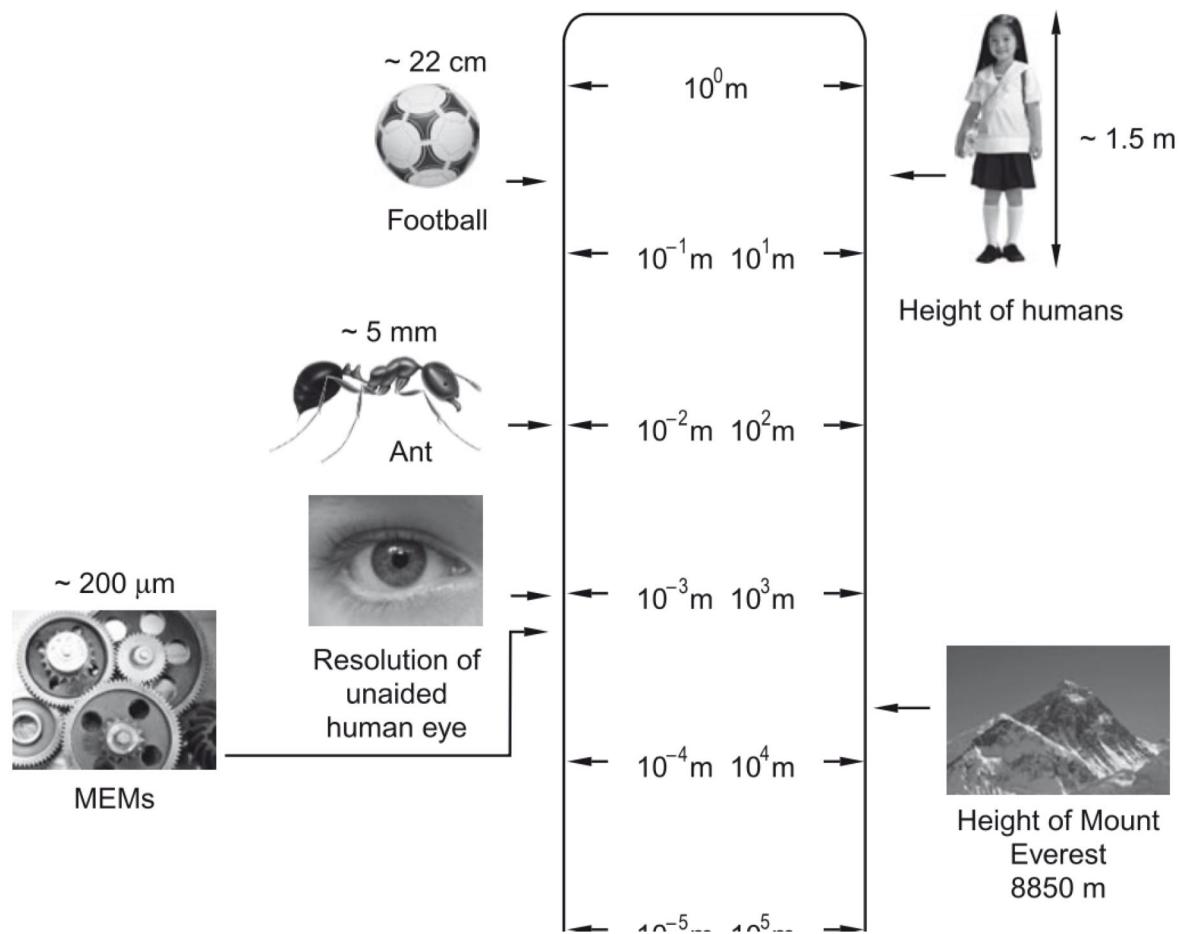


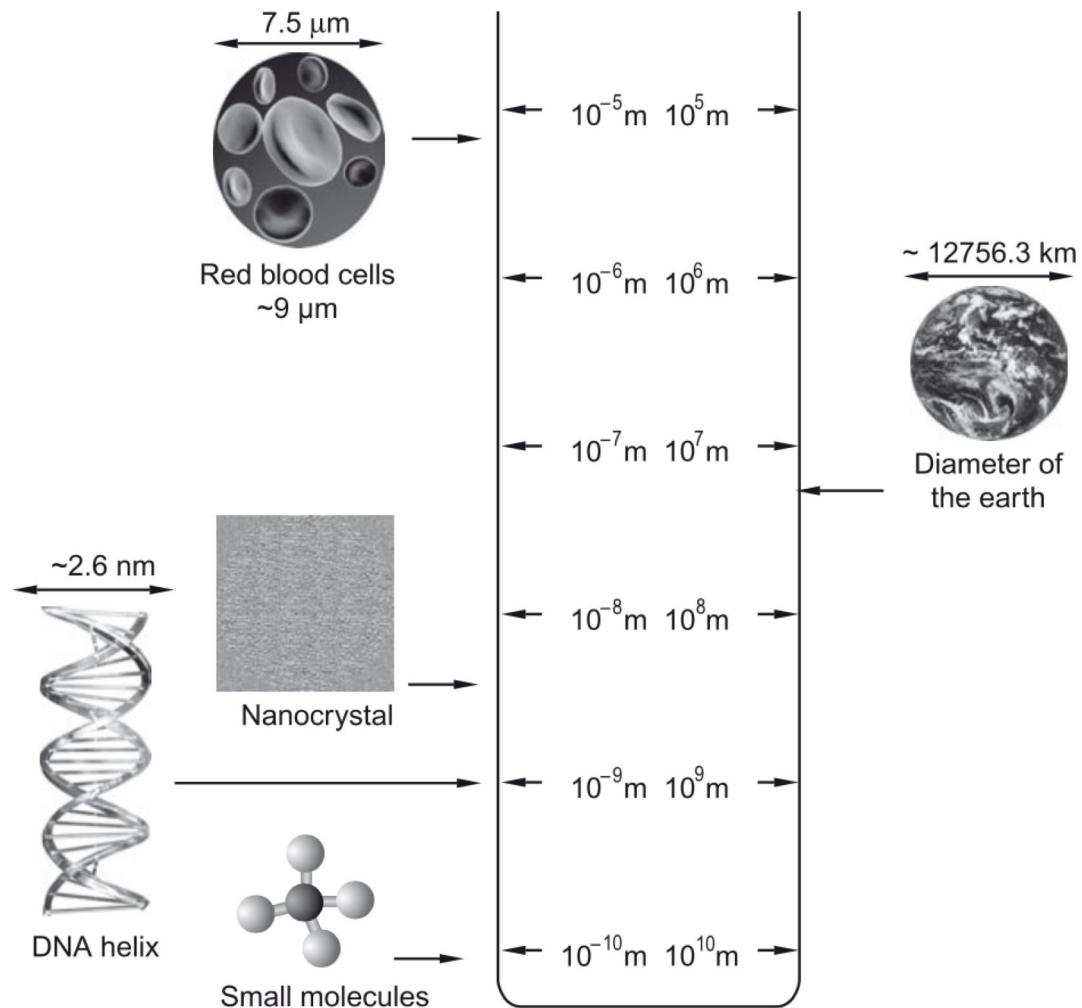
# Nanophysics and Nanotechnology

# Books

1. Charles P. Poole and Frank J. Owens, Introduction to Nanotechnology, Wiley-Interscience, 2003
2. Nano Science and Nanotechnology: Fundamentals to Frontiers, M.S. Ramachandra Rao and Shubra Singh, Wiley, 2015

## Objects in different scale



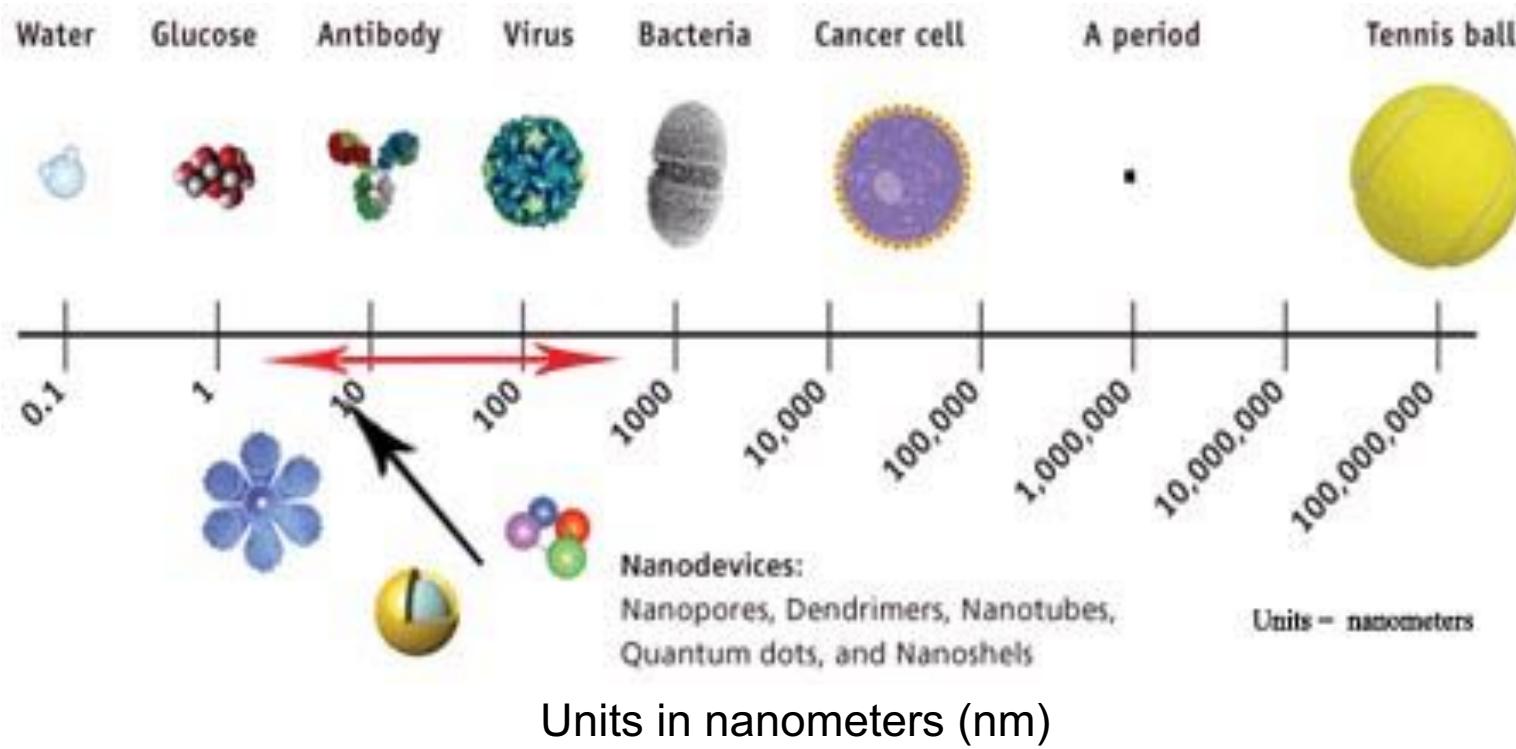


## What is Nano?

meter	m	1	$1 \times 10^0$
decimeter	dm	$1/10$	$1 \times 10^{-1}$
centimeter	cm	$1/100$	$1 \times 10^{-2}$
millimeter	mm	$1/1000$	$1 \times 10^{-3}$
micrometer	$\mu\text{m}$	$1/1000000$	$1 \times 10^{-6}$
nanometer	nm	$1/1000000000$	$1 \times 10^{-9}$
angstrom	$\text{\AA}$	$1/10000000000$	$1 \times 10^{-10}$

One (nm) equals to  $1/1000000000$  ( $10^{-9}$ ) meter

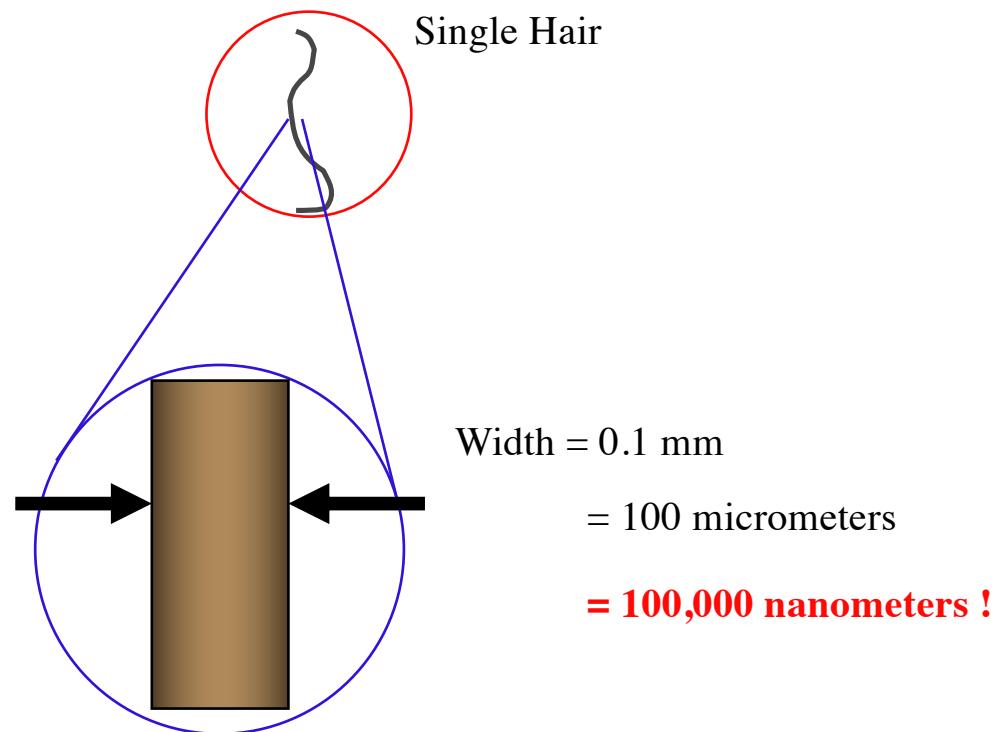
# The nanometre scale



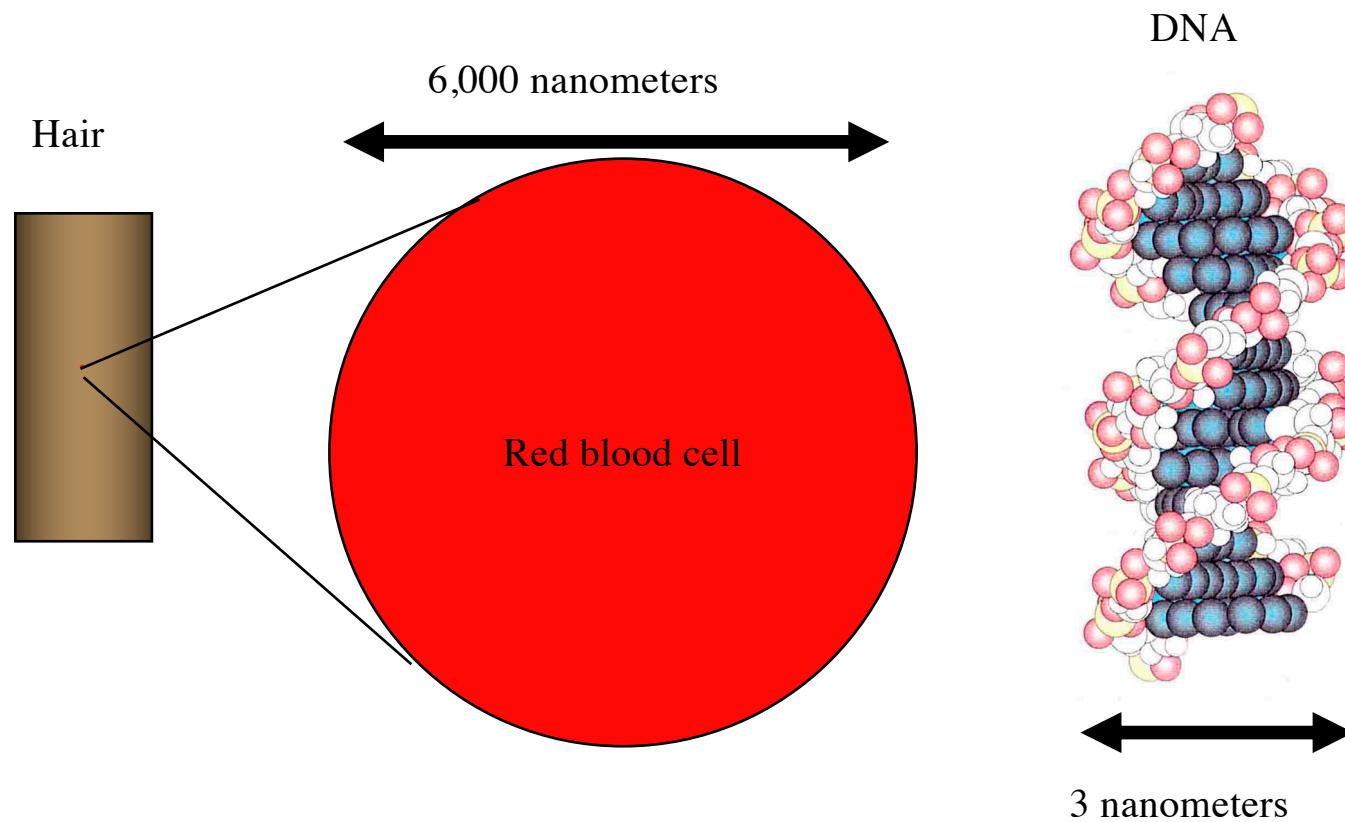
## Terminology

- **Nanoscale** - at the 1-100 nm scale, roughly
- **Nanostructure** - an object that has nanoscale features
- **Nanoscience** - the behavior and properties of nanostructures
- **Nanotechnology** - the techniques for making and characterizing nanostructures and putting them in applications.
- **Nanomanufacturing** - methods for producing nanostructures in commercially ways for technical applications.

# How small are nanostructures?



# Smaller still....

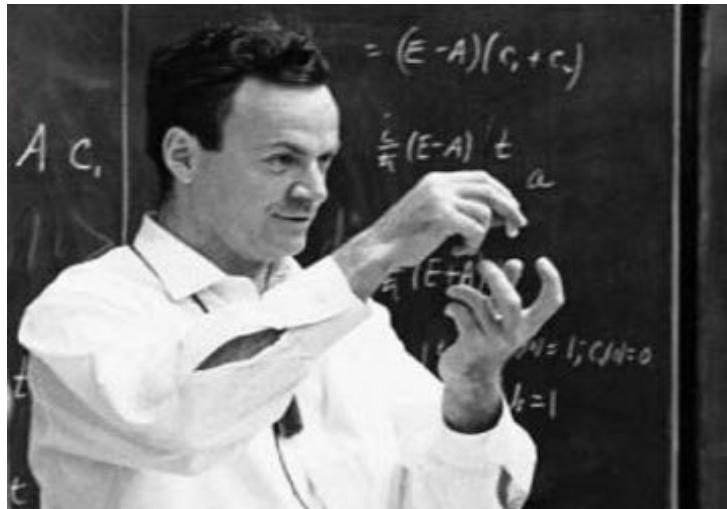


## Some Examples

- A sheet of newspaper is about 100,000 nanometers thick.
- On a comparative scale, if a marble were a nanometer, then one meter would be the size of the Earth.
- Our fingernails grow at the rate of 1 nm per second

Who gave this term ‘Nano’?

The first person to *identify and discuss the ‘nanometer-scale world* was Richard Feynman in his talk during a conference of the American Physical Society : “*There’s plenty of the room at the bottom*” in 1959.



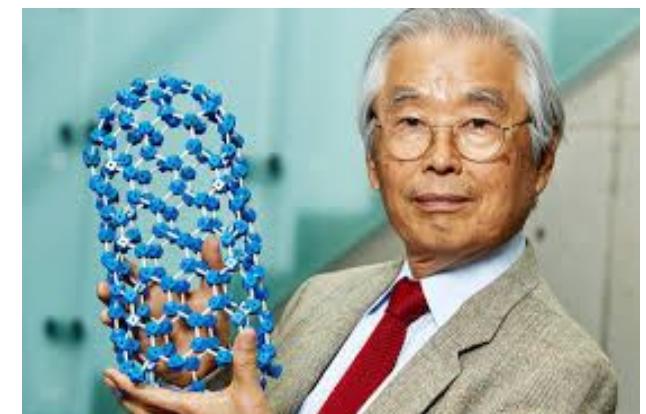
Physicist Richard Feynman, **the father of nanotechnology**

## Pioneers of Nanoscience & Nanotechnology

**Norio Taniguchi** defined it as that which consists of the “processing of separation, consolidation and deformation of materials by one atom or one molecule”



**K. Erik drexler-** pioneer of productive nanosystems. Authored “**Engines Of creation: The Coming Era of Nanotechnology**”, possibly the first book in the field (1980’s).



**Sumio Iijima**

# Nanoscience and Nanotechnology

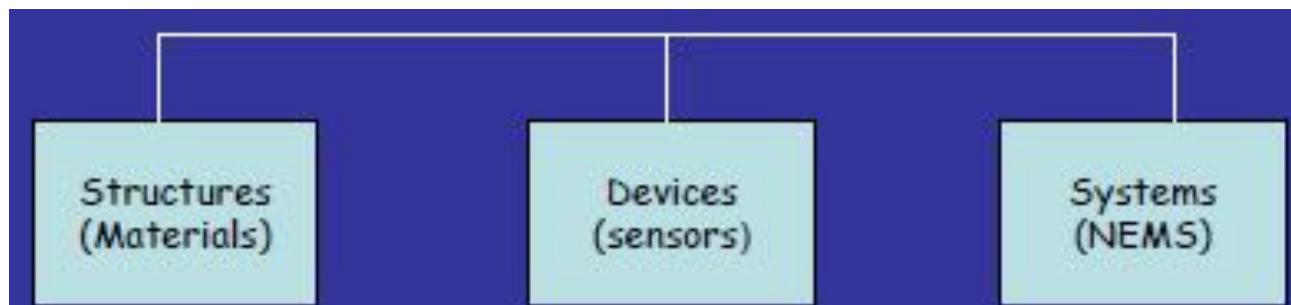
- Nanoscience is the study the structures and properties of matter with dimensions in the nanometer range or about phenomena occurring in nanoseconds.

In Nanophysics, we study physical properties of the nanostructures and develops various devices and instruments through various fabrication techniques.

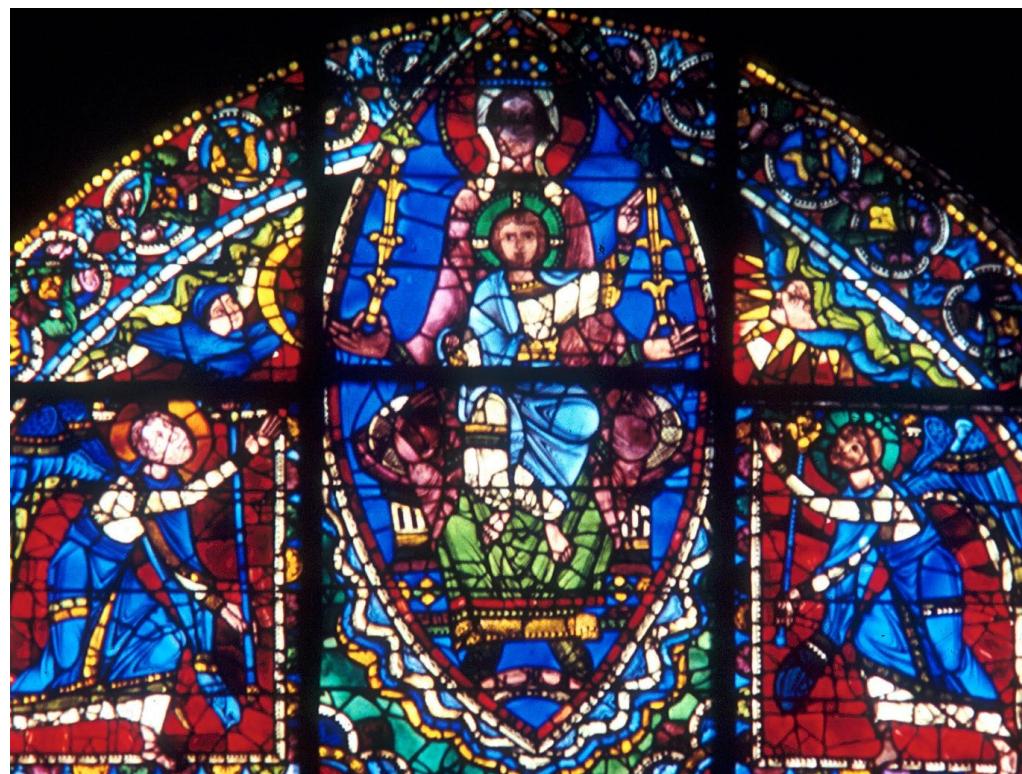
- Nanotechnology is the understanding and control of matter at nanoscale, where unique phenomena enable novel applications.

