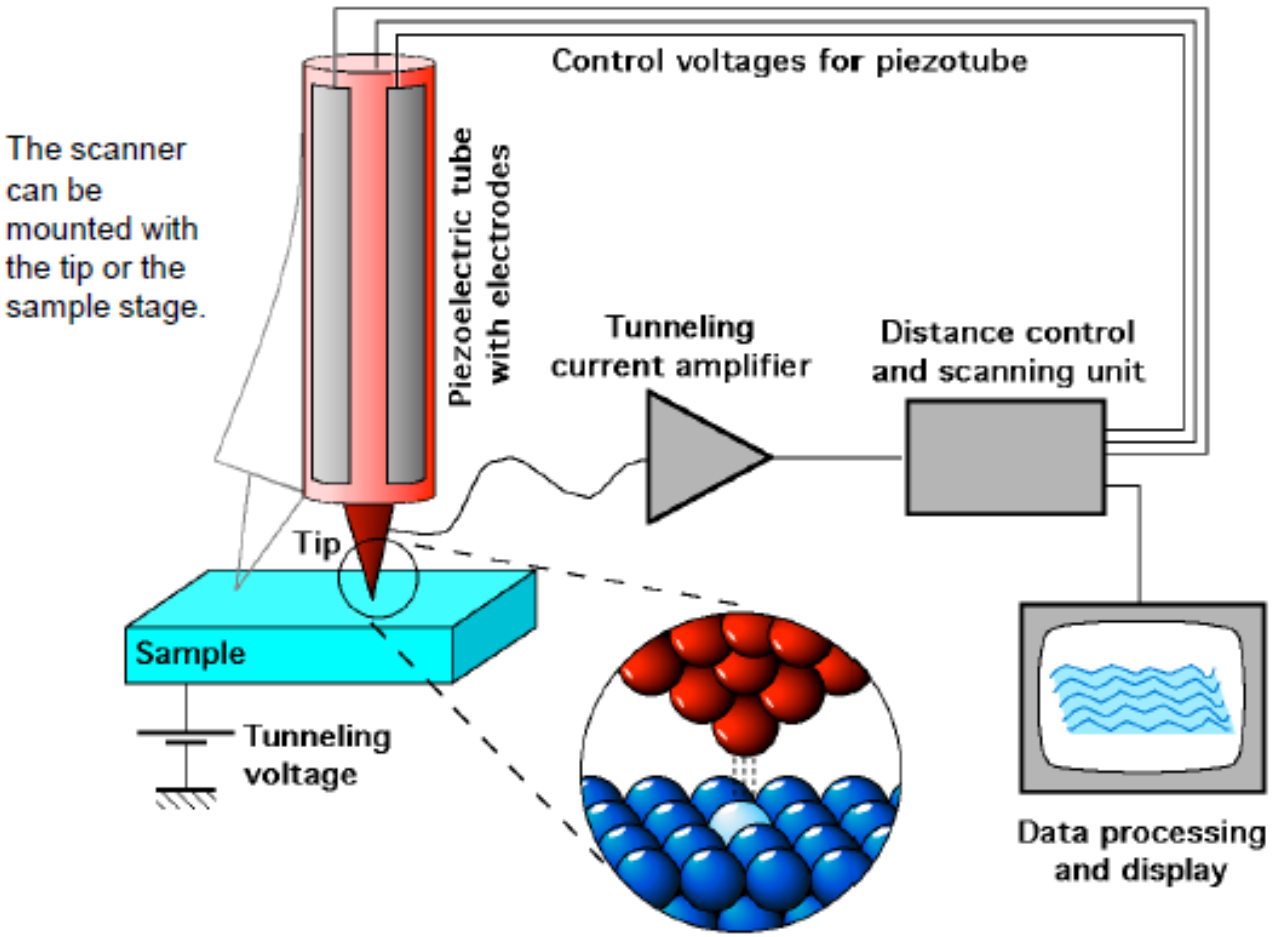
Tunneling Current

- **A thin metal tip is brought in close proximity of the sample surface. At a distance of only a few Å, the overlap of tip and sample electron wavefunctions is large enough for an electron tunneling to occur.**
- **When an electrical voltage *V* is applied between sample and tip, this tunneling phenomenon results in a net electrical current, the 'tunneling current'. This current depends on the tip-surface distance *d*, on the voltage *V*, and on the height of the barrier.**

STM Tip:

- **STM tip should be conducting (metals, like Pt);**
- **STM plays with the very top (outermost) atom at the tip and the nearest atom on sample; so the whole tip is not necessarily very sharp in shape.**

Basic components of STM:



Five basic components:

1. Metal tip,
2. Piezoelectric scanner,
3. Current amplifier (nA),
4. Bipotentiostat (bias),
5. Feedback loop (current).

- Tunneling current from tip to sample or vice-versa depending on bias;
- Current is exponentially dependent on distance;
- Raster scanning gives 2D image;
- Feedback is normally based on constant current, thus measuring the height on surface.

Applications:

- STM provides remarkable detail about the surface of a material, they are very useful for studying friction, surface roughness, defects, and surface reactions in materials like catalysts.
- STMs are also very important tools in semiconductors and microelectronics research.
- The scanning tunneling microscope (STM) is widely used in both industrial and fundamental research to obtain atomic-scale images of metal surfaces

Advantages:

- STM provides three dimensional profile of a surface, which allows researchers to examine a multitude of characteristics, including roughness, surface defects and determining things about the molecules such as size and conformation.
- STM is versatile technique . They can be used in ultra high vacuum, air, water and other liquids and gasses.
- STM can be operated in temperatures as low as zero Kelvin up to a few hundred degrees Celsius.

Disadvantages:

- There is a very specific technique that requires a lot of skill and precision.
- STMs require very stable and clean surfaces, excellent vibration control.
- STMs use highly specialized equipment that is fragile and expensive.