## Development

*Nanoscience → Nanophysics → Nanotechnology*



## Nanotechnology from the perspective of Medieval Period



Coloured stained glasses

## Medieval Period: Lycurgus cup

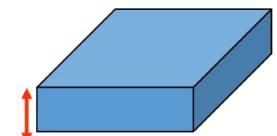
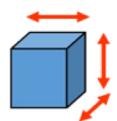


# Nanomaterials

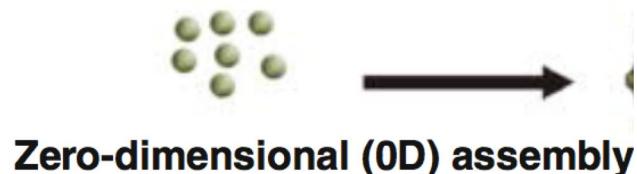
A nanomaterials are the object that have at least one dimension in the nanometre scale.

Nanomaterials are categorised according to their dimensions as follows:

Nanomaterial dimension	Example
All three dimensions < 100 nm	Nanoparticles, quantum dots, nanoshells, nanorings, microcapsules
Two dimensions < 100 nm	Nanotubes, fibres, nanowires
One dimension < 100 nm	Thin films, layers and coatings



## Classification of nanostructured materials



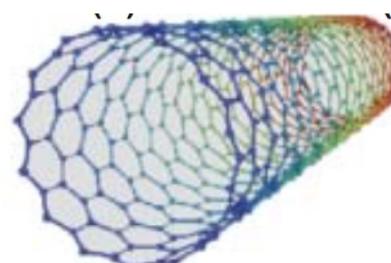
**Zero-dimensional (0D) assembly**



Quantum dot



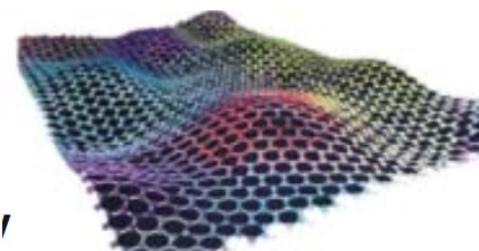
**One-dimensional (1D) assembly**



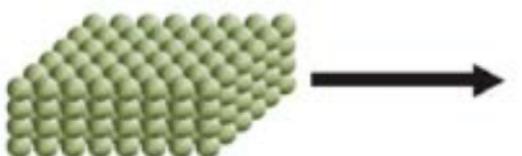
Nanotube



**Two-dimensional (2D) assembly**



Nanofilm



**Three-dimensional (3D) assembly**



Nanodiamond

## **Nanomaterials can be of two types:**

- 1. Non-intentionally-made nanomaterials** - which refers to nano-sized particles or materials that belong naturally to the environment. Example: proteins, viruses, nanoparticles produced during volcanic eruptions, etc
  
- 2. Intentionally-made nanomaterials** - which refers to nanomaterials produced deliberately through a defined fabrication process.

## What makes ‘nano’ special

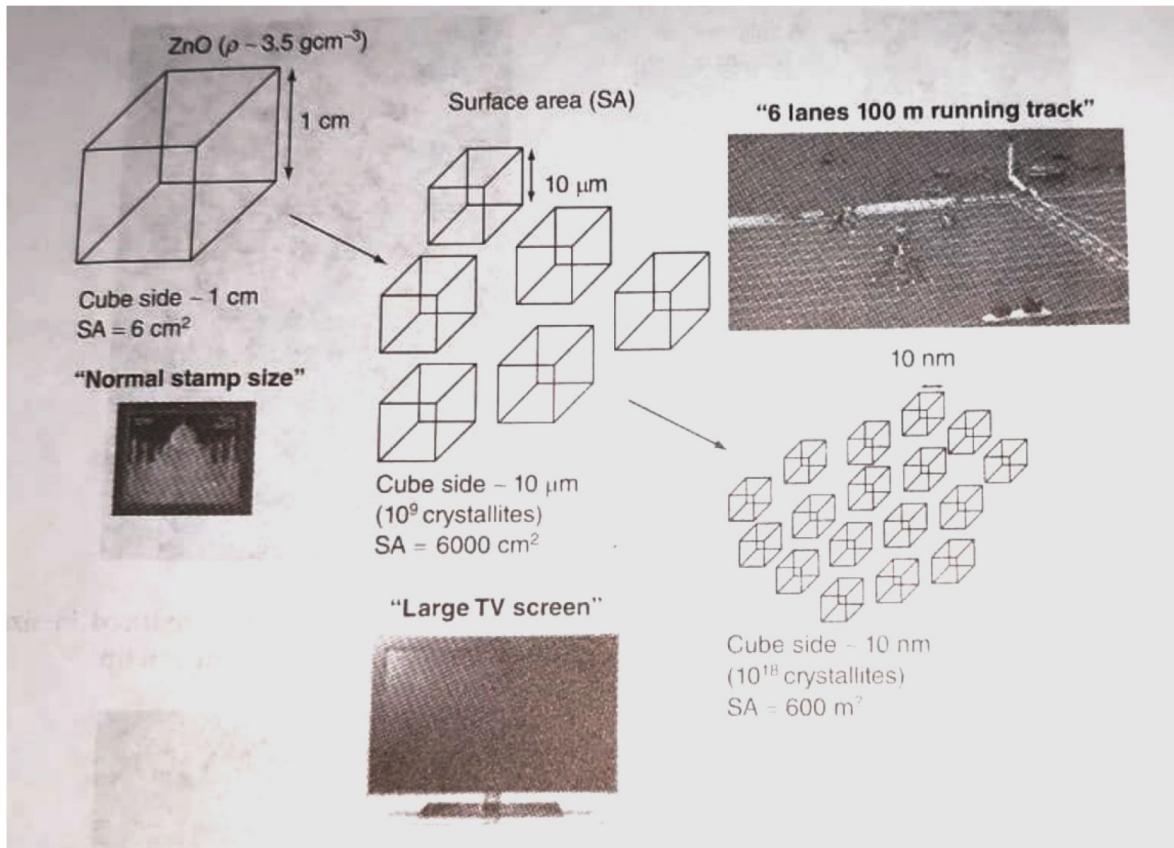
There are various reasons why nanoscience and nanotechnologies are so promising in materials, engineering and related sciences.

1. First, at the nanometre scale, properties like electrical conductivity, colour, strength and weight are changed.
2. The second exceptional property of nanomaterials is that they can be fabricated atom by atom by a process called **bottom-up**.

## What actually happens when objects turn so small?

- Objects usually have constant physical properties regardless of its size.
- But properties of materials change as their size approaches the nanoscale as there is a vast **increase** in ratio of surface area to volume

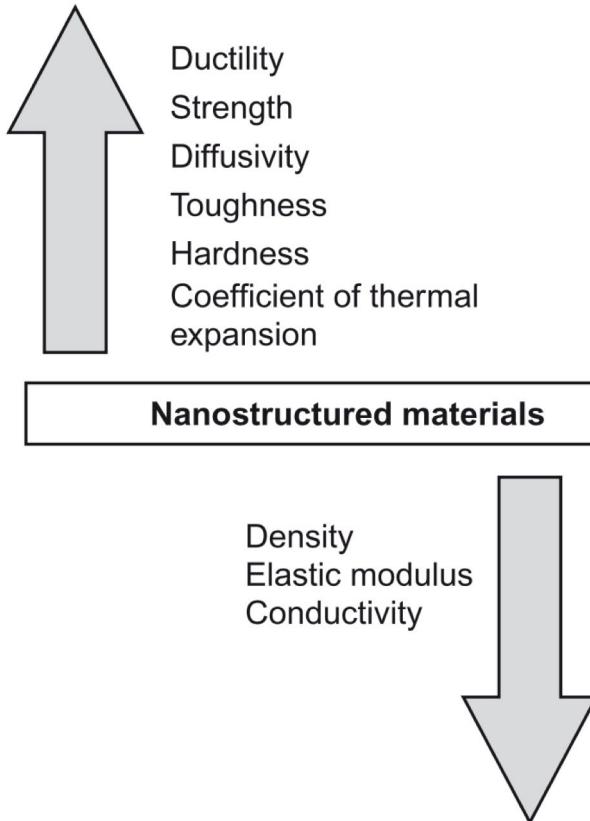
## Changes in surface area in going from bulk to nanocrystals



Spherical nanoparticles are expected to have large surface-to-volume ratio given as

$$\frac{\text{Surface}}{\text{Volume}} = \frac{4 \pi R^2}{4/3 \pi R^3} \propto \frac{1}{R}$$

## Properties affected in the Nano-regime



## Properties of Ni as the grain size reduces to nanoscale

**Table 1.2** Change in properties of Ni as grain size is changed from 10  $\mu\text{m}$  to 10 nm

Property	Change in property in comparison to bulk
Hardness	5 times increase
Strength	3–10 times increase
Wear resistance	170 times increase
Frictional coefficient	Reduced to half
Corrosion resistance	Reduced or localised corrosion is stopped
Magnetic properties	Lower coercivity, saturation magnetisation reduced by 5%
Electrical properties	Resistivity increased by 3 times
Hydrogen diffusion	Higher
Electrocatalytic properties	Improved electrocatalytic activities for hydrogen evolution

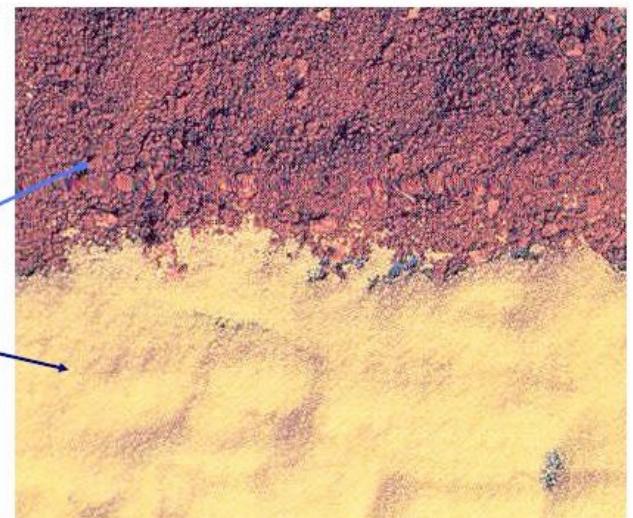
## Nano-sizing causes changes in:

1. Colour
2. Melting point
3. Magnetism
4. Crystal Shape
5. Conductivity
6. Chemical Reactivity

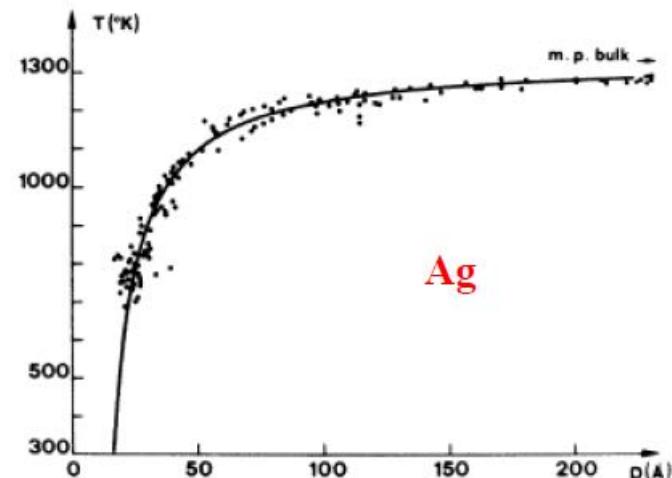
**size-dependence of color**

powered cadmium selenide

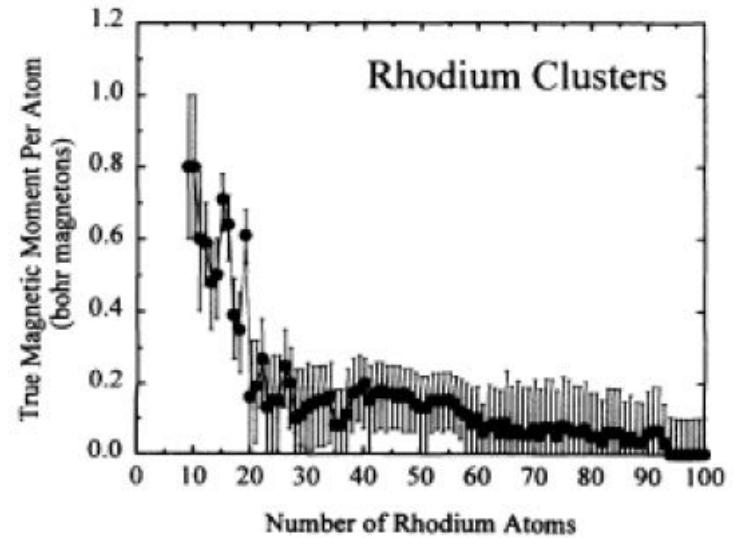
larger  
 $(\mu m)$   
smaller  
 $(nm)$



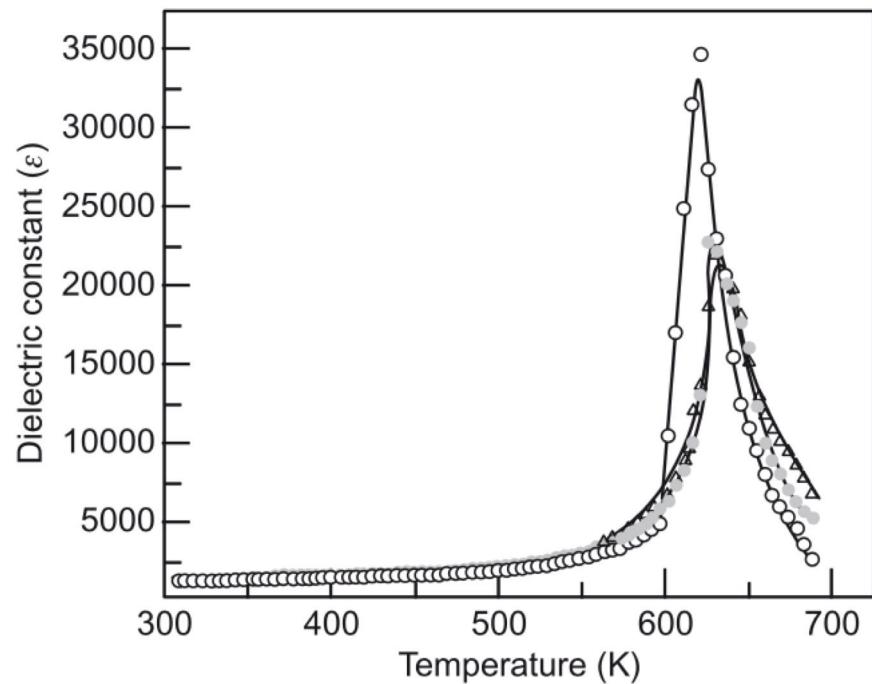
## size-dependence of melting temperature



## size-dependence of magnetism



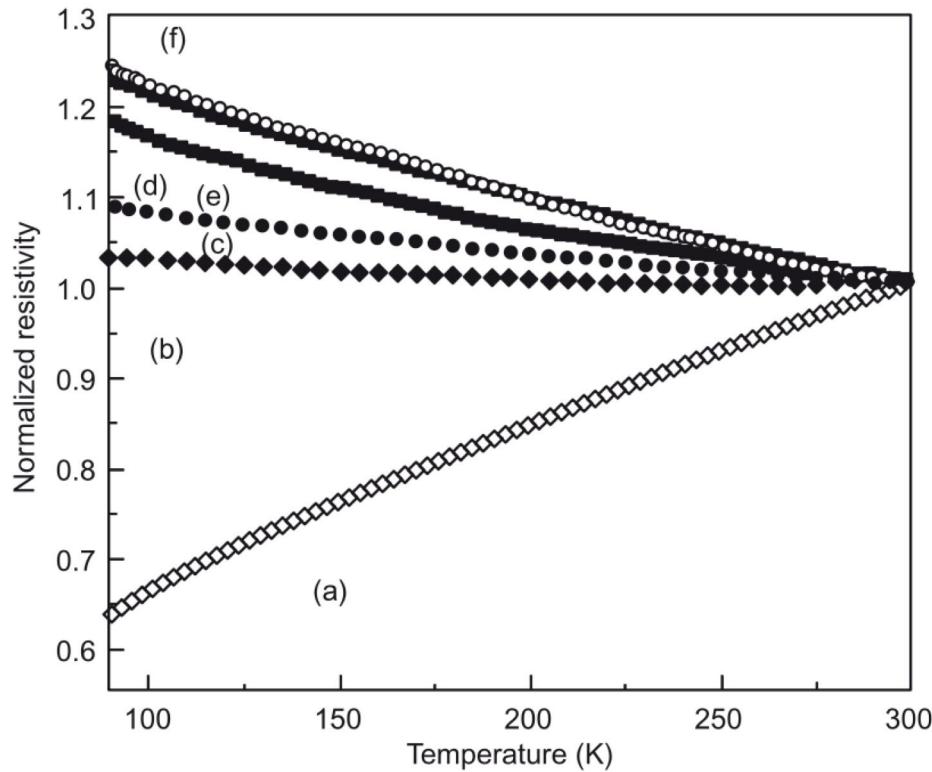
## High dielectric constant in nanocrystalline PZT



The nanocrystalline PZT (Lead zirconium titanate) with an average particle size of about 10 nm shows a dielectric constant of about 35,000 at  $T_c$ .

In contrast, bulk PZT has a dielectric constant of only about 1000 at the same temperature.

## Change in electrical resistivity



A metallic Al-Cu-Fe alloy is converted to a semiconductor with a negative temperature coefficient of electrical resistivity in the nanocrystalline phase.

In the figure:

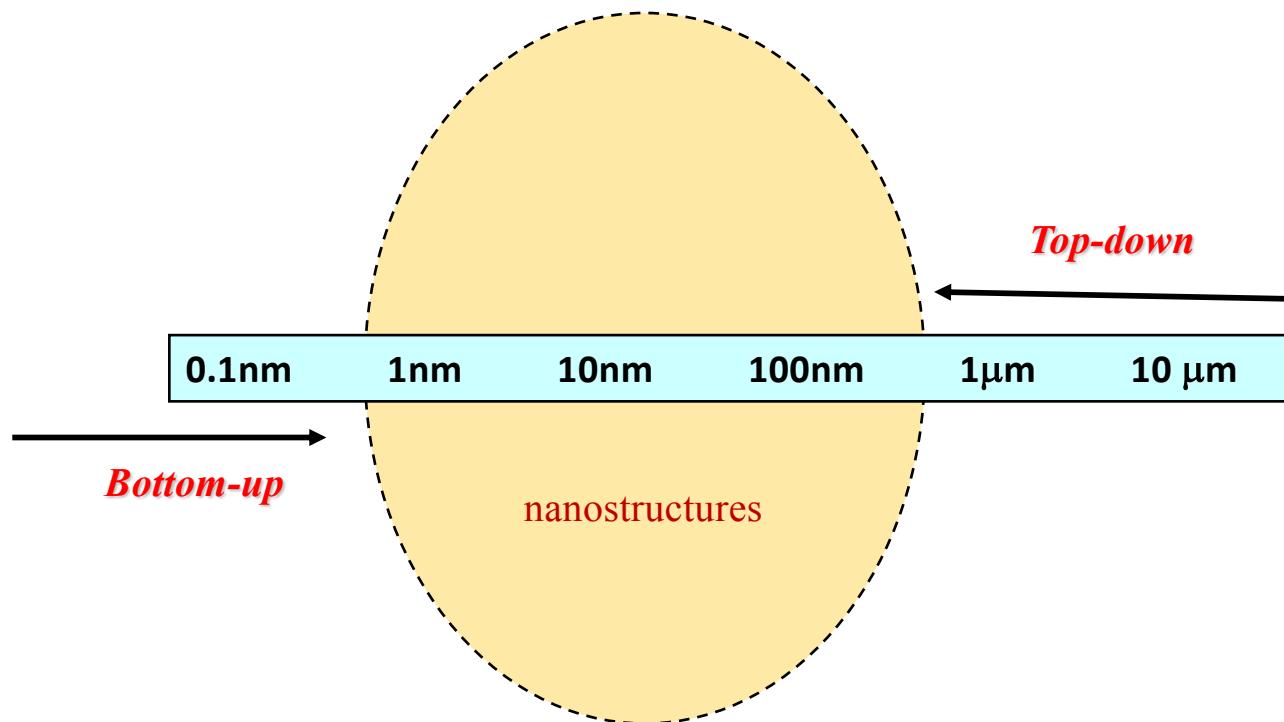
(a) : bulk alloy

(b)-(f): Different fractions of nanocrystalline phases

# Making Nanostructures: Nanofabrication

Nanomaterials can be fabricated by two methods:

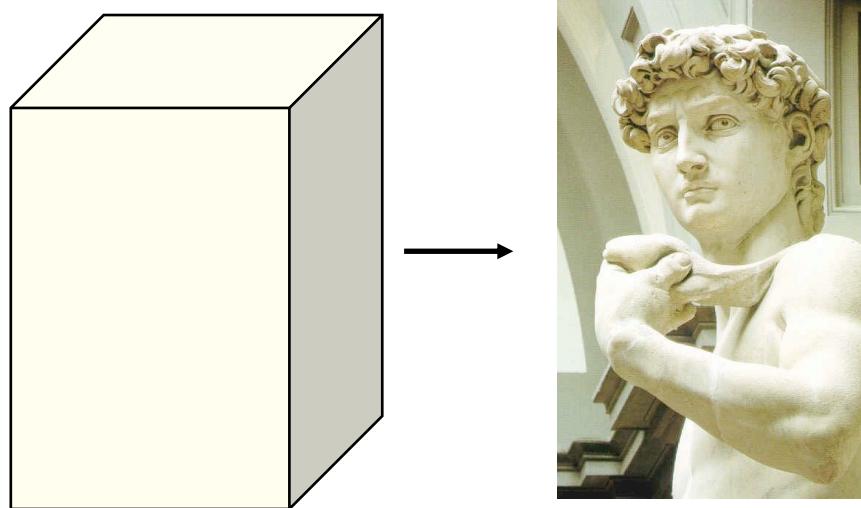
1. Top-down approach
2. Bottom-up approach



**1. Top- down approach:** In this technique generally a bulk material is taken and machined to modify into desired shape and product.

**Examples of this type:**

- Ion-beam Lithography
- Ball milling
- Etching
- Microfabrication

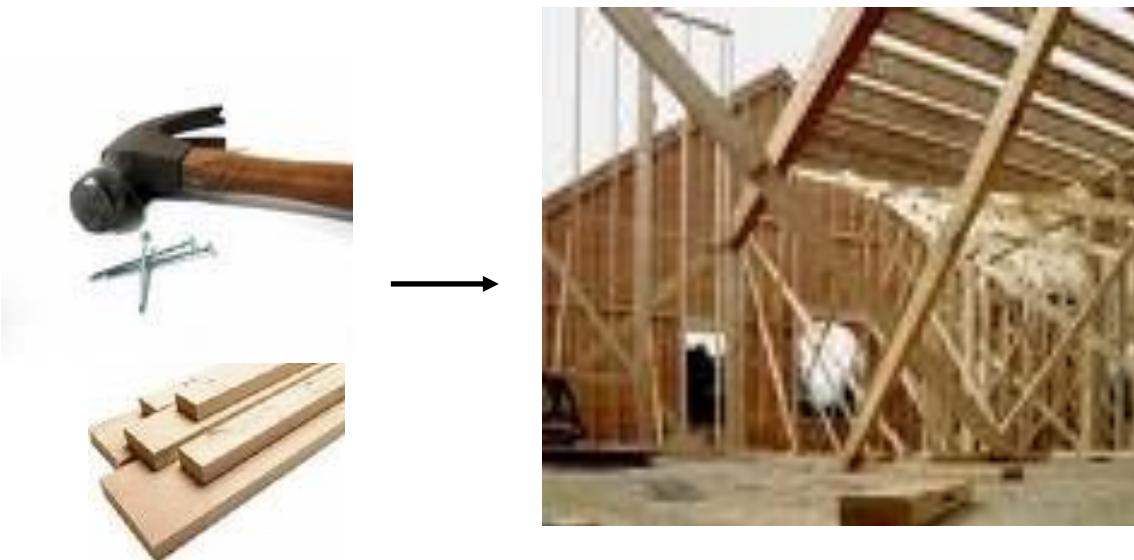


Top- down approach

**1. Bottom –up approach:** Bottom –up technique is used to build something from basic materials

**Examples of this type:**

- Sol-Gel synthesis
- Hydrothermal growth
- Thin film growth:
  - Physical vapor deposition
  - Chemical vapor deposition
  - Pulsed laser deposition



## Bottom- up approach

# Top- down approach: Lithography

Lithography is a printing method that uses chemical processes to create an image.

## Steps in Lithography:

- (i) Coating a substrate (Si wafer or glass) with a sensitive polymer layer (the resists).

Ex: photoresists are radiation-sensitive organic polymer

- (ii) Exposing the resist to light, electrons or ion beams
- (iii) Developing the resist image with a suitable chemical developer

Classification of resists based on their solubility after exposure:

**(a) Positive resists :**

**(b) Negative resists:**

There are two type of Lithographic processes:

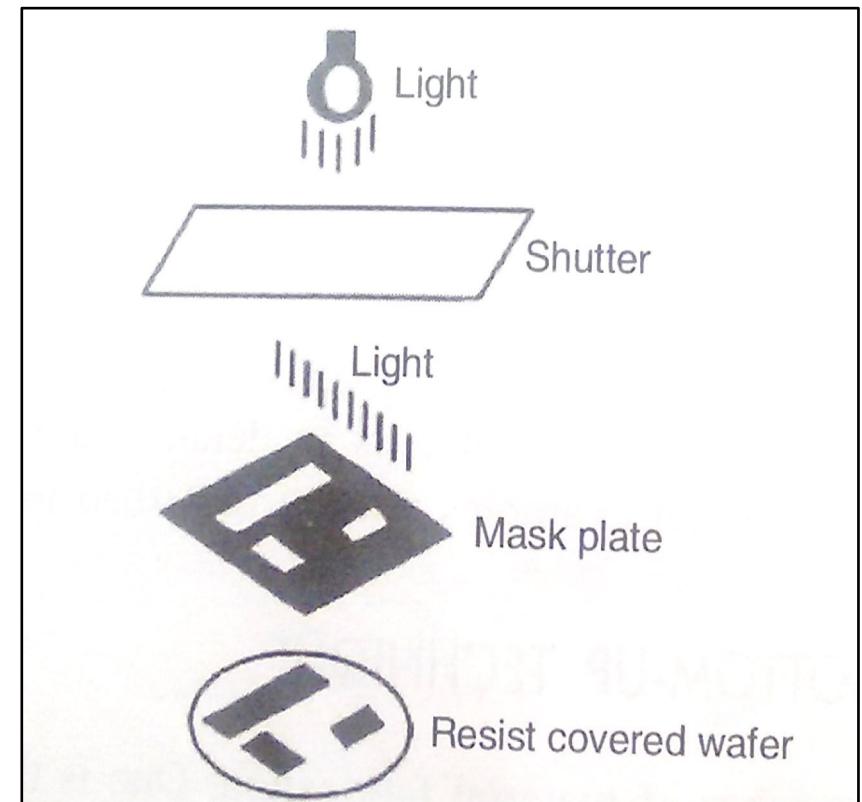
1. Photolithography
2. Electron beam Lithography

# 1. Photolithography

- It uses light to transfer a geometric pattern from photomask to a light-sensitive chemical on the substrate.
- Depending on pattern on the photomask, various structure can be generated on the substrate, which is further used to develop various silicon –based photonic and electronic devices.
- This process is limited to minimum size down to 50 nm.
- This technique is commonly used for fabricating semiconductor microchips and devices of microelectromechanical systems (MEMS).

- **Light source:** Photolithography uses UV(360-460 nm), deep UV, extreme UV or X-ray light source to expose a layer of radiation-sensitive polymer (photoresist) through a mask.
- **Mask :** A nearly optically flat glass (or quartz) plate with the desired pattern on a UV-transparent background.

(Note: pattern is made of an absorber metal)

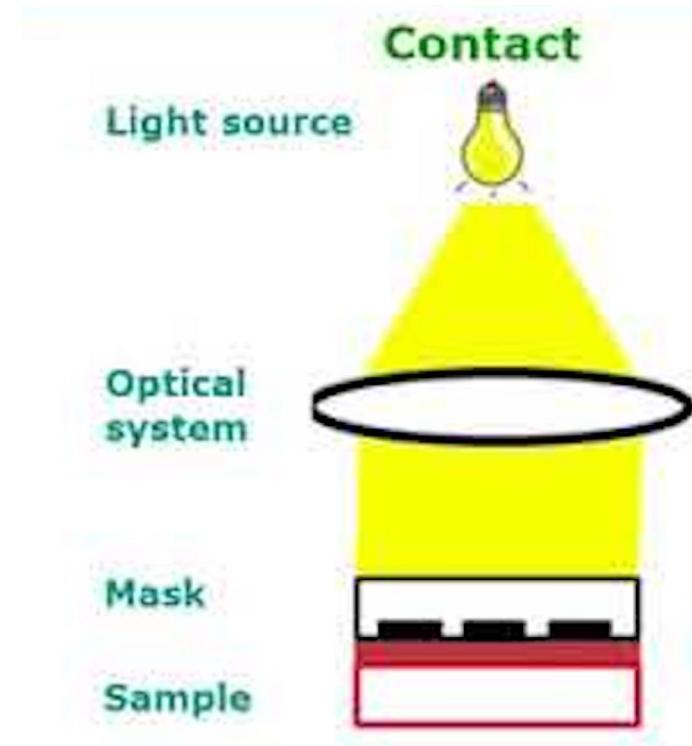


## Types of Photolithography

### (i) Contact mode photolithography:

Mask is in physical contact with the resist. Hence the image is replicated as it is. The resolution is typically  $0.5 - 0.8 \mu m$  when UV light is used.

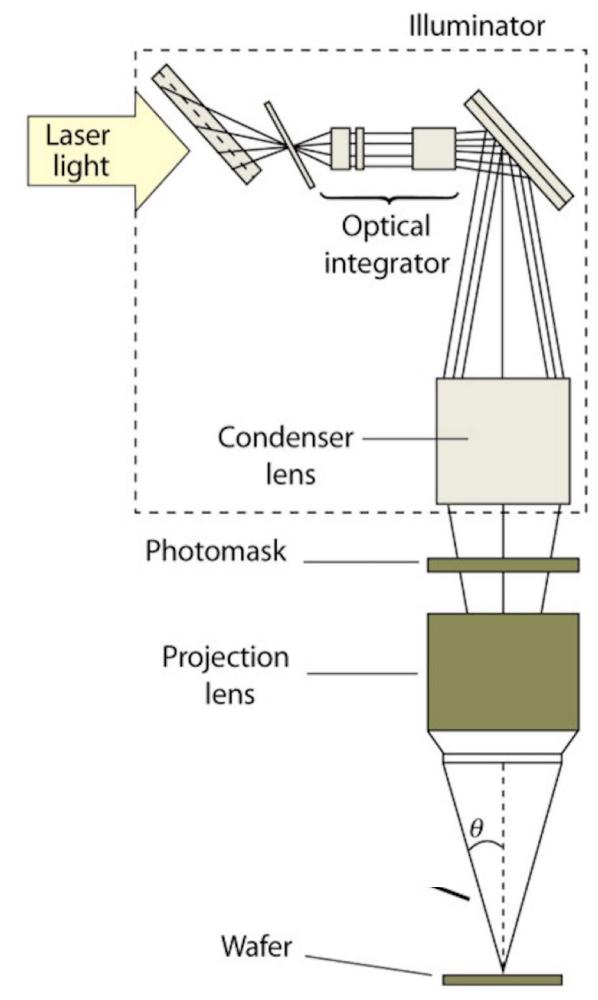
**Limitation:** Higher resolutions cannot be achieved because of the inability to reduce the gap between the mask and the flat substrate below  $\sim 1 \mu m$ .



## Types of Photolithography

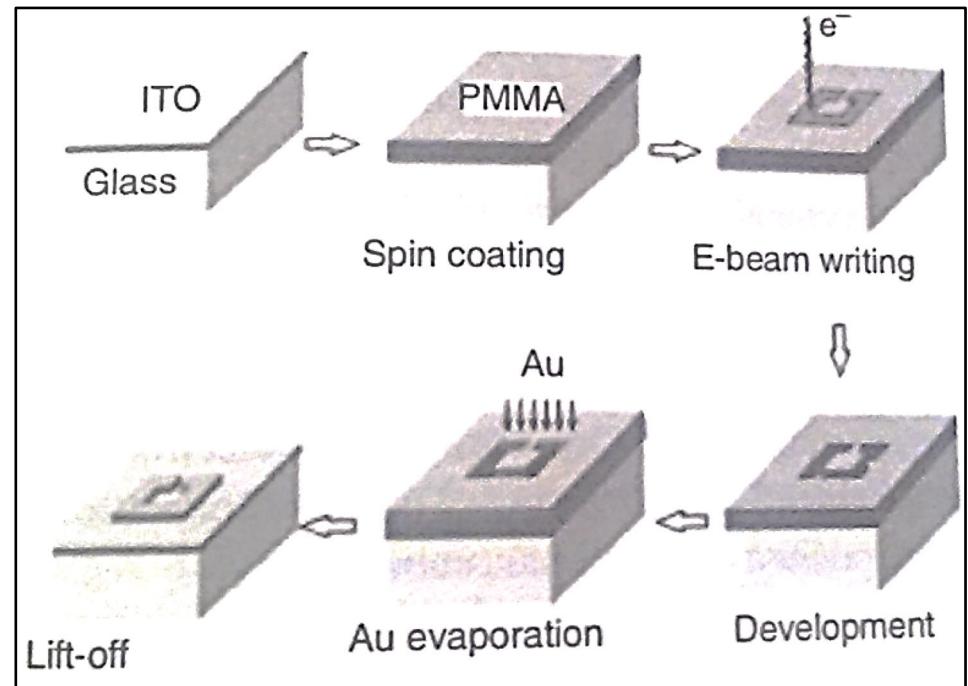
### (ii) Projection-mode photolithography:

Projected to the resist layer through an optical system. The image on the mask is reduced usually by a factor of 5 or 10.



## 2. Electron beam Lithography

- Electron beam Lithography (EBL) is the process of using a beam of electron to generate pattern on the surface.
- These systems have produced linewidths of  $\sim 20$  nm, but it is not suitable for very small size nanostructures
- Therefore, alternative **non-lithographic approaches** to nanostructure fabrication are the need of the time.

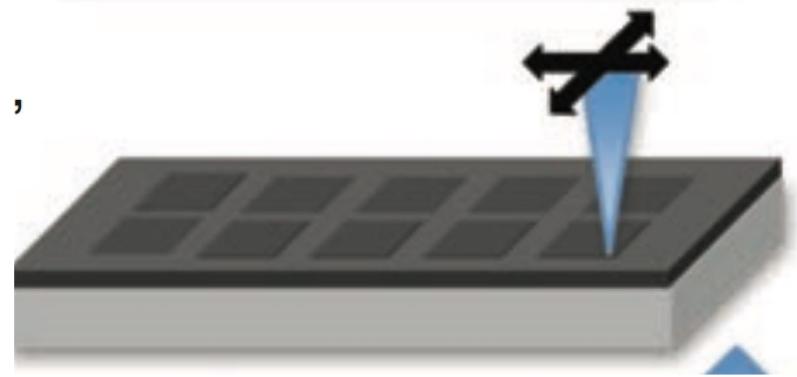


- EBL relies on materials (“resists”) that are chemically altered when they are exposed to an electron beam.
- Chemical change renders them soluble in a previously insoluble solvent—called positive resist or vice versa.
- The first electron beam resist, the organic material polymethyl methacrylate (PMMA), was discovered in 1968.
- It is a positive resist when used with the solvent methyl isobutyl ketone (MIBK) .



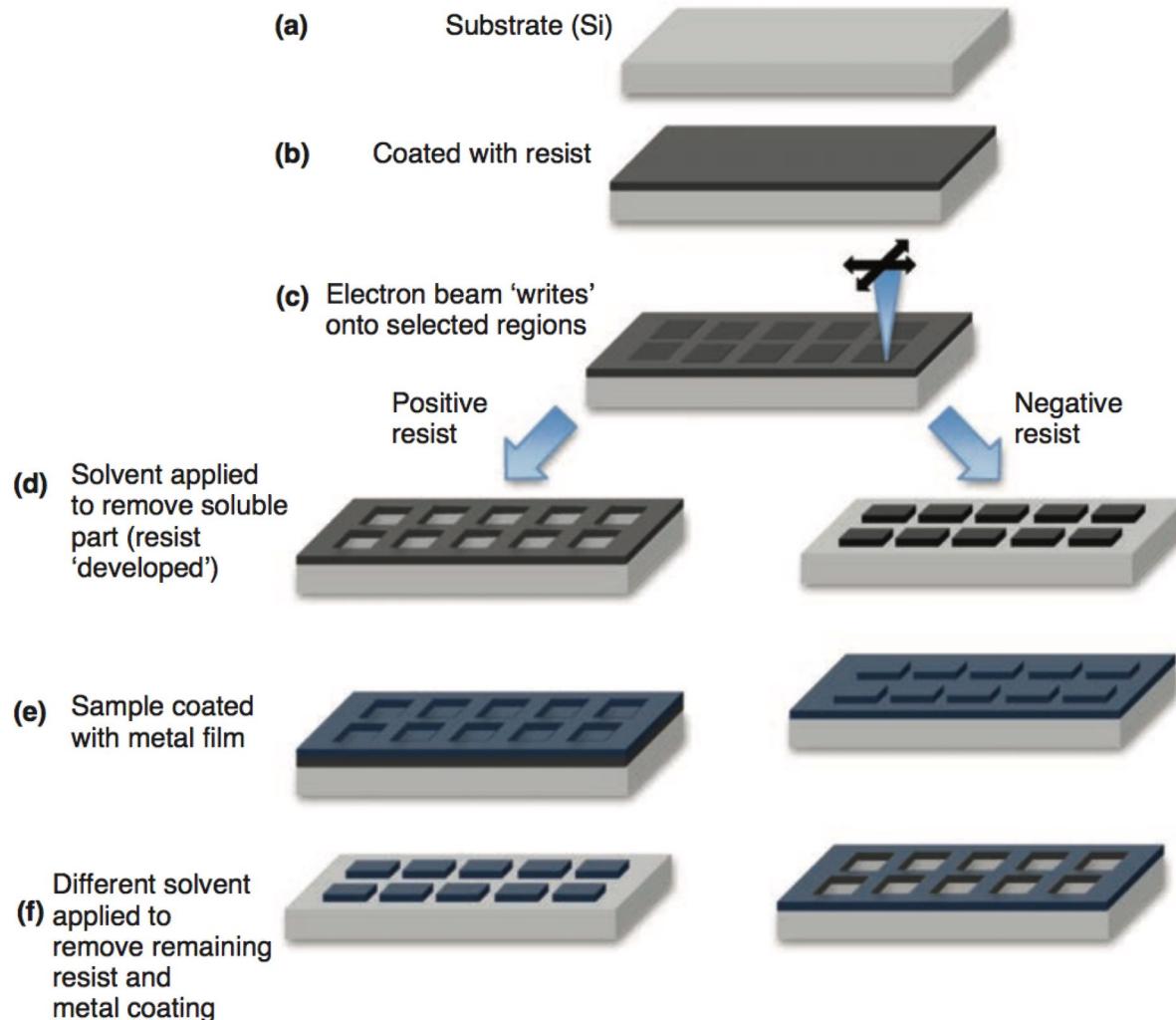
Substrate coated with resist

- A resist can be switched from positive to negative by altering the electron exposure-
  - (i) at low doses it is a positive resist
  - (ii) Becomes negative if given a sufficiently high dose.
- A highly focused electron beam (a spot  $\sim 5$  nm across) usually at an energy of about 100 keV and a beam current of a few picoamperes is used to “write” the desired nanostructures.

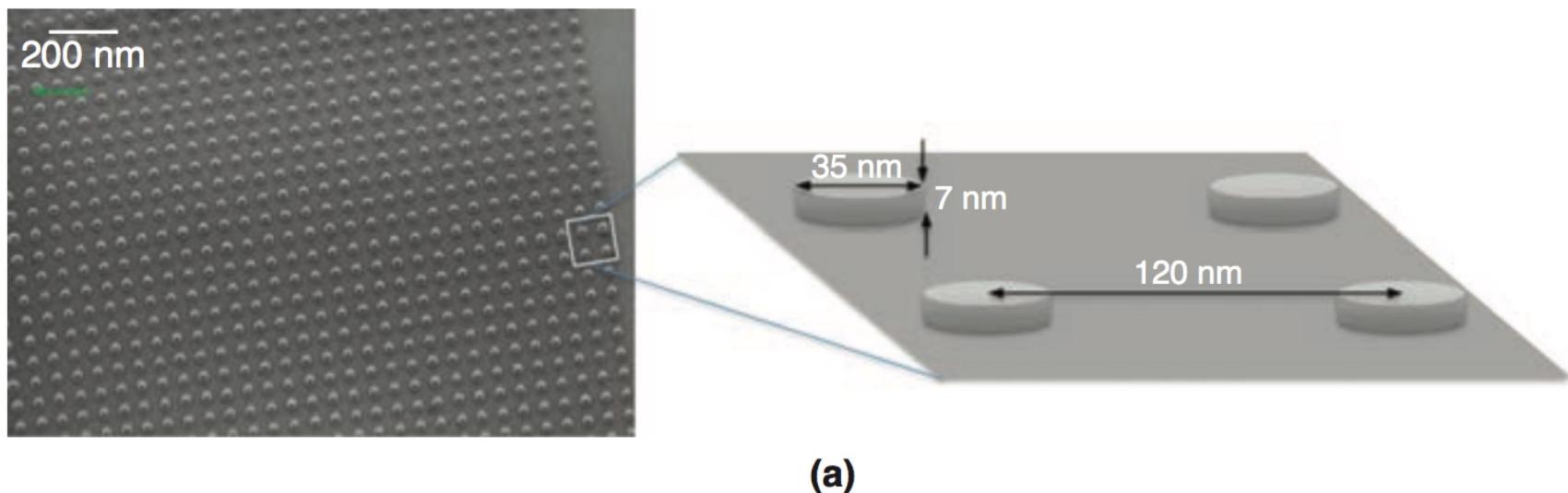


Electron beam “writes”

## EBL to create metal nanostructures on a surface using positive and negative resists



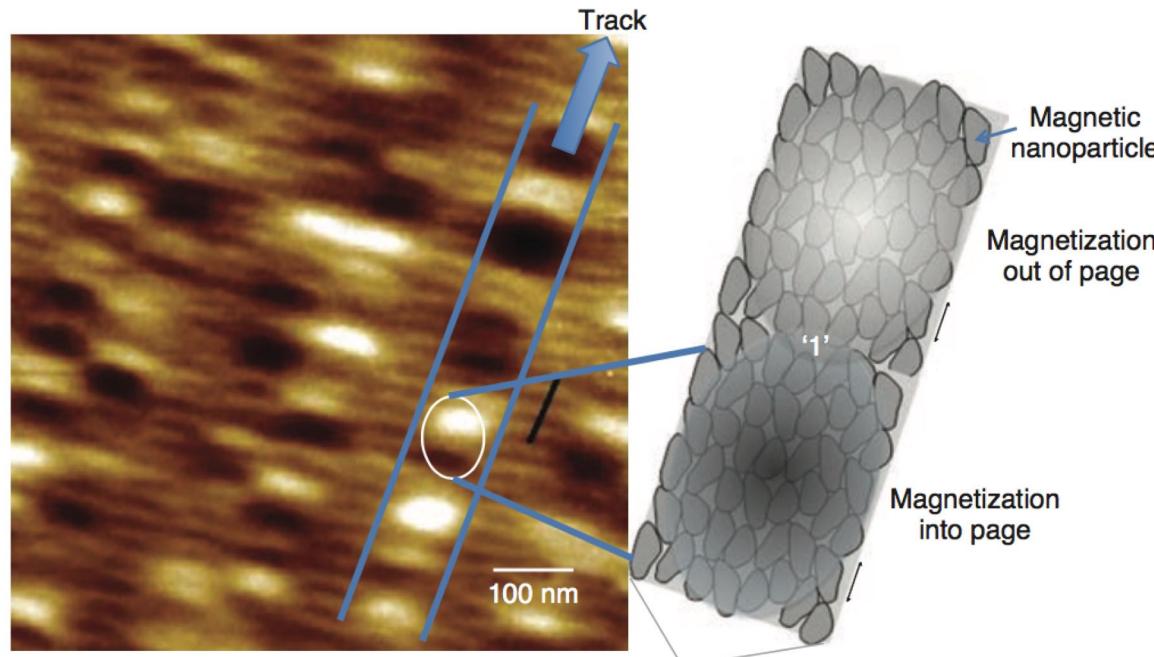
## Application of EBL: 40 nm CoPt magnetic dots produced by EBL



SEM image of array of CoPt nanoparticles using PMMA (positive resist) on Si surface.

## Data Storage On Magnetic Nanoparticles

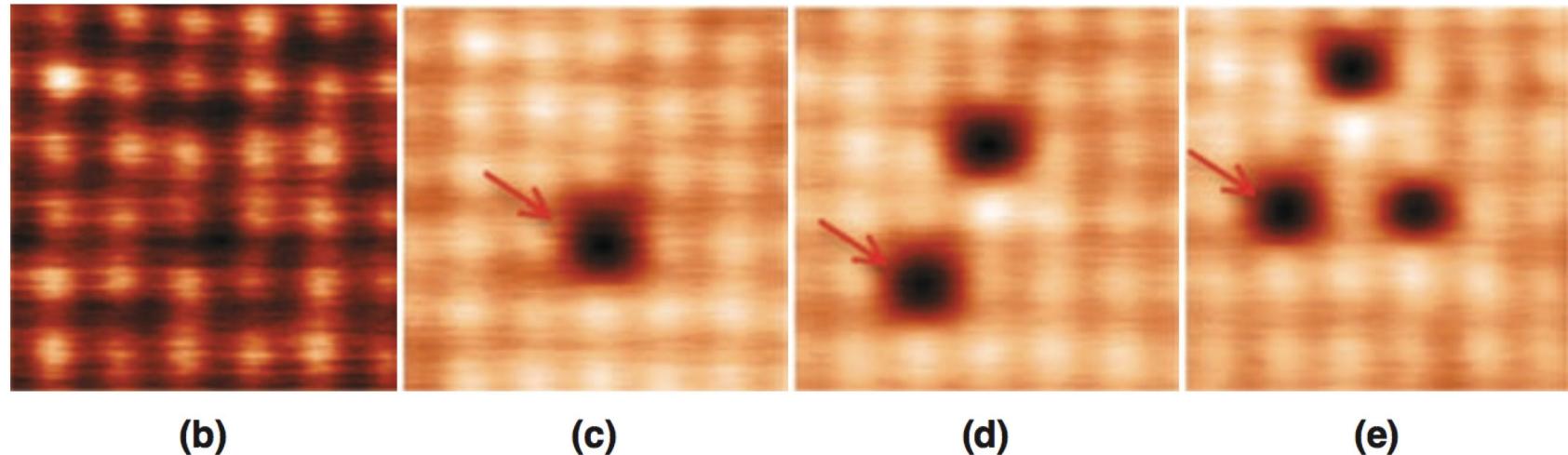
The first hard disk magnetic storage system had a storage density of  $2000 \text{ bits/in}^2$ , in 1956.  
Fifty years later, typical storage densities  $\sim 200 \text{ Gb/in}^2$   
Recently, Seagate demonstrated a disk system with a storage density of  $421 \text{ Gb/in}^2$



Each data bit is written onto  $\sim 100$  nanoparticles, each of size in the range 10-20 nm.

**Magnetic Force Microscopy(MFM) image of magnetization pattern of a Seagate hard disk**

## Writing to CoPt nanoparticle using Magnetic Force Microscopy(MFM)

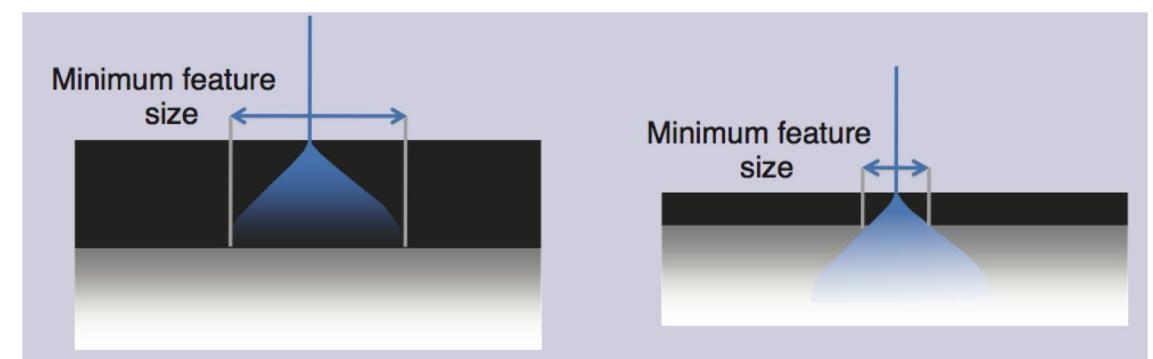
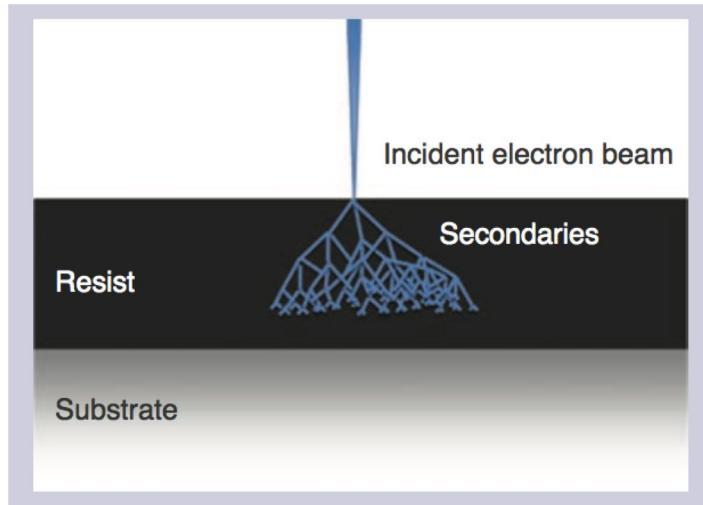


(b) 700 nm x 700 nm MFM scan of array with every nanodisk initially magnetized in the same direction

The first particle reversed is indicated by a red arrow in each frame. The space occupied by Each bit corresponds to a storage density of  $\sim 40 \text{ Gb/in}^2$ .

## Limitations of EBL

### 2. Electron scattering within resist and beam broadening



## Non-lithographic approaches: Bottom up approach

This technique is divided in two groups:

1. Vacuum based synthesis
2. Solution based synthesis

## Vacuum based synthesis:

1. Deposition takes place under high vacuum,  $10^{-8}$  to  $10^{-11}$  mbar
2. Process is very clean
3. Probability of deposition of foreign and undesired material is very low
4. It is costly and complicated
5. Needs vacuum pumps, pressure gauge and leak-proof accessories.

Examples of vacuum based synthesis to deposit nanocrystalline thin films:

1. Chemical vapor deposition
2. Pulsed laser deposition
3. Molecular beam epitaxy
4. Plasma arc methods

## 2. Solution based synthesis

1. It is a wet-chemical synthesis
2. Based on chemical reaction in liquid phase
3. Simple and cost-effective
4. Large range of the material can be synthesized
5. Not very clean process
6. Undesired and foreign materials can affect the properties

Examples of Solution based synthesis to deposit micro/nanocrystalline thin films:

:

1. Sol-gel dip coating
2. Spin coating
3. Spray pyrolysis
4. Electrodeposition

## Sol-gel Method

- This technique was first identified by Ebelmen during hydrolysis and polycondensation of tetraethyl orthosilicate (TEOS).
- Ebelman produced the first silica gel in 1846, and Cossa synthesized alumina gel in 1870.
- This sol–gel process depends on the precursor material, solvent, and catalysts (if necessary).
- The precursor, consisting of metal or metalloid elements. Alkoxides are mostly used for this purpose.
- Hydrolysis and polycondensation are the two important steps, involved in the sol–gel process, those prefer water as solvent medium.

## Sol-gel Method

- The sol-gel process involves:
  - ✓ the evolution of inorganic networks through the formation of a colloidal suspension(Sol) and
  - ✓ gelation of sol to form a network in a continuous liquid phase(gel)

## Steps involved:

Step 1: Synthesis of the colloid from precursors (usually ions of a metal)



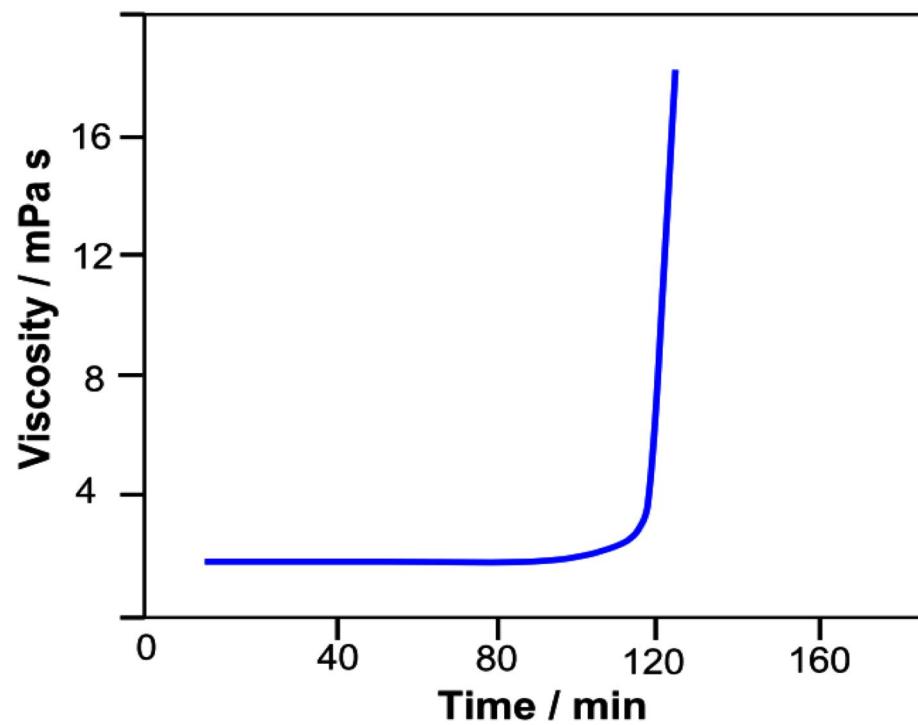
MOR : Metal alkoxides such as aluminates, titanates and borates

Other precursors are : alkoxysilanes such as tetramethoxysilane (TMOS) and tetraethoxysilane (TEOS), which form silica gel.

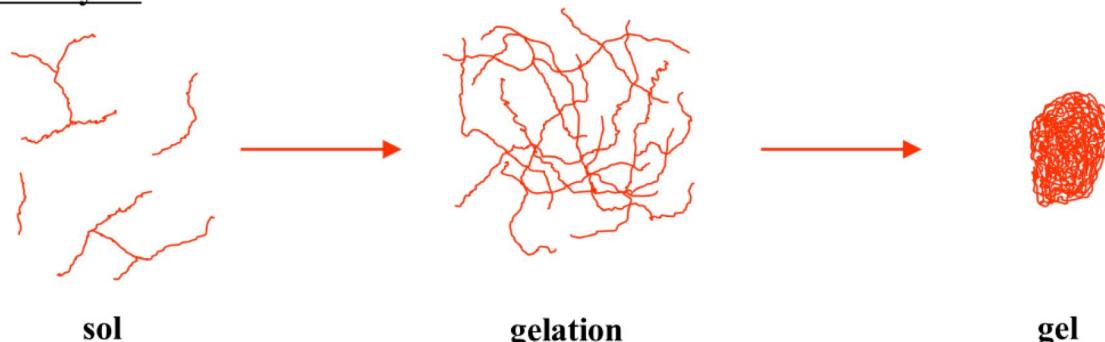
Step 2:  $MOH + ROM \rightarrow M - O - M + ROH$  (condensation)

The sharp increase in viscosity during sol-gel transition.

**Typical viscosity curve of a sol**



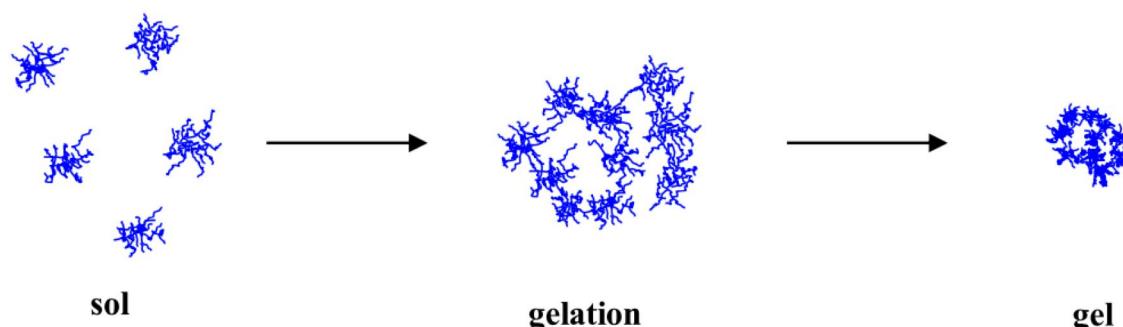
Acid catalyzed



Acid catalyzed hydrolysis

Favours formation of linear or weakly branched silica species.  
Gelation is via entanglements

Base catalyzed



Base catalyzed hydrolysis

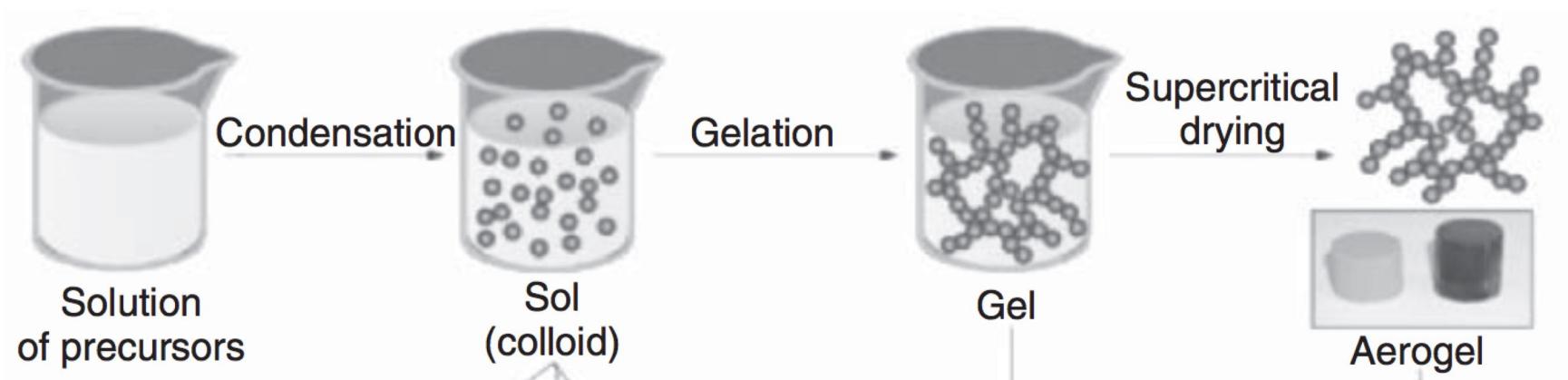
Gelation occurs via formation of agglomerated clusters which condense to form a 3D network

### Step 3: Syneresis (aging of the gel)

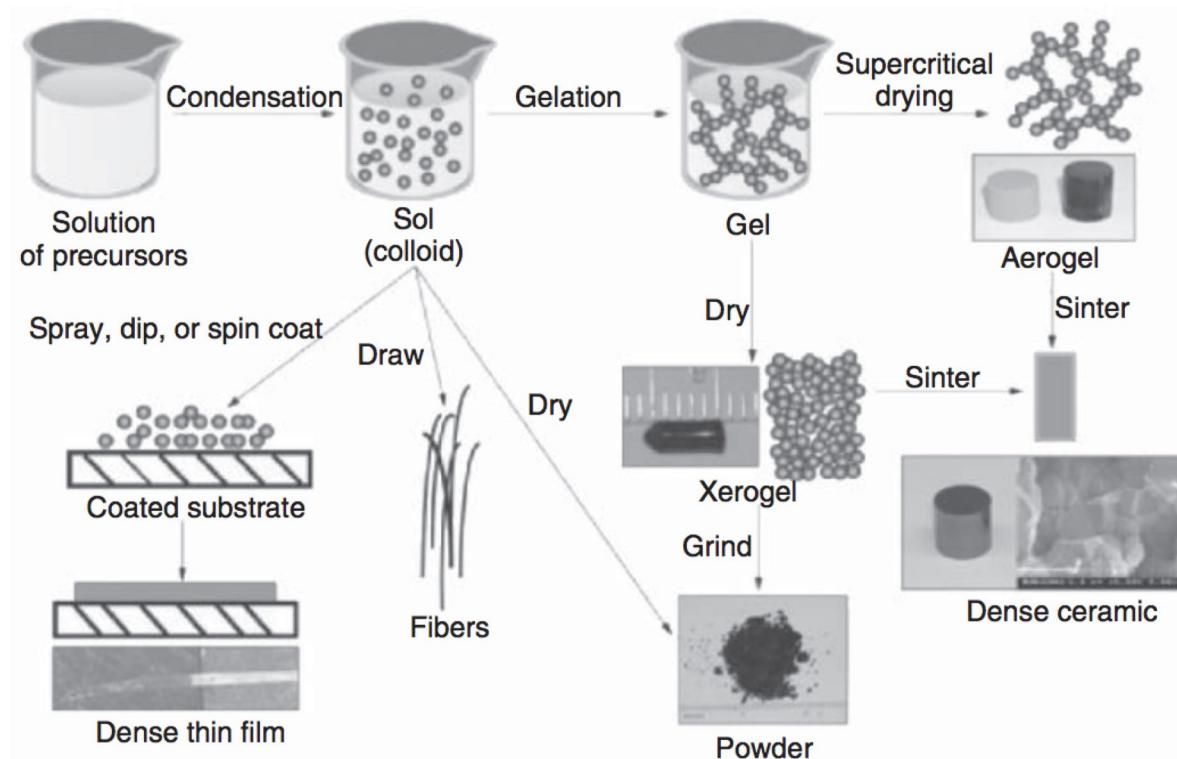
Accompanied by the contraction of the gel network and expulsion of the solvent from gel pores. The aging process of gels can exceed 7 days and is critical to the prevention of cracks in gels.

### Step 4: Calcining/Drying of the gel at temperatures upto 800 °C

During this step, water and other volatile liquids are removed from the gel network. If the solvent is extracted under supercritical conditions, the product is an aerogel.



# Sol-gel process

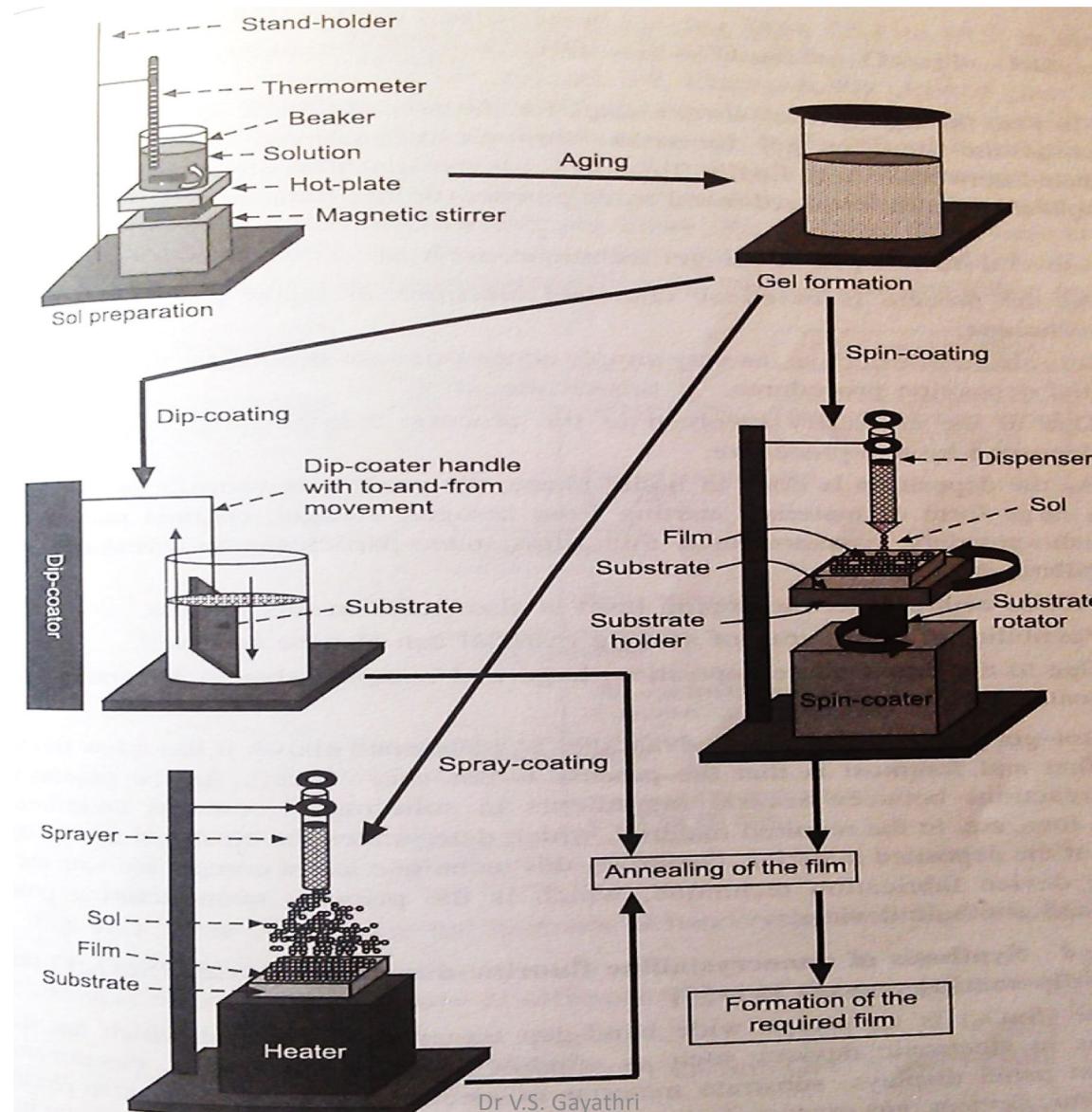


## Types of products:

1. Supercritical drying of gel result in Aerogel. It retains 3D structure, porous, catalytically active and can withstand 100 times its own weight. If Aerogel is heated at high T(sintering), it can form dense solid (dense ceramic).
2. Simple drying of gel result in Xerogel. Further if Xerogel is heated at high T, it can form dense solid.
3. Upon passing sol through a mold, it forms fibers of oxides and metal fibers.
4. If sol is dried, it forms nanocrystalline powders

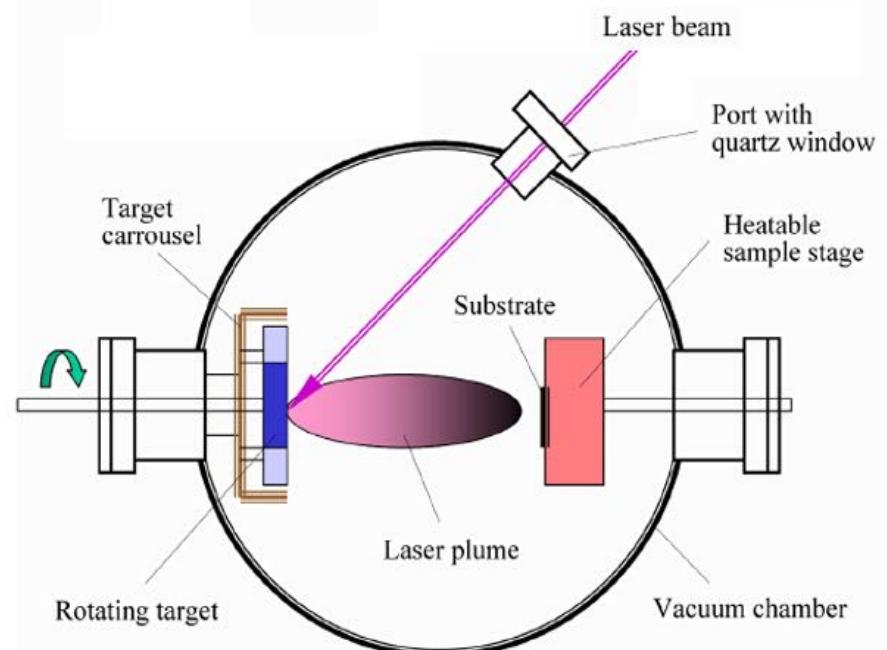
## Sol-gel dip coating

- In this process, the substrate is generally dipped into the sol and taken out to coat it with required material.
- Depending on the number of the dipping, the thickness of the film is determined
- Thereafter, the coated substrate is annealed to get the required film.
- In dip coating, spin coating and spray coating: *film thickness , annealing temperature and annealing time* determine the nanocrystallinity of the deposited film.



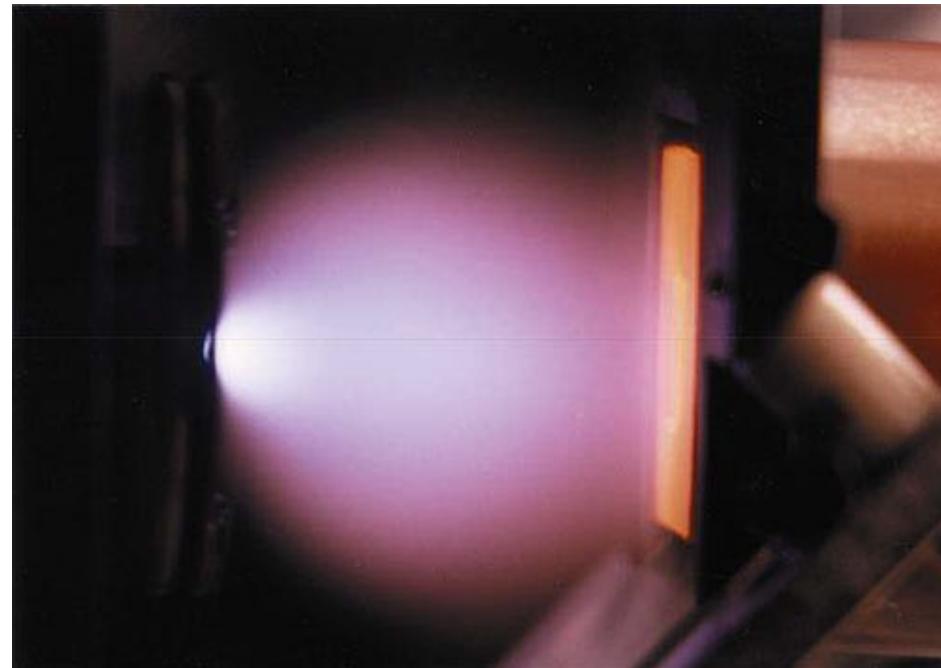
# Pulsed laser deposition method

1. Physical Vapor Deposition Technique for nanostructured thin films.
2. High Powered Laser is focused on target (material to be deposited) in vacuum.
3. Material is vaporized into plasma plume which extends from target.
4. Proceeds to deposit on substrate forming a thin film.
5. Highly Advantageous

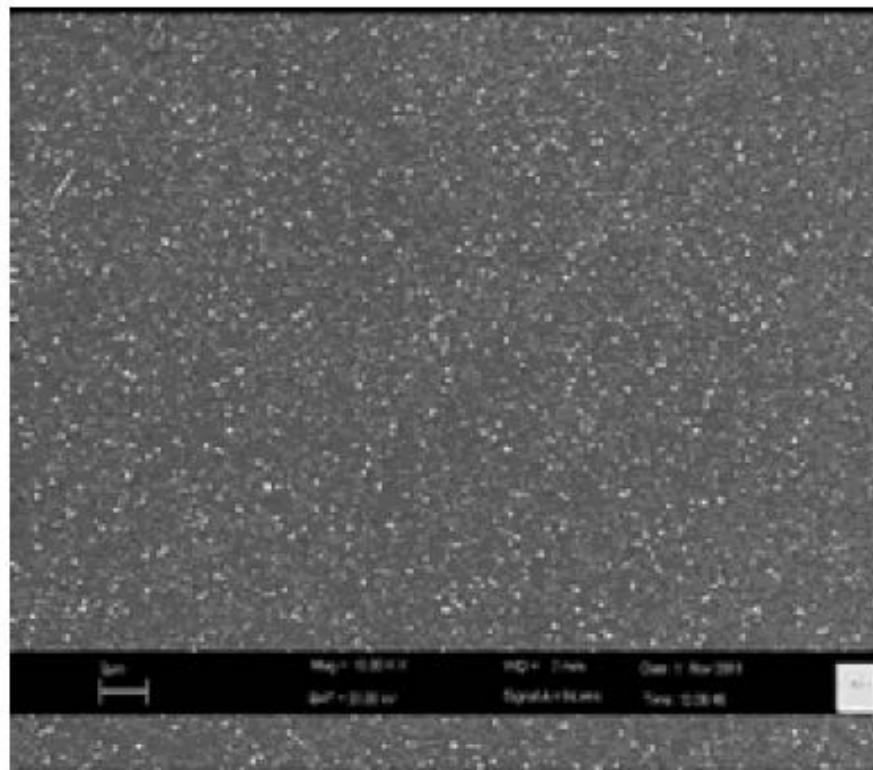


- At low laser flux, the material is heated by the absorbed laser energy and evaporates or sublimates. At high laser flux, the material is typically converted to a plasma.
- In an ultrahigh vacuum (UHV of about  $10^{-9}$  mbar) chamber, elementary or alloy targets are struck at an angle of 45°C by a pulsed and focused laser beam.
- The atoms and ions ablated from the target are deposited on substrates.
- Typical target-to-substrate distance is 2-10 cm.

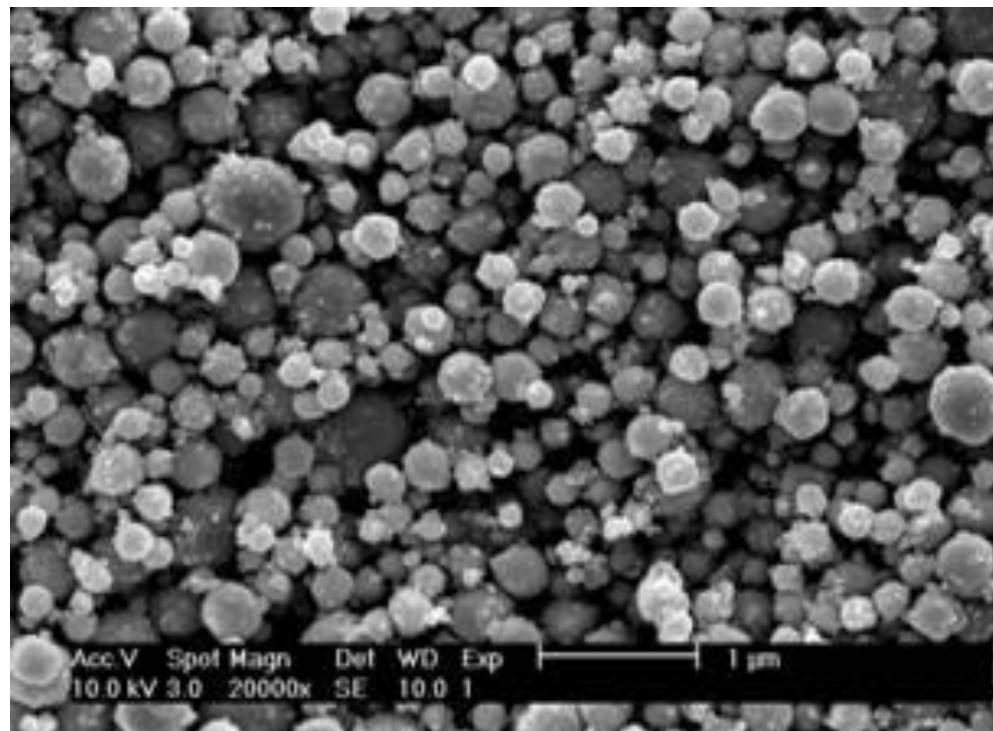
# laser ablated plasma



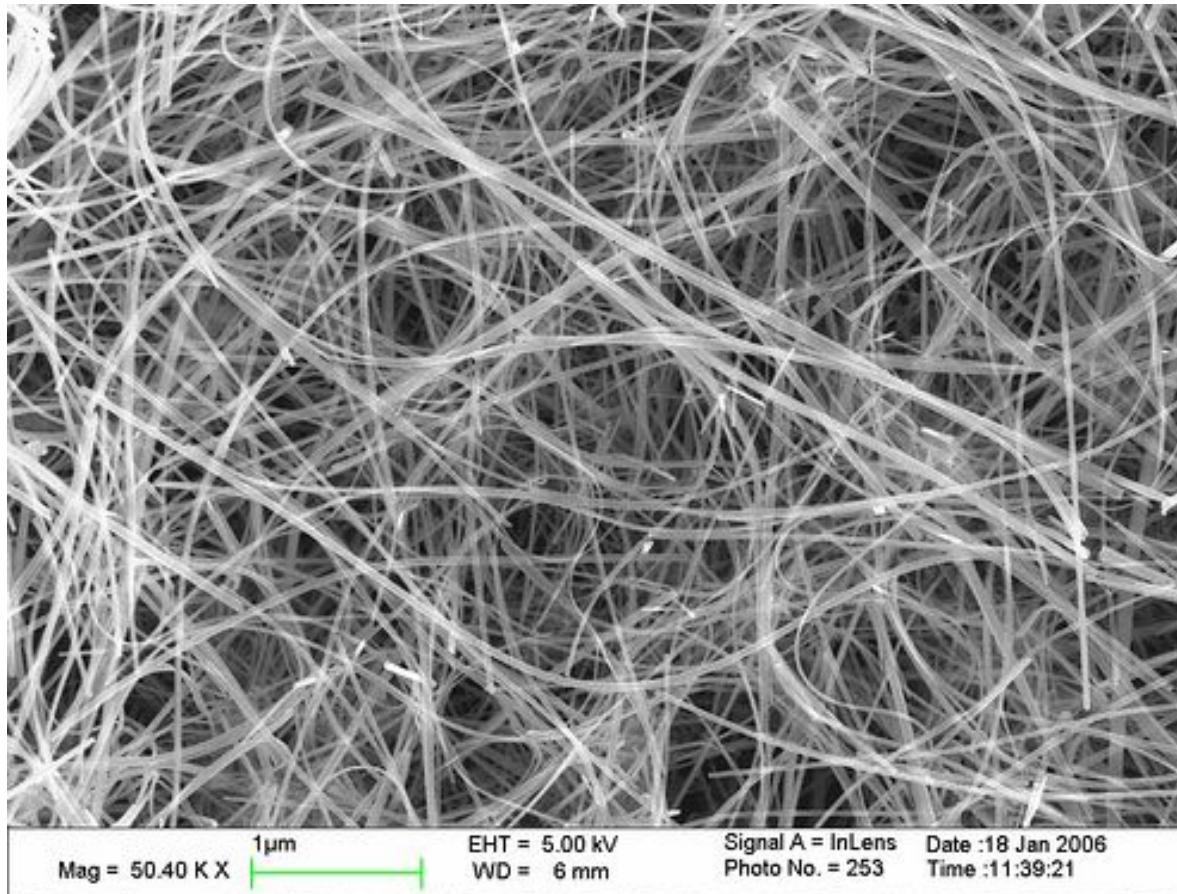
# Thin Film



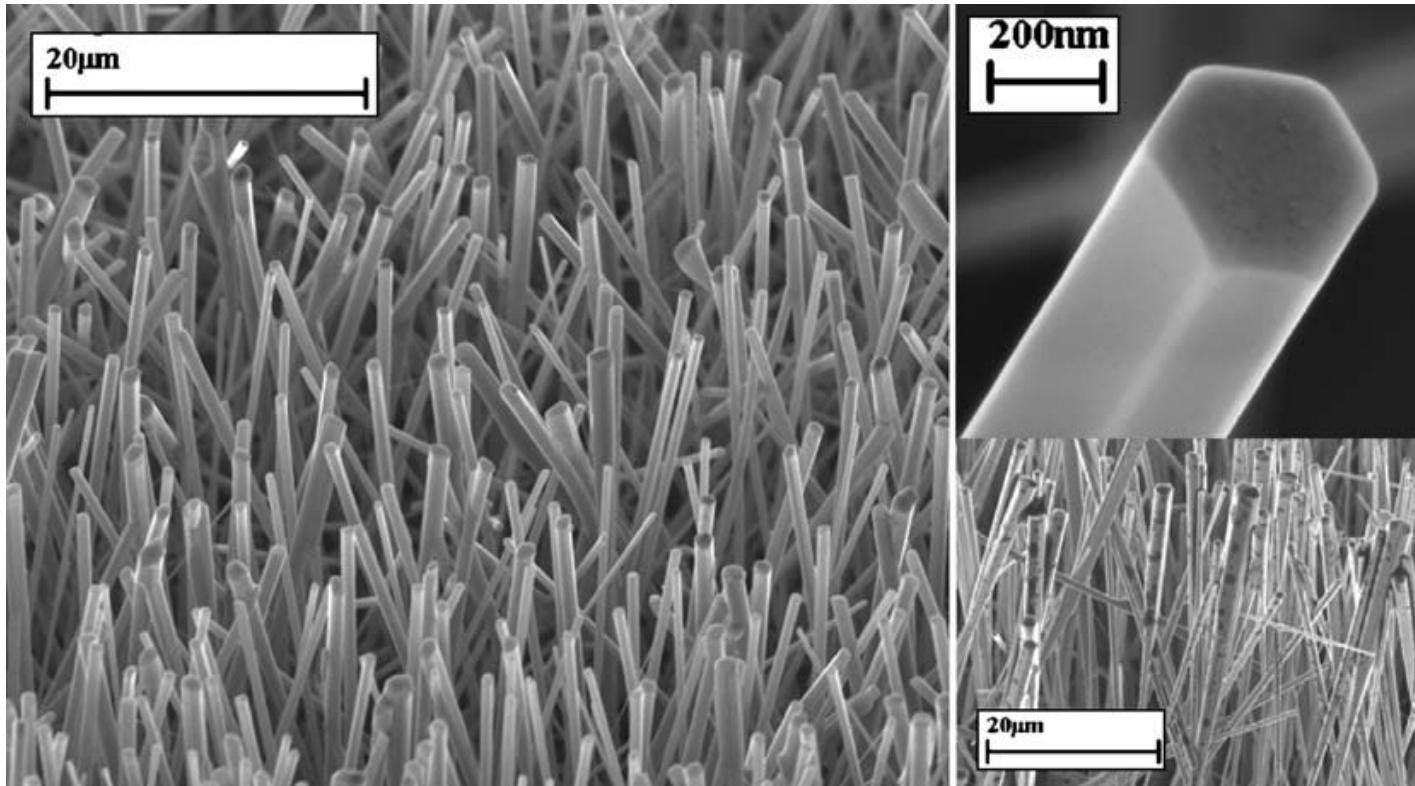
# Nanoparticles



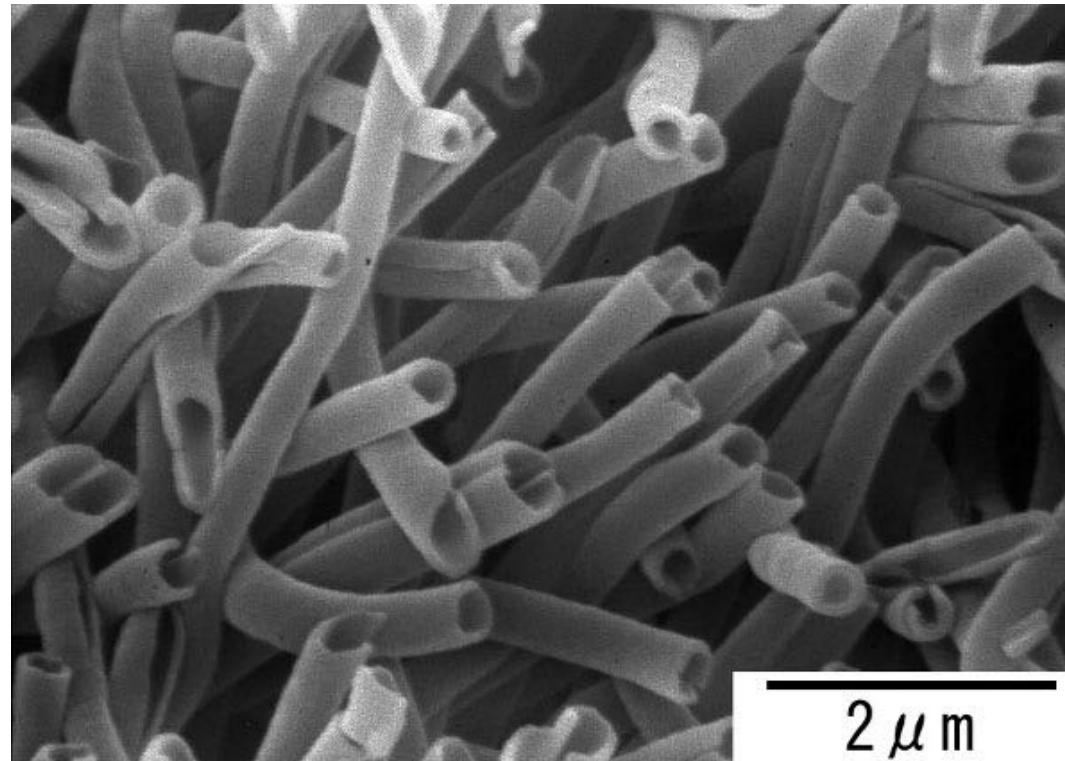
# Nano wires



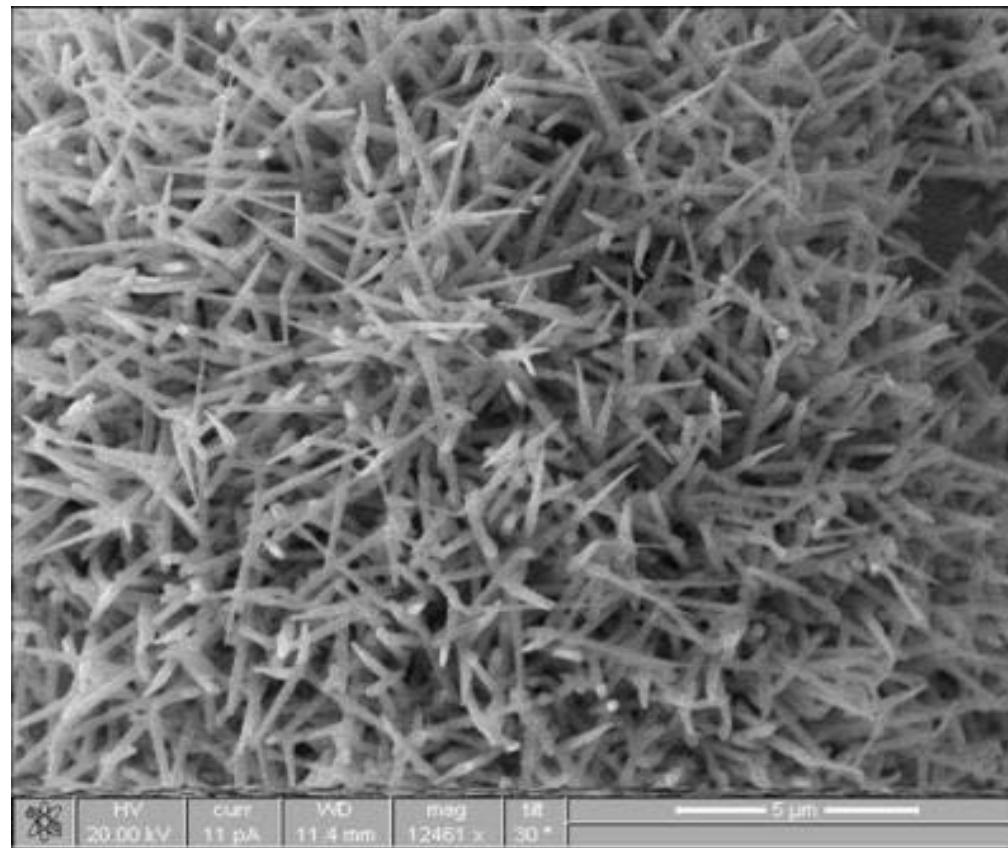
# Nano rods



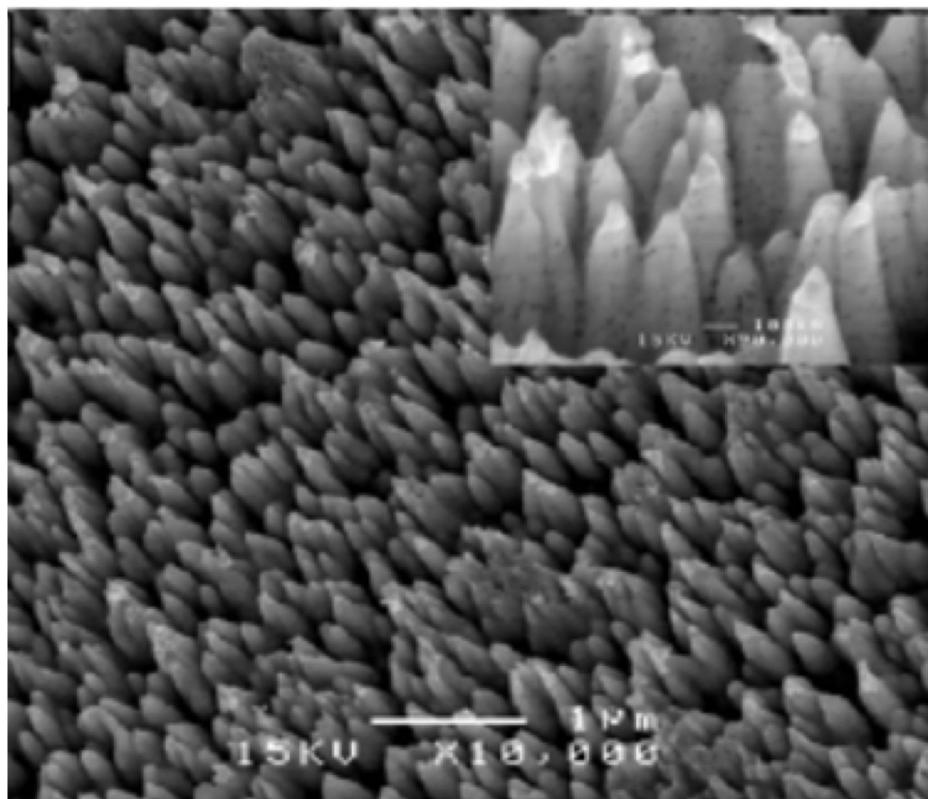
# Nano tubes



# Nano needles



# Nano cones



# Nanoscale Characterization techniques

- Scanning Electron Microscope (SEM)
- Transmission Electron Microscope (TEM)
- Atomic Force Microscopy(AFM)
- X-rays Diffraction (XRD)

# Electron microscope (EM)

- Electron microscopes(OM) are scientific instruments that use a beam of energetic electrons to examine objects on a very fine scale.
- In the early 1930s, Electron microscopes were developed due to the limitations of Optical Microscopes.
  - There was a scientific need to see the fine details of the interior structures of organic cells (nucleus, mitochondria...etc.).
  - This required 10,000x plus magnification which was not possible using current optical microscopes.

## DIFFERENCES BETWEEN OM AND EM

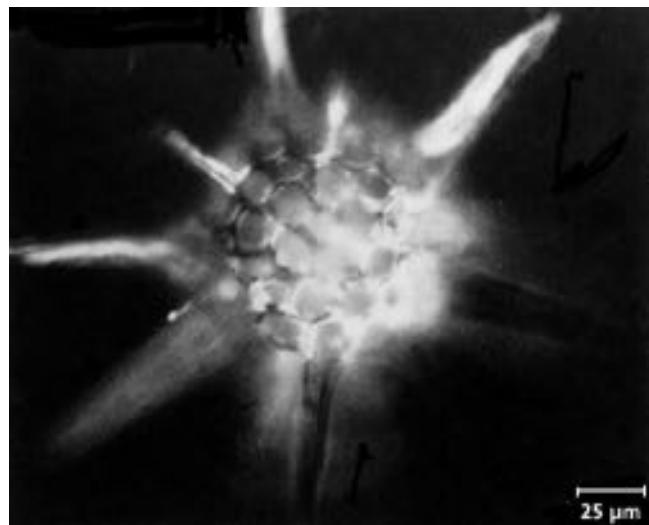
OPTICAL MICROSCOPE	ELECTRON MICROSCOPE
<ol style="list-style-type: none"><li>1. The source of light.</li><li>2. The specimen.</li><li>3. The lenses that makes the specimen seem bigger.</li><li>4. The magnified image of the specimen that you see.</li></ol>	<ol style="list-style-type: none"><li>1. The light source is replaced by a beam of very fast moving <b>electrons</b>.</li><li>2. The specimen usually has to be specially prepared and held inside a <b>vacuum chamber</b> from which the air has been pumped out (because electrons do not travel very far in air).</li><li>3. The lenses are replaced by a series of coil-shaped <b>electromagnets</b> through which the electron beam travels.</li><li>4. The image is formed as a photograph (called an electron micrograph) or as an image on a <b>TV screen</b>.</li></ol>

- Maximum usable Magnification = 
$$\frac{\text{Resolving power of naked eye}(\sim 250 \mu\text{m})}{\text{Resolving power of instrument}}$$
- If the resolving power of light microscope is 250nm, magnification is of the order of 1000.
- For an electron energy of 50,000V the theoretical resolving power of an electron microscope would be 0.0027 nm, reaching a magnification of the order of  $10^9$ .

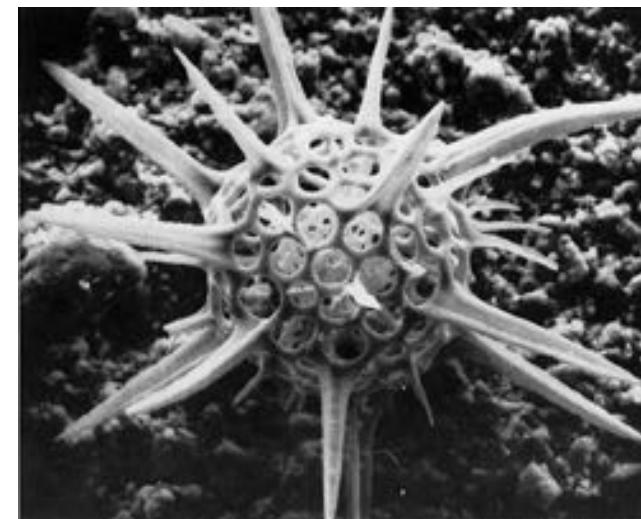
## Advantages of Using EM over OM

- 

Magnification	Depth of Field	Resolution
OM: 4x - 1400x	0.5mm	0.2 $\mu$ m
SEM: 10x - 500Kx	30mm	1.5nm

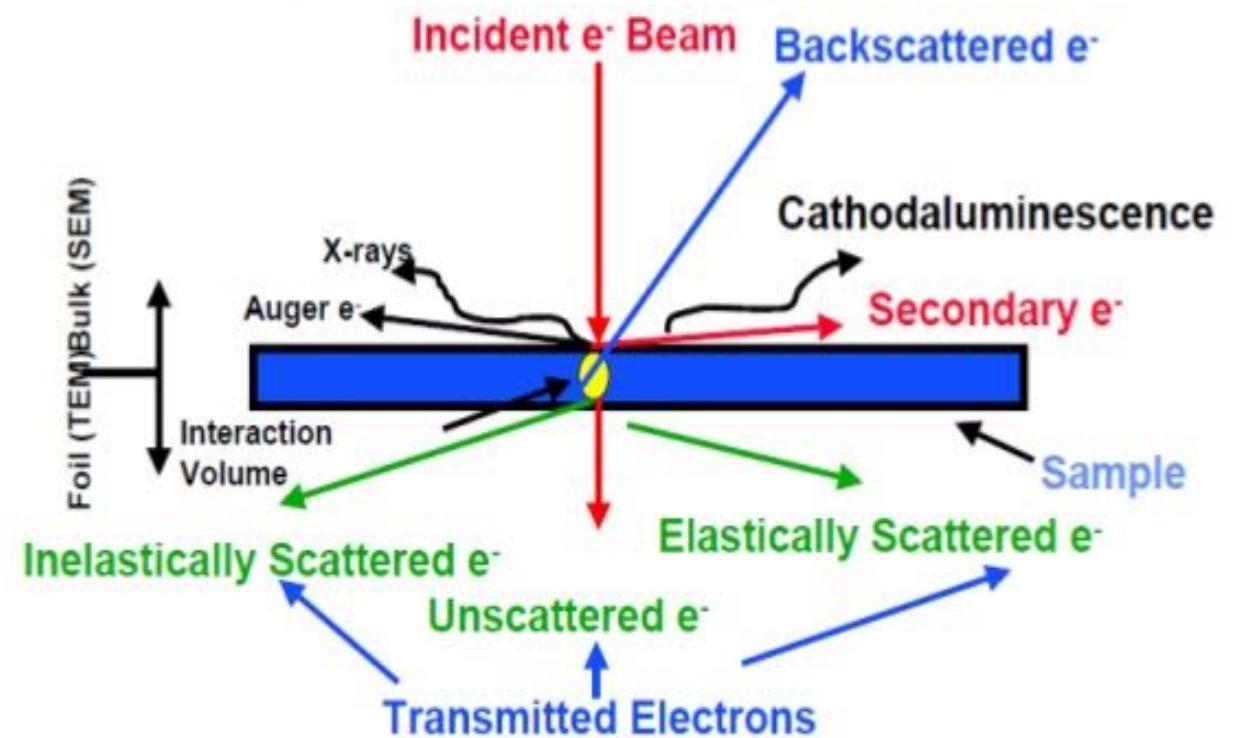


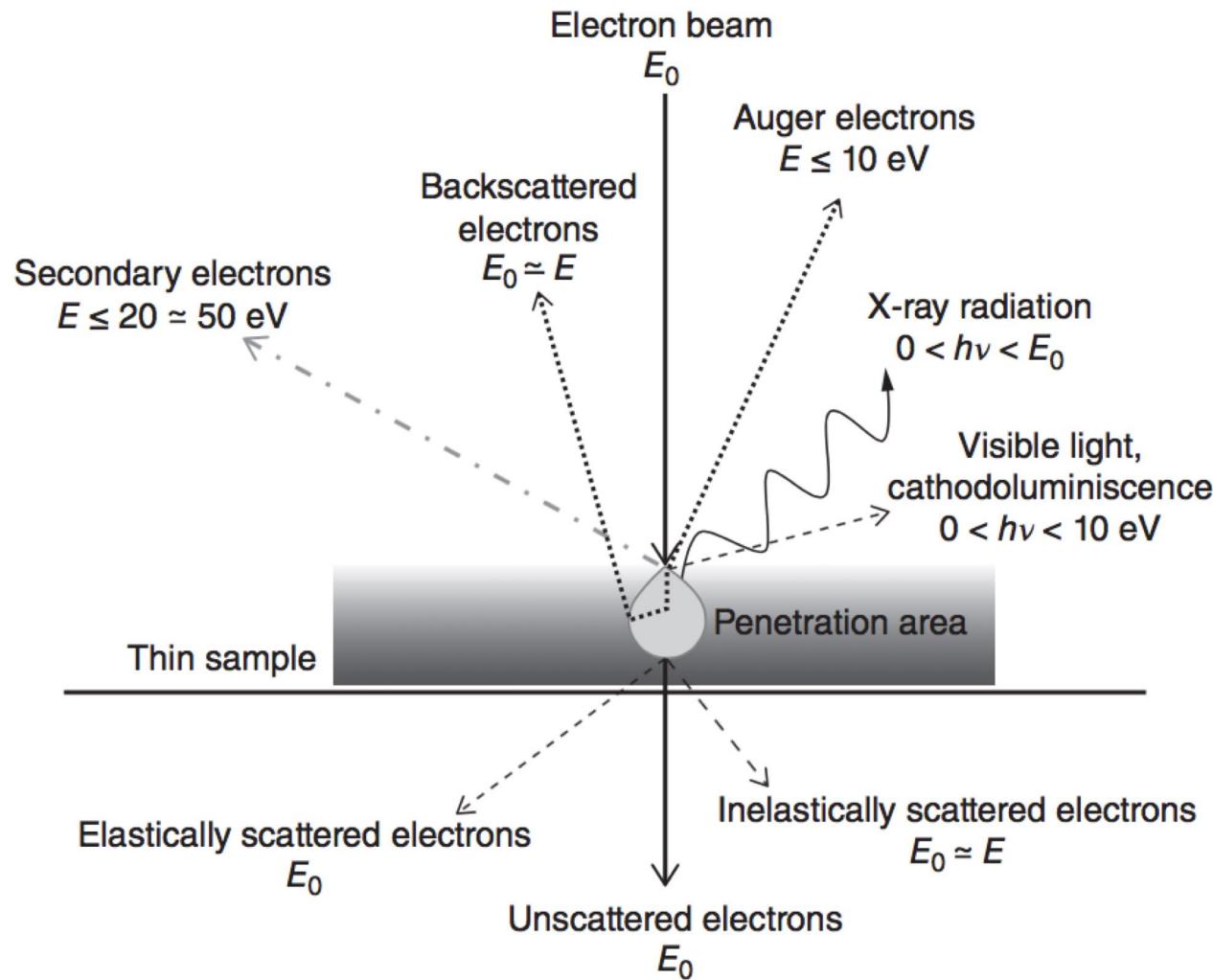
**OM image**



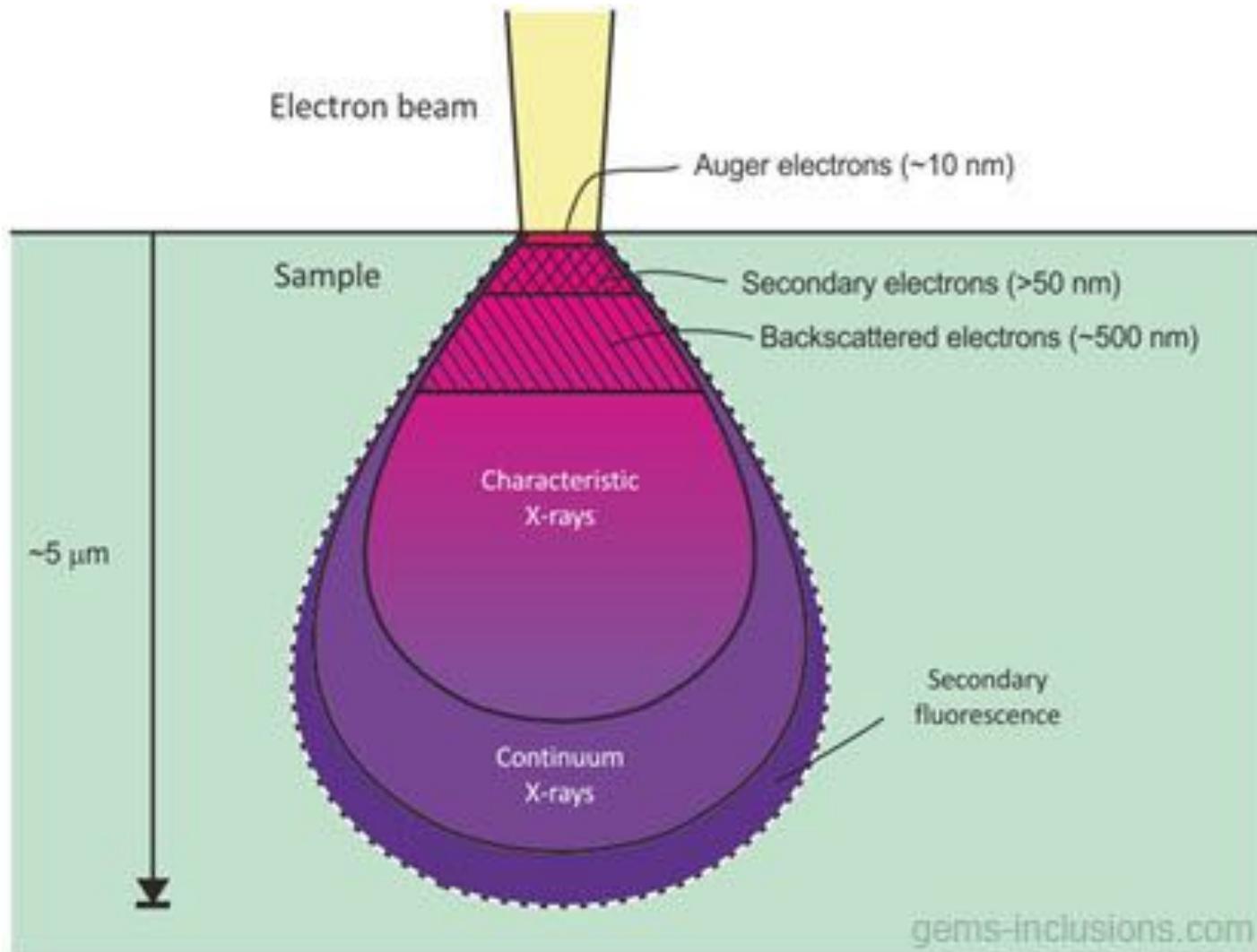
**SEM image**

## Electron stimulated Signals when it strikes a sample





## A cross section of the interaction volume



## Types of Electron microscopy

### 1. Transmission electron microscope (TEM)

It forms images using electrons that are transmitted through the specimen.

### 2. Scanning electron microscope (SEM)

It utilizes electrons that have bounced off the surface of the specimen.

## History

- The **transmission electron microscope (TEM)** was the first type of Electron Microscope to be developed.
- It 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**.
- The **first scanning electron microscope (SEM)** debuted in **1938** ( **Manfred Von Ardenne**) with the first commercial instruments around **1965**.
- Its late development was due to the electronics involved in "scanning" the beam of electrons across the sample.

# SCANNING ELECTRON MICROSCOPE (SEM)

- SEM is one of the most widely used techniques for the characterization of nanomaterials and nanostructures.
- It is a type of electron microscope that images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern.
- When a finely focused beam of electrons impinges on the surface of the solid sample and interacts with the atom of sample, several signals in the form of backscattered electrons, secondary electrons, Auger electrons and characteristic X-rays are generated from the surface, which contains information about surface topography and composition of specimen.
- It shows detailed 3D images with a resolution of few nm.
- Has higher magnification upto  $\times$  300,000 as compared to light microscope (upto  $\times$  10,000).

## **Characteristics that can be viewed on SEM-**

1. **Topography:** The surface features of an object or "how it looks", its texture; detectable features are limited to a few nm.
2. **Morphology:** The shape, size and arrangement of the particles making up the object that are lying on the surface of the sample; detectable features limited to few nm.
3. **Composition:** The elements and compounds that the sample is composed of and their relative ratios, in areas  $\sim 1 \mu m$  in diameter and depth.
4. **Crystallographic Information:** The arrangement of atoms in the specimen and their degree of order; only useful on single-crystal particles  $>> 20\mu m$ .

## **In SEM, different type of signal gives different information:**

- a. Secondary electrons: surface structure.
- b. Backscattered electrons: surface structure and average elemental information. The production of backscattered electrons varies directly with the specimen's atomic number. They may be used to detect the contrast between the areas with different average atomic numbers.
- c. X-rays and Auger electrons: elemental composition with different thickness-sensitivity.

## SEM Sample Preparation

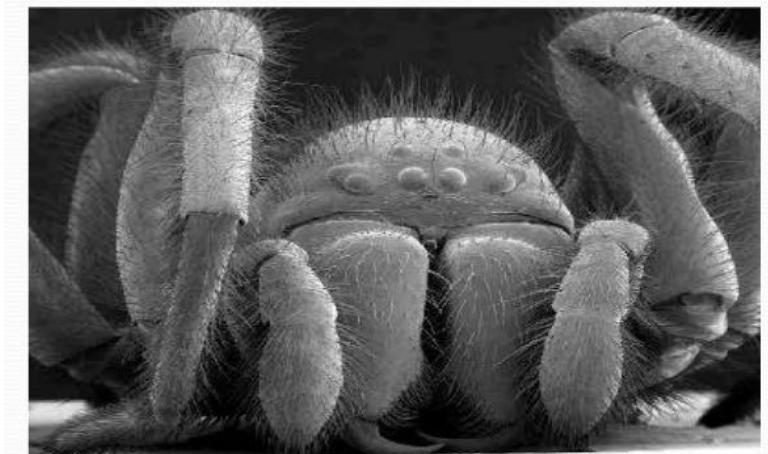
1. Cleaning the surface of the specimen
2. Stabilizing the specimen
3. Rinsing the specimen
4. Dehydrating the specimen
5. Drying the specimen
6. Mounting the specimen
7. Coating the specimen

- The specimen for SEM should be conductive for the electron beam to scan the surface.
- Nonconductive solid specimen is generally coated with a layer of conductive material by low-vacuum sputter coating or high-vacuum evaporation.
- The sample stage can be moved in the x-,y- and z- directions and it can be rotated about each axis. ∴ the surface of most samples can be viewed from almost any perspective.

- Typically, specimens are coated with a thin layer of approximately 20 nm to 30 nm of a conductive metal (e.g., gold, gold-palladium, or platinum).



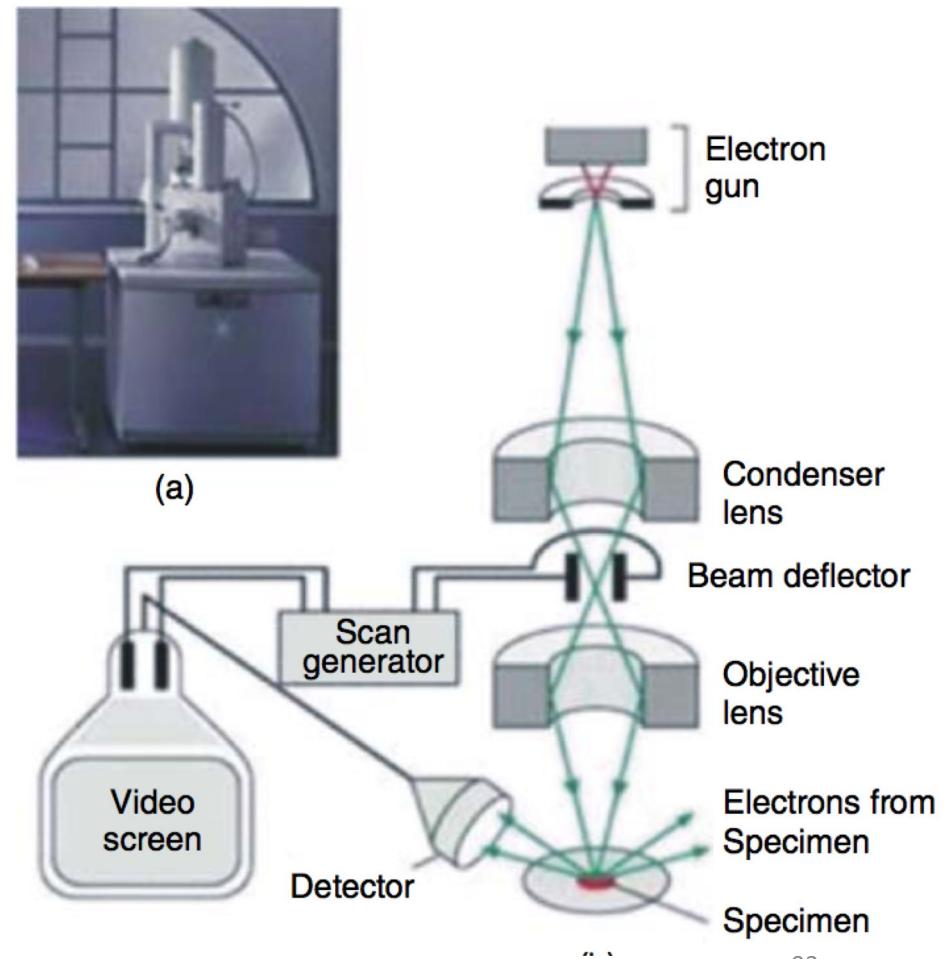
A spider coated in Gold



SEM image

## Experimental set up of Scanning Electron Microscope(SEM)

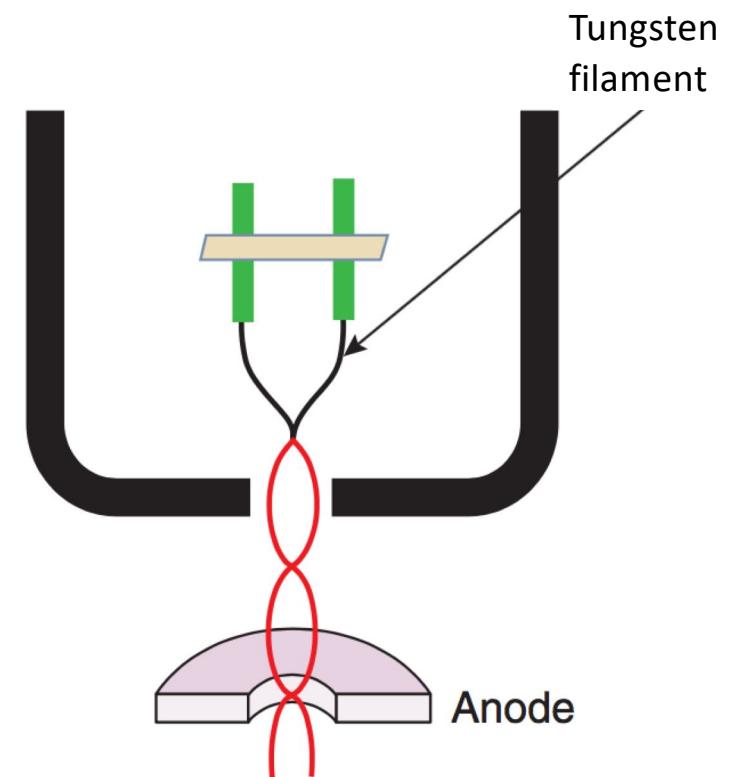
- In a typical SEM, a source of electrons is focused into a beam, with a finite spot size of  $\sim 5\text{nm}$ .
- Their energy range from a few hundred eV to 50 keV
- Two sets of scan coils to scan a square surface of the sample: (i) for raster (ii) for deflection
- As the electron strikes and penetrate the surface, a number of interactions occur.
- The SEM images are produced by collecting the emitted electrons on a cathode ray tube (CRT).



## Schematic of electron gun : A Thermionic Gun

Thermionic electron gun has three parts:

- (i) A heated ( $\sim 2000\text{-}2700\text{ K}$ ) tungsten filament of  $100\text{ }\mu\text{m}$  diameter and bent into a shape of hairpin with a V-shaped tip.
- (ii) A grid cap (Wehnelt cap) biased negatively w.r.t filament
- (iii) The anode held at ground potential



The cathodic filament is maintained at a potential of 1-50kV w.r.t anode. The electrons are accelerated to energy between 1 and 30 keV.

## Electromagnetic lenses

Electromagnetic lens consists of a coil of copper wires enclosed in a cylindrically symmetrical iron casting.

Current through the coils create a magnetic field—weak in the center of the gap and becomes stronger close to the bore.

In magnetic field, an electron experiences Lorentz force F:

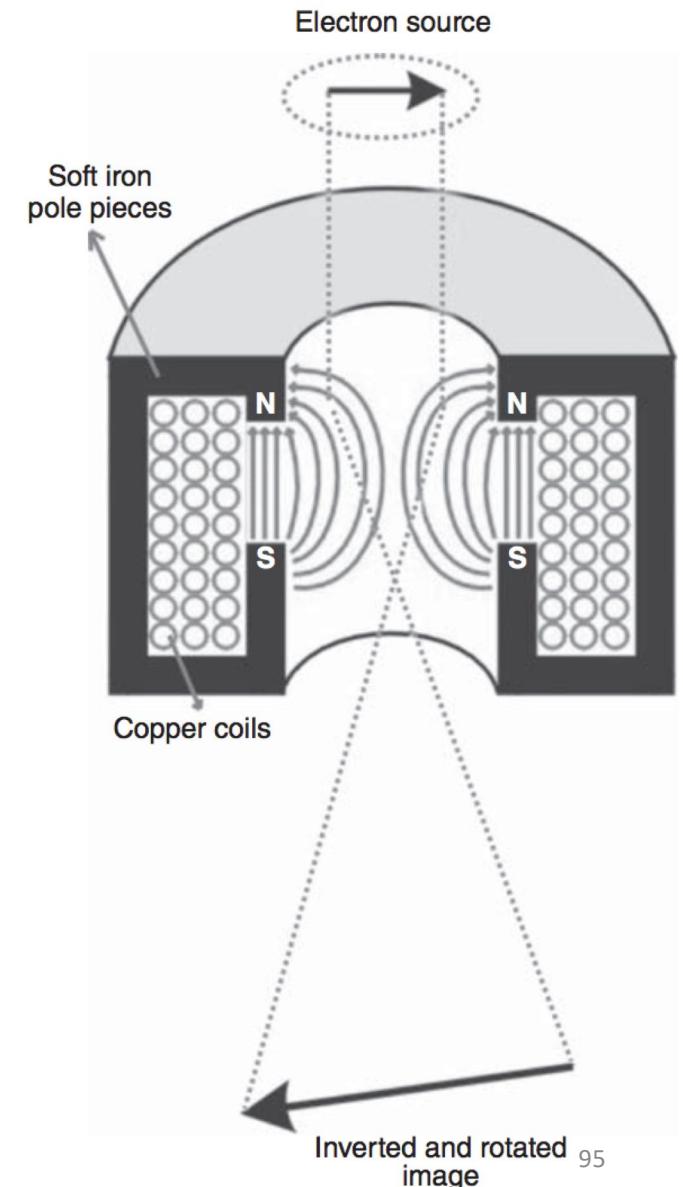
$$\mathbf{F} = -e(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

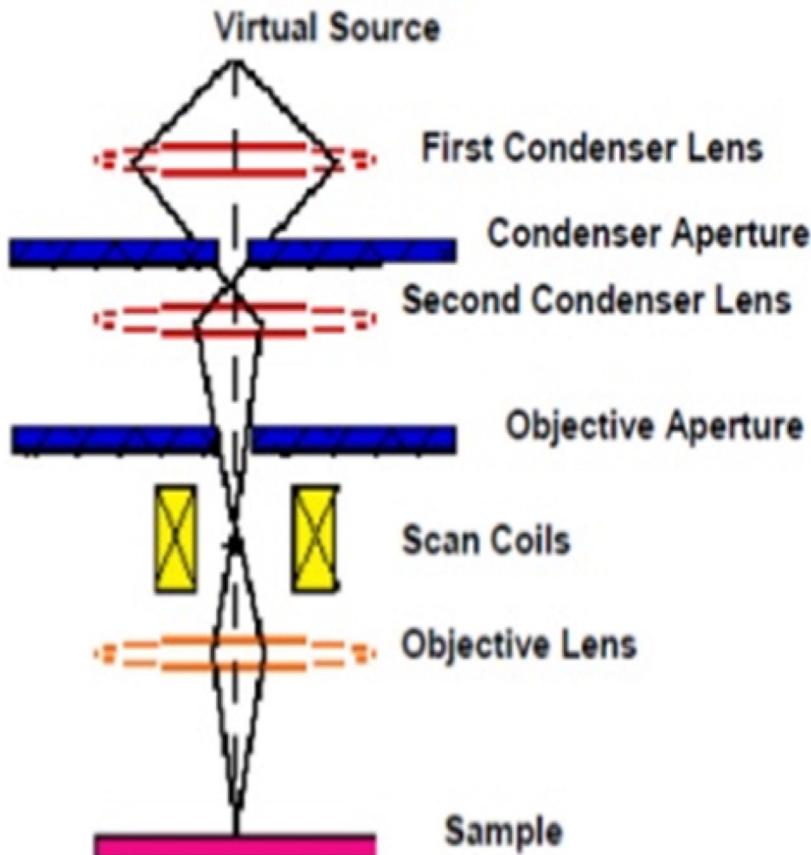
F leads to helical trajectory of the electrons and to the magnetic rotation.

The focal length can be changed by altering the strength of the current.

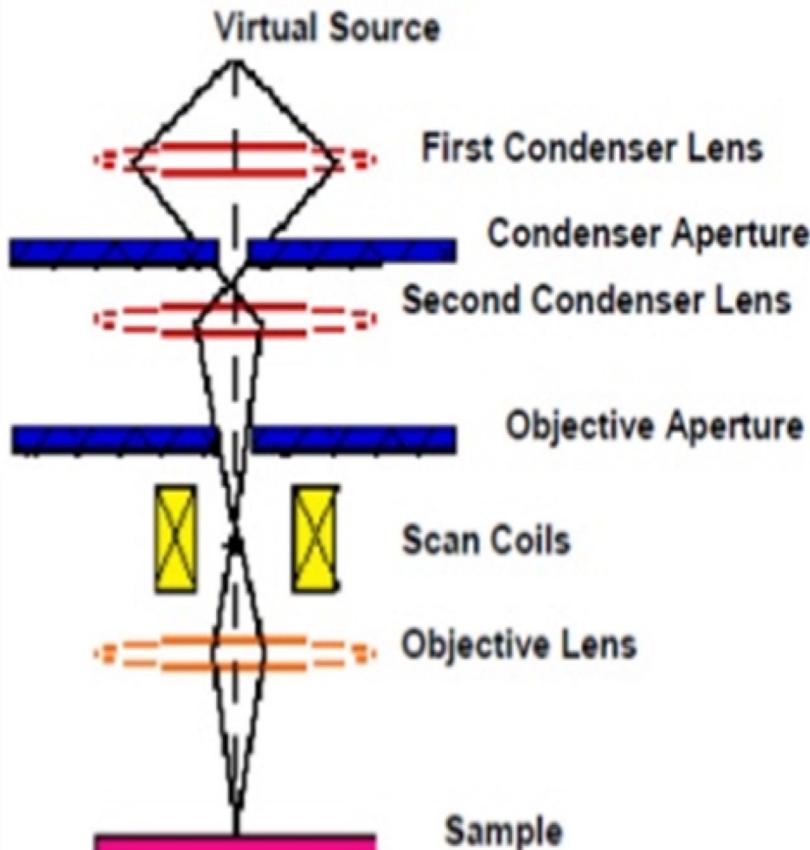
Dr VS Gayathri

30/01/22

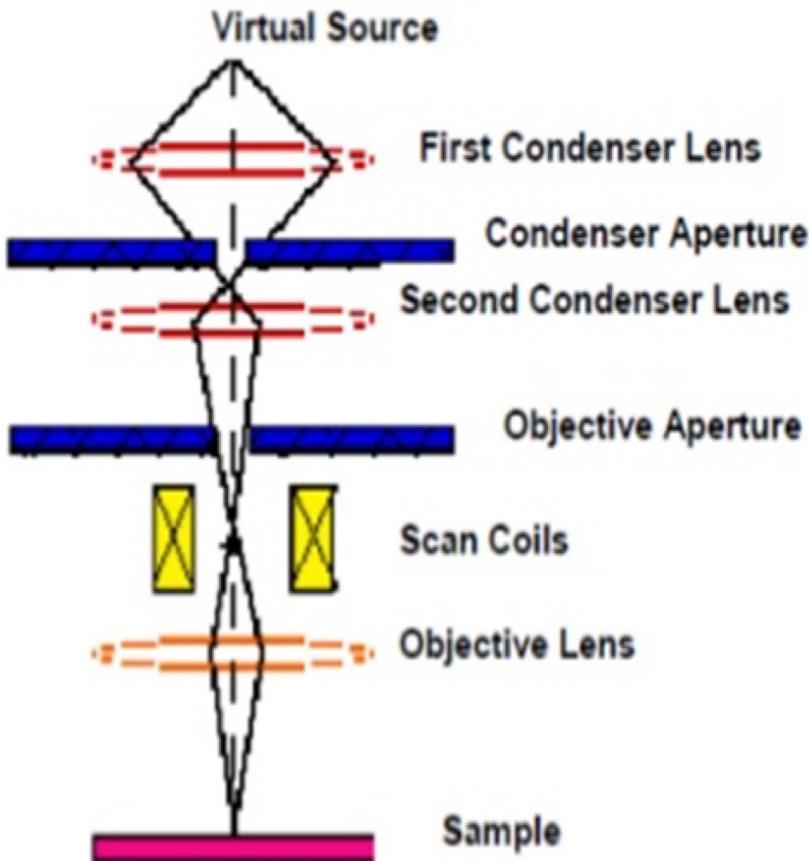




- 1) The "Virtual Source" at the top represents the electron gun, producing a stream of monochromatic electrons.
- 2) The stream is condensed by the first condenser lens (usually controlled by the "coarse probe current knob"). This lens is used to both form the beam and limit the amount of current in the beam. It works in conjunction with the condenser aperture to eliminate the high-angle electrons from the beam.



- 3) The beam is then constricted by the condenser aperture (usually not user selectable), eliminating some high-angle electrons.
- 4) The second condenser lens forms the electrons into a thin, tight, coherent beam and is usually controlled by the "fine probe current knob".
- 5) A user selectable objective aperture further eliminates high-angle electrons from the beam.



6) A set of coils then "scan" or "sweep" the beam in a grid fashion (like a television), dwelling on points for a period of time determined by the scan speed (usually in the microsecond range).

7) The final lens, the objective, focuses the scanning beam onto the part of the specimen desired.

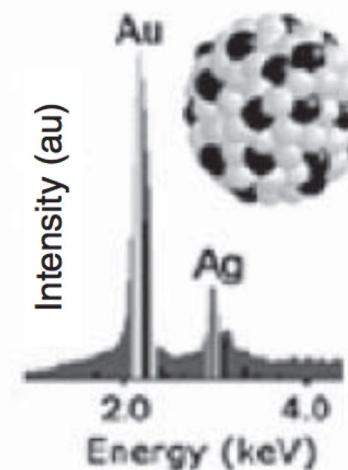
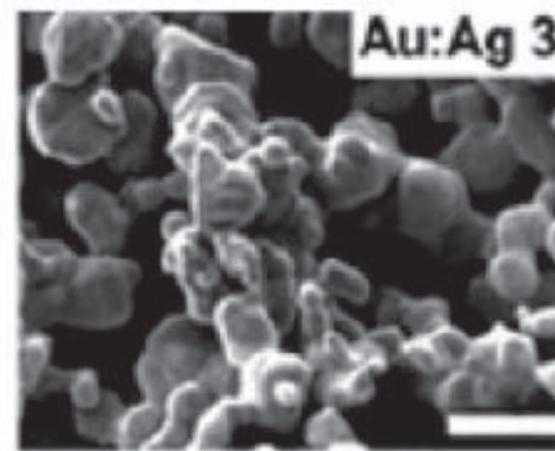
**8) When the beam strikes the sample (and dwells for a few microseconds) interactions occur inside the sample and are detected with various instruments.**

**10) This process is repeated until the grid scan is finished and then repeated, the entire pattern can be scanned 30 times/sec.**

**9) Before the beam moves to its next dwell point these instruments count the number of e<sup>-</sup> interactions and display a pixel on a CRT whose intensity is determined by this number (the more reactions the brighter the pixel).**

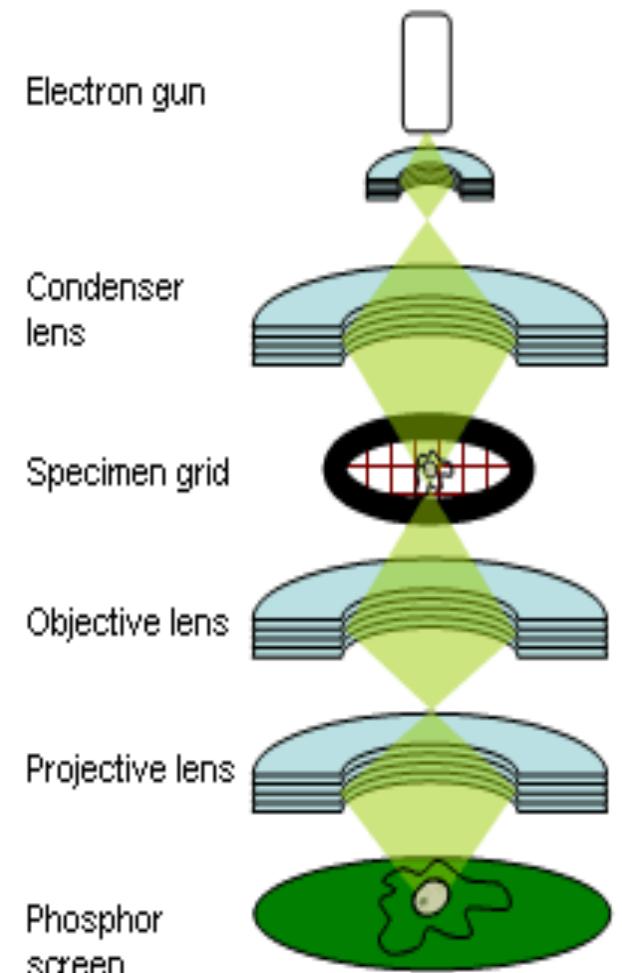
## Energy dispersive X-ray analysis (EDX):

- In SEM, the incident beam may cause the emission of the characteristic X-rays.
- Those rays are characteristic of the element.
- Chemical composition can be analysed using EDX analysis when it is attached with SEM.

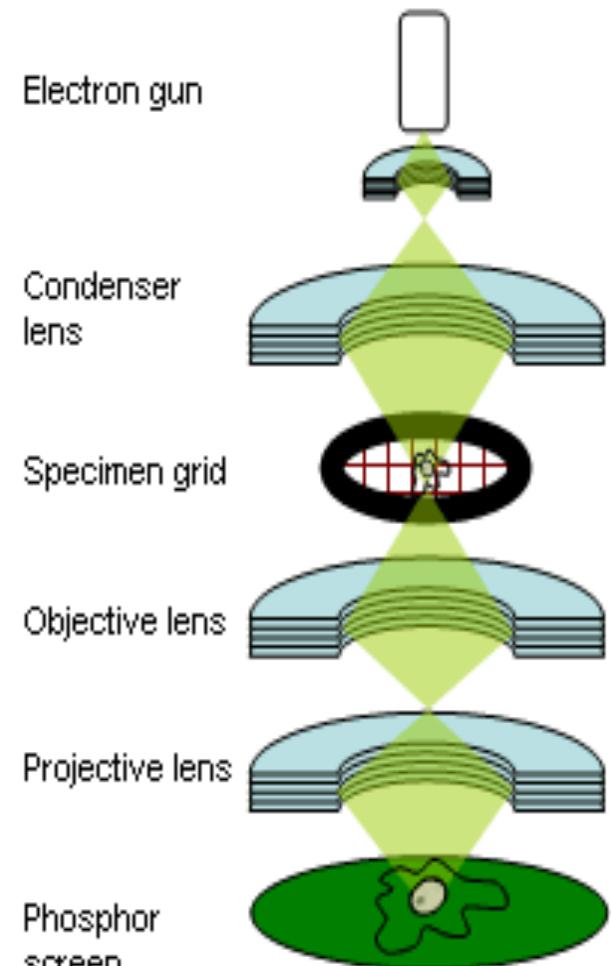


# Transmission electron microscope (TEM)

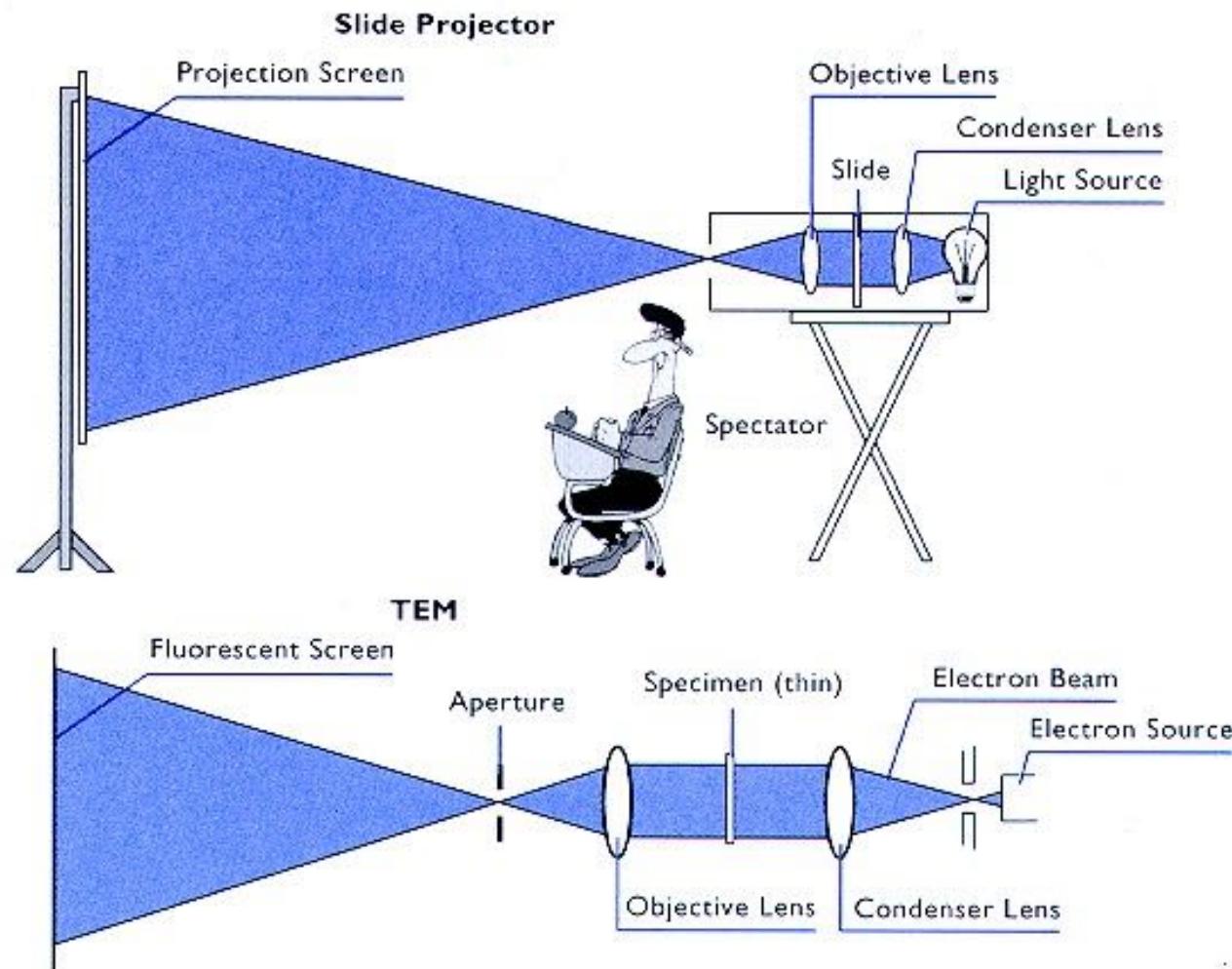
- Transmission electron microscopy (TEM) is a electron microscopic technique in which a energetic beam of electrons is transmitted through an ultra-thin specimen (<200nm) and provides *morphologic, compositional and crystallographic information of the samples.*
- An image is formed from the interaction of the electrons transmitted through the specimen. The image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD.
- TEMs produce high-resolution, two-dimensional images, allowing for a wide range of educational, science and industry applications.



- Electrons are accelerated from 100 keV to 1 MeV.
- They penetrate the sample either scattered or unscattered.
- Elastic scattering give rise to diffraction patterns
- Inelastic scattering leads to a spatial variation in the intensity of transmitted electrons. To minimize this scattering, the specimen thickness of the specimen should be between 10 nm and 1  $\mu\text{m}$ . High resolution demands specimen thickness in nm region.
- Provides higher magnification (X 1000,000)



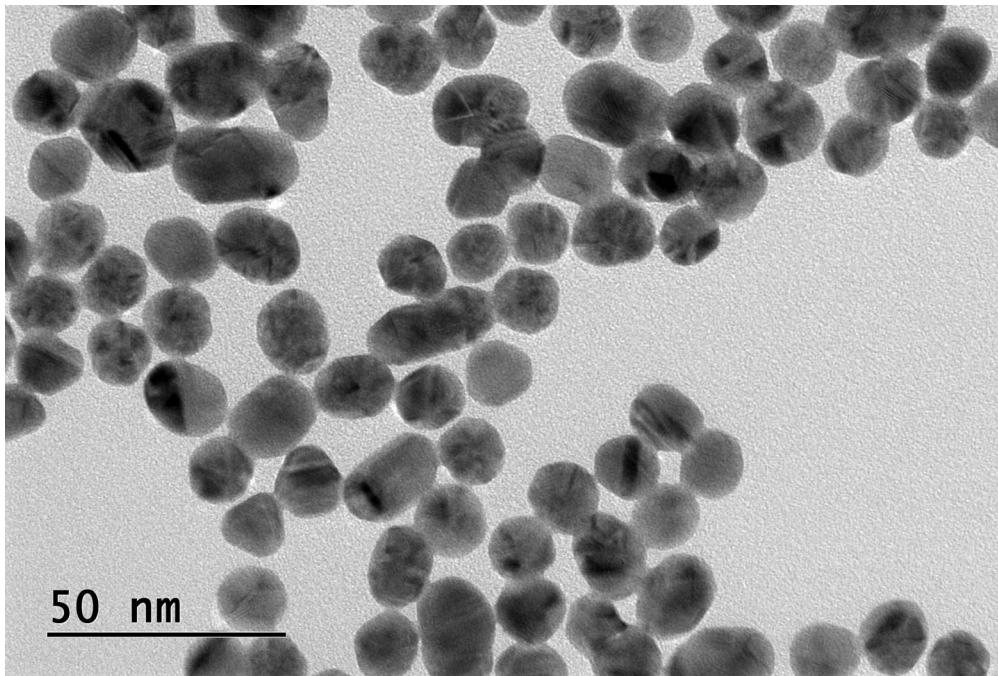
## A transmission Electron Microscope is analogous to a slide projector



## Difference between SEM and TEM

- SEM is based on *scattered electrons* while TEM is based on *transmitted electrons*.
- SEM focuses on the *sample's surface and its composition* whereas TEM provides the details about *internal composition*.
- 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.

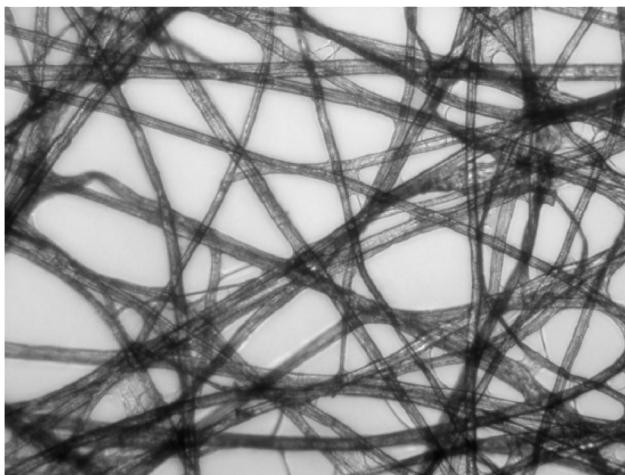
- SEM is used for *surfaces, powders, polished & etched microstructures, IC chips, chemical segregation* whereas TEM is used for imaging of *dislocations, tiny precipitates, grain boundaries and other defect structures* in solids.
- In TEM, pictures are shown on *fluorescent screens* whereas in SEM, picture is shown on *monitor*.
- SEM also provides a *3-dimensional image* while TEM provides a *2-dimensional picture*.
- TEM has much *higher resolution* than SEM.



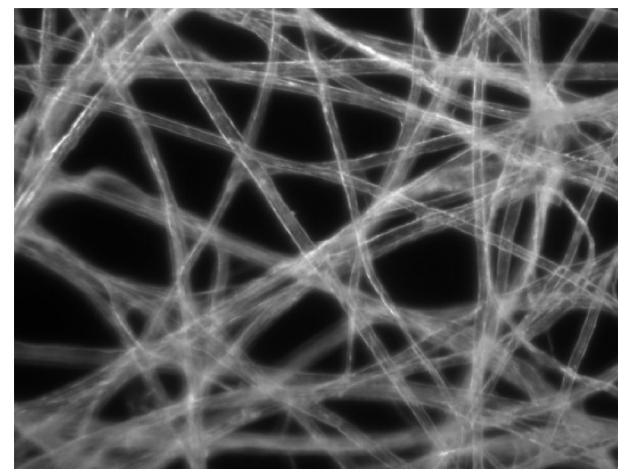
An TEM Image

## TEM images of Tissue paper

**Bright-field mode**



**dark-field mode**



## The Atomic Force Microscope (AFM)

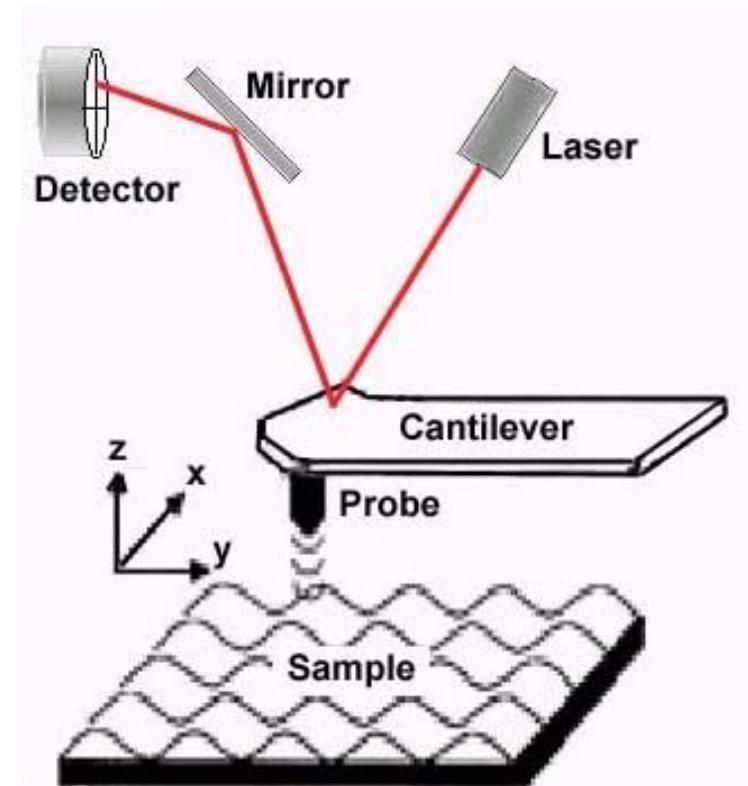
- The Atomic Force Microscope (AFM) belongs to the family of the **Scanning Probe Microscopy (SPM)**.
- **Scanning probe microscopy (SPM)** is a new branch of microscopy that forms images of surfaces using a physical probe of nanometer dimensions is scanned over the surfaced material/ specimen.
- An image of the surface is obtained by mechanically moving the probe in a **raster scan** of the specimen, line by line, and recording the probe-surface interaction as a function of position.
- This technique is capable of resolving details of surface down to atomic level and reveal 3D details unlike OM &EM.

- The atomic force microscope (AFM) or scanning force microscope (SFM) was developed in **1986** by **Binnig, Quate and Gerber**.
- AFM raster scans a sharp probe over the surface of a sample and **measures the changes in interatomic forces** between the probe tip and the sample.
- It does not require the surface to be conductive.
- It operates in air and not under vacuum.
- It is a **non-destructive** technique with a very high 3D spatial resolution.
- We can gain information on size, surface area and volume distributions.
- A wide range of particle sizes (**1nm to 8  $\mu m$** ) can be characterized in the same scan.

# Basic set-up and working of an AFM

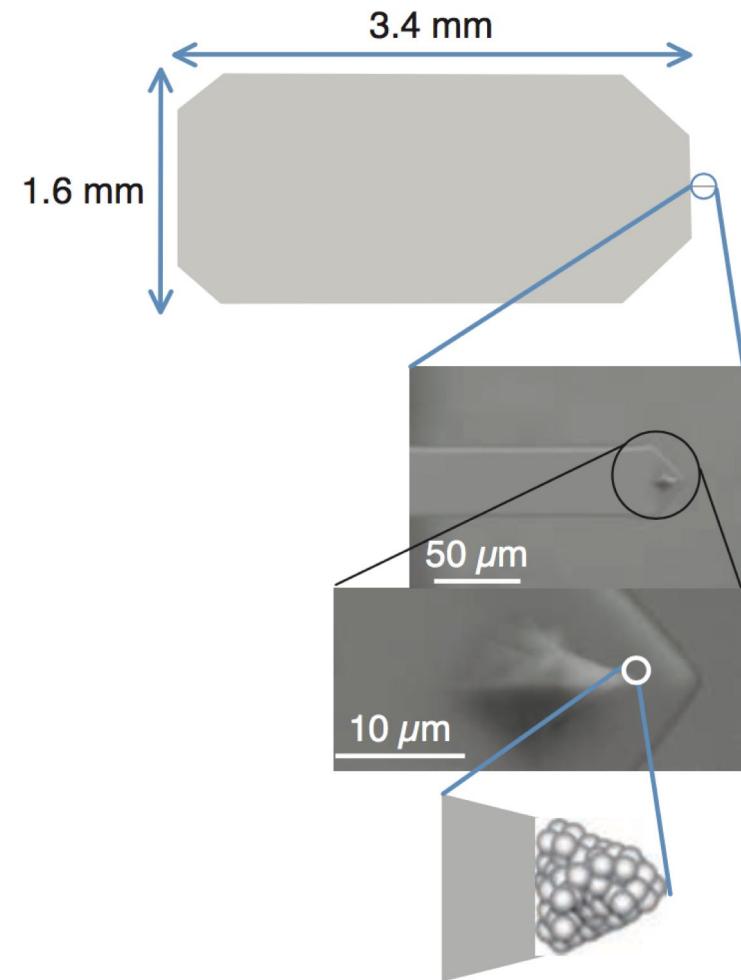
## Parts of AFM

1. **Laser** – deflected off cantilever
2. **Mirror**—reflects laser beam to photodetector
3. **Photodetector**—dual element photodiode that measures differences in light intensity and converts to voltage
4. **Cantilever** —moves as scanned over sample and deflects laser beam
5. **Probe**—tip - scans sample, made of Si
6. **Sample** to be analysed



## Basic set-up and working of an AFM

- An ultra-sharp tip is mounted on a cantilever and moved along the surface.
- A standard commercial cantilever fabricated on a Si chip with a thickness of  $\sim 300 \mu\text{m}$ .
- The cantilever is typically  $100 - 300 \mu\text{m}$  long with the tip fabricated on the end.



- In principle, the AFM resembles a record player and a stylus profilometer.
- The ability of an AFM to achieve near atomic scale resolution depends on the three essential components:
  - i. a cantilever with a sharp tip,
  - ii. a scanner that controls the  $x$ - $y$ - $z$  position, and
  - iii. the feedback control and loop.

i. Cantilever with a sharp tip:

- The stiffness of the cantilever needs to be less.
- The tip should have a radius of curvature less than 20-50 nm a cone angle between 10-20 degrees.

ii. Scanner:

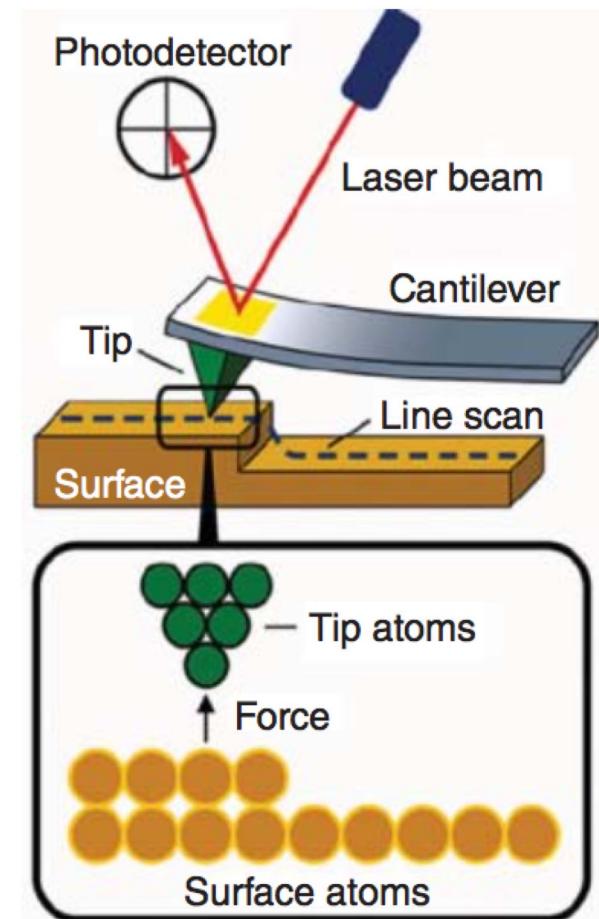
- The movement of the tip or sample in the x, y, and z-directions is controlled by a piezo-electric tube scanner.
- For typical AFM scanners, the maximum ranges are 80 mm x 80 mm in the x-y plane and 5 mm for the z-direction.

### iii. Feedback control.

- The forces that are exerted between the tip and the sample are measured by the amount of bending (or deflection) of the cantilever.
- By calculating the different signal in the photodiode quadrants, the amount of deflection can be correlated with the height .
- Because the cantilever obeys Hooke's Law for small displacements, the interaction force between the tip and the sample can be determined.

## Basic set-up and working of an AFM

- As the tip is brought towards a sample, at separations below  $\sim 50$  nm there is initially an attractive force that bends the cantilever a detectable amount towards the surface.
- Typically the bend in the cantilever is kept constant.
- A laser beam is reflected off a spot on the cantilever to a segmented photodiode that detects the motion of the probe.
- The output from the photodiode then controls the force applied to the tip so that it remains constant. The instrument measures how much the cantilever needs to be moved up and down to achieve constant bending.

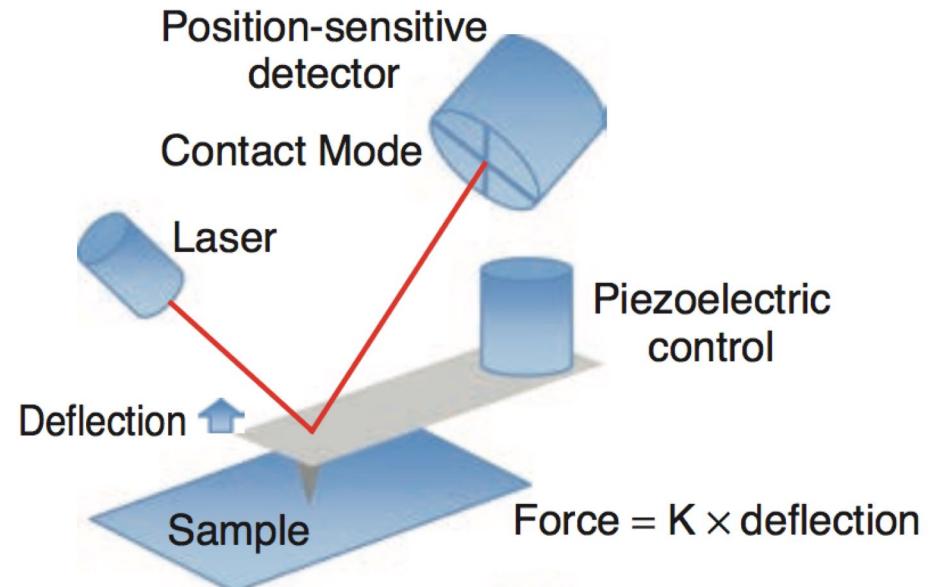


## AFM modes

The common modes are :

### (i) static mode : Contact mode

- The tip is approached towards the surface until it touches the surface. There is repulsive force between them in this mode.
- Then it is scanned in x and y with the control system moving the cantilever in z to maintain a constant cantilever deflection.
- The piezoelectric control is used to position the cantilever and tip in x, y and z with a precision of  $\sim 0.1$  nm.
- The z-piezo voltage vs x-y is used to obtain the image.  
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**(ii) Dynamic modes :** The probe is not simply dragged onto the surface but oscillated vertically w.r.t surface while it is scanned. So, allows imaging of biomolecules and cells.

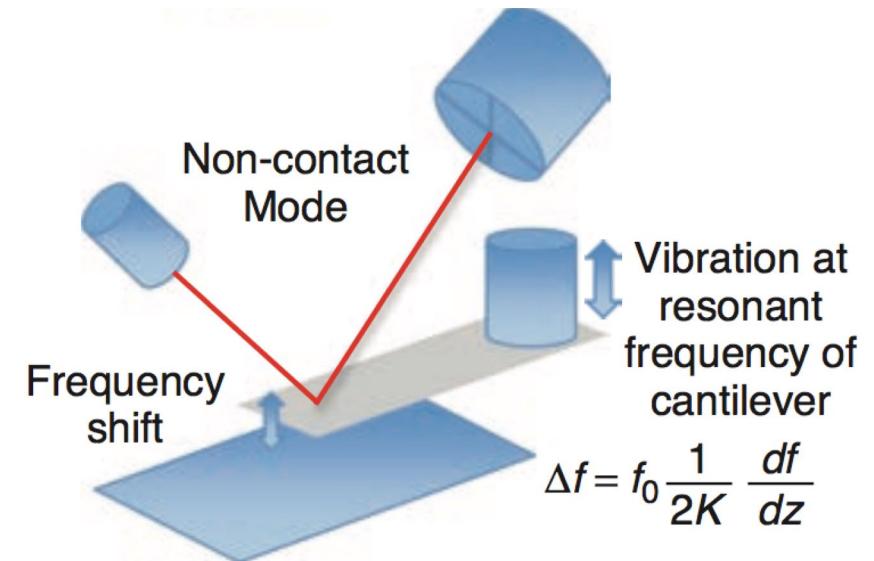
**(a) non-contact mode :** The cantilever is oscillated at either its resonant frequency (usually 10-100 kHz) or just above where the amplitude of oscillation is typically < 10nm to a few picometers.

Forces act to decrease the frequency.

The feedback loop system maintains a constant amplitude or frequency by adjusting the average tip-to-sample distance.

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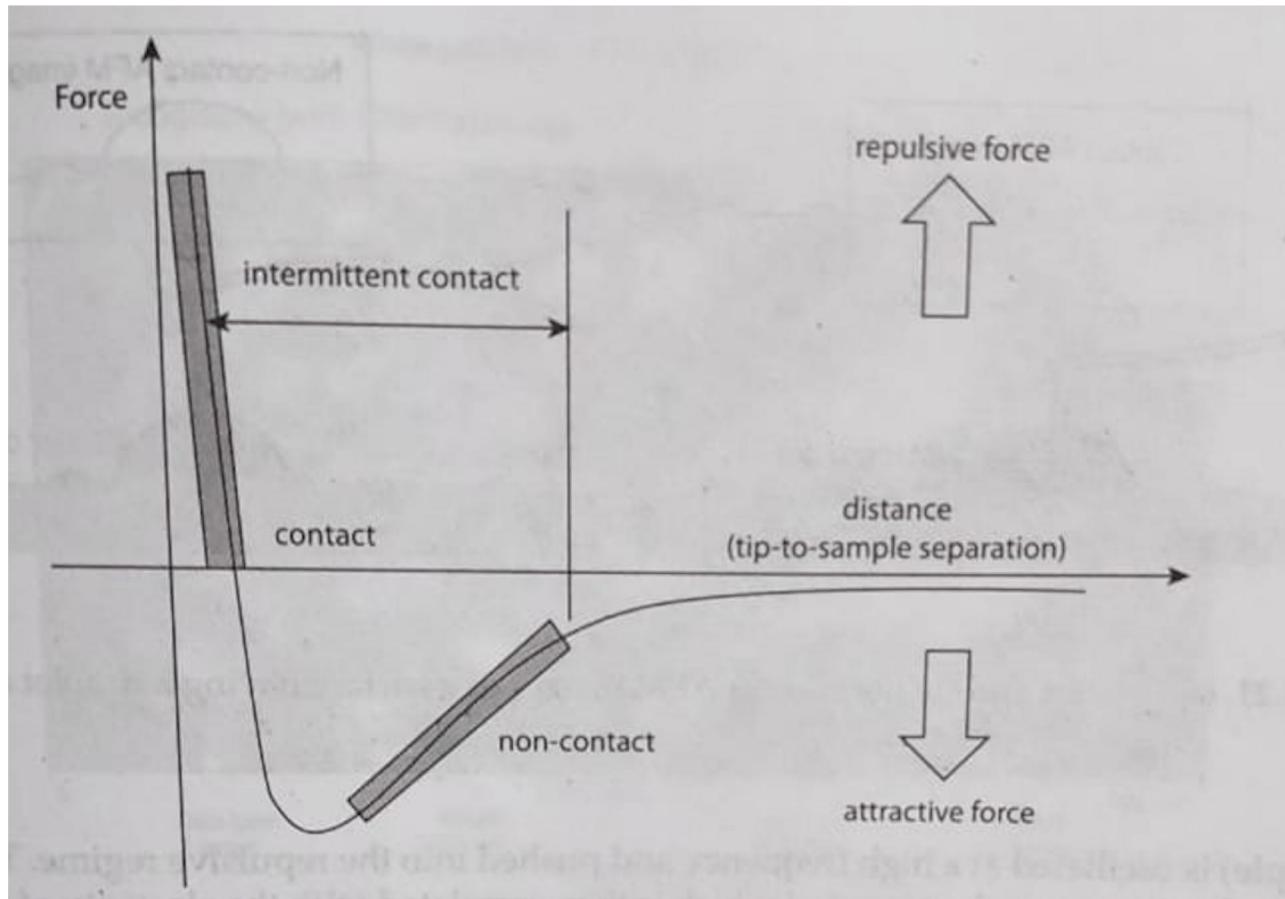


$$\Delta f = f_0 \frac{1}{2K} \frac{df}{dz}$$

$\Delta f$ :shift in frequency  
 $df$ : gradient of force

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## Contact and noncontact modes for surface imaging of AFM



## **(b) Tapping mode**

The cantilever is driven to oscillate up and down at or near its resonance frequency by a small piezoelectric element.

The amplitude of oscillation is typically 100-200 nm.

The forces acting on the cantilever causes the amplitude to decrease.

A piezoelectric actuator controls the height of the lever above the sample.

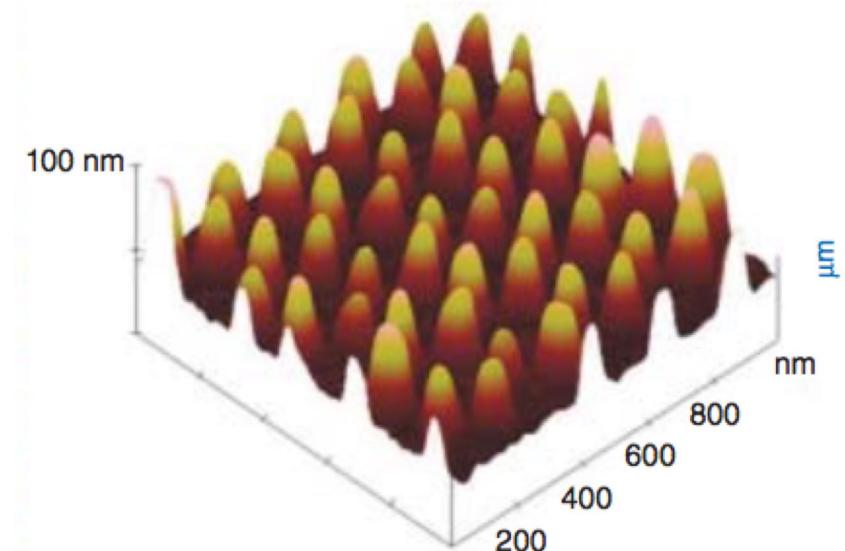
∴ A tapping AFM image is produced by imaging the force of the contacts of the tip with the sample surface.

In both contact & non-contact modes, it is possible to scan at constant height and plot force or the frequency shift as a function of x and y.

## Applications of AFM

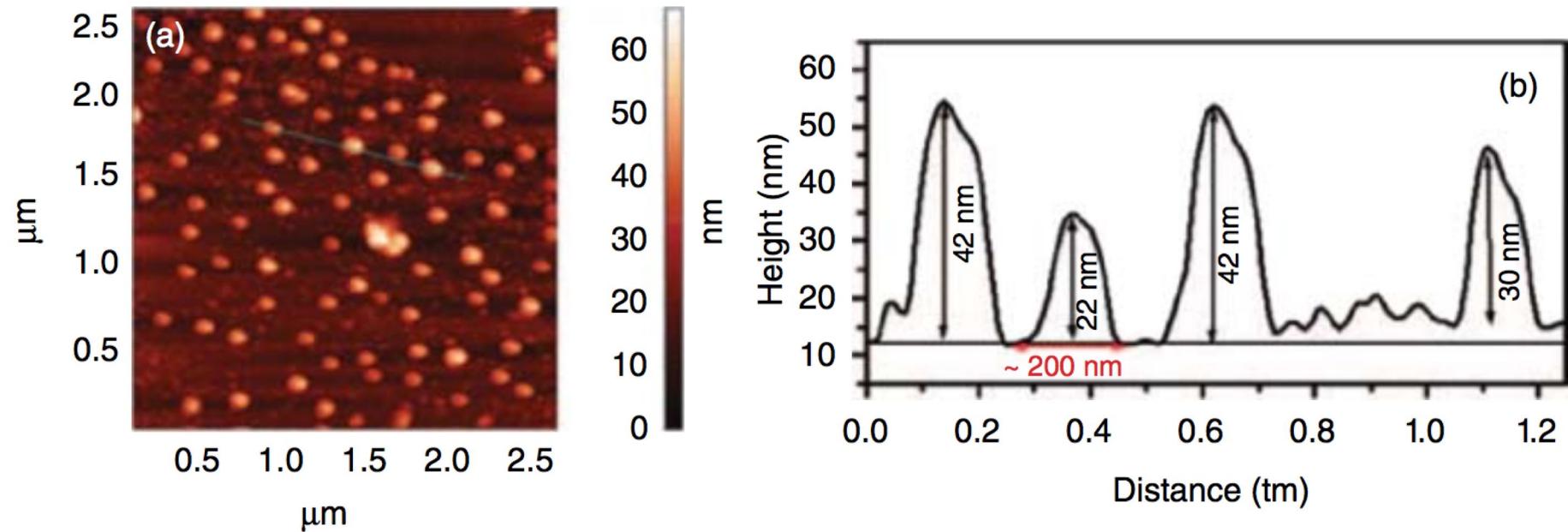
### Qualitative analysis:

- Resolution in the vertical z-axis is < 0.1 nm and the x-y resolutions are around 1 nm.
- Individual and groups of particles can be resolved.
- The AFM can distinguish between different materials, providing spatial distribution information on composite materials.



AFM image showing Pt nanoparticles coated with Si nanopillars

## Quantitative analysis:



AFM image of graphene balls with height bar

# X-ray diffraction(XRD)

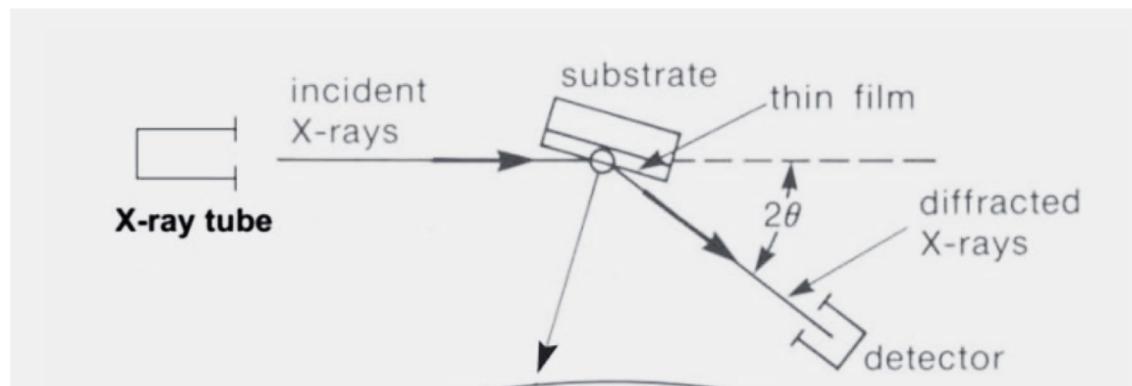
## X-ray diffraction(XRD)

- ❖ X-ray diffraction is an important experimental tool used in determining crystal structures of material systems in **bulk and nano-regimes**.
- ❖ It is a non-destructive technique and does not require detailed sample preparation.
- ❖ The wavelengths of X-ray ( $1-2 \text{ \AA}^\circ$ ) are in the same order as the size of nanostructures.
- ❖ Types of X-ray Diffractometers:
  1. X-ray thin film diffractometers
  2. X-ray powder diffractometers

## XRD diffractometer

It has three basic elements:

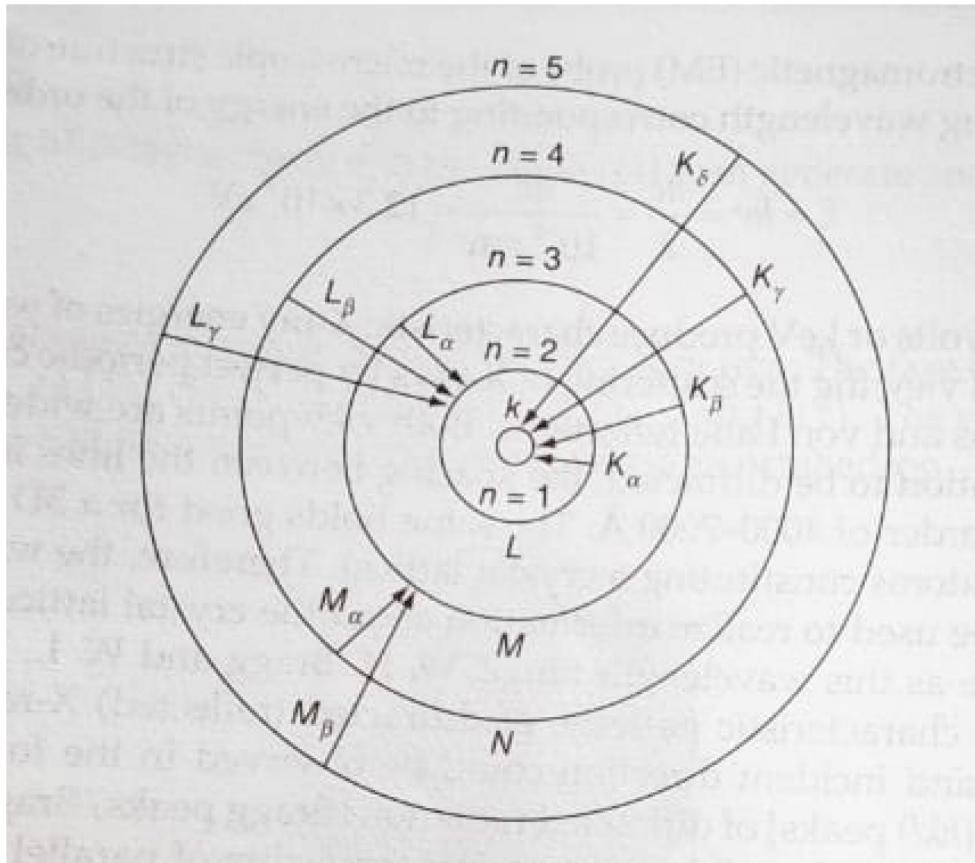
(a) X-ray tube. (b) Sample holder. ( c) X-ray detector



In X-ray tube, electrons are accelerated to a potential diff. of 20-40 kV.

The accelerated electrons impinge on a metal target.

## Production of several characteristic X-ray lines ( $K_{\alpha}, K_{\beta}, L_{\alpha} \dots$ )

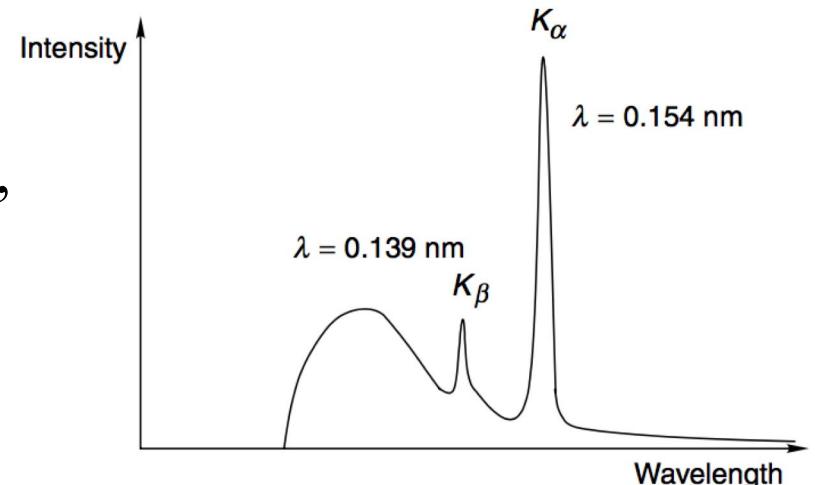


Xrays emitted by certain heavy elements consist of a continuous wavelength range known as **Bremsstrahlung or white radiation**

The minimum wavelength in the continuous wavelength spectrum is inversely proportional to the applied voltage.

## X-ray emission spectrum from copper

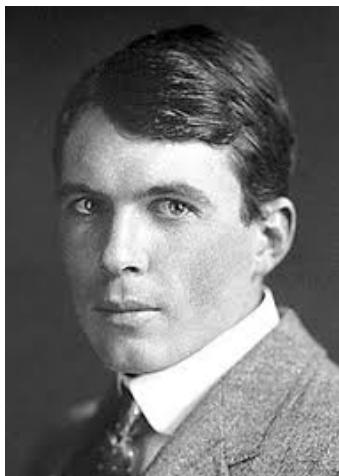
For high voltage, in addition to continuum, a characteristic radiation is also emitted.



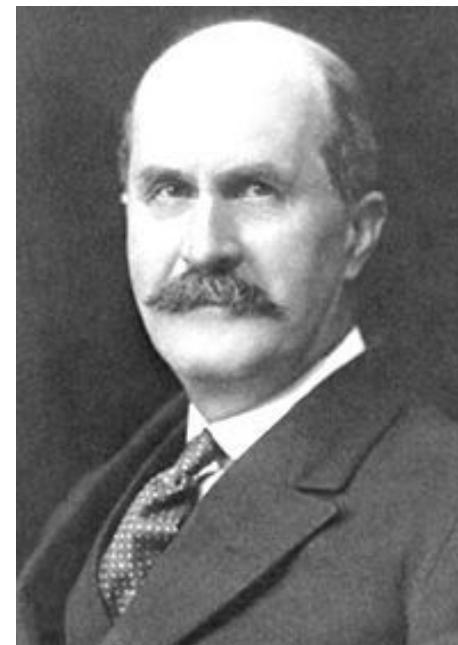
### Target metals and their characteristic $K_{\alpha}$ wavelengths

Target Metals	Characteristic $K_{\alpha}$ wavelengths				
	Mo	Cu	Co	Fe	Cr
$K_{\alpha}$ wavelength ( $\text{\AA}$ )	0.71	1.54	1.79	1.94	2.29

## Nobel Prize in Physics - 1915



**William Lawrence Bragg**



**Sir William Henry Bragg**

## Bragg's Law

For a sharp intense peak of the diffracted X-ray beam (**Bragg peak**) , there should be constructive interference between the diffracted rays originating from successive planes.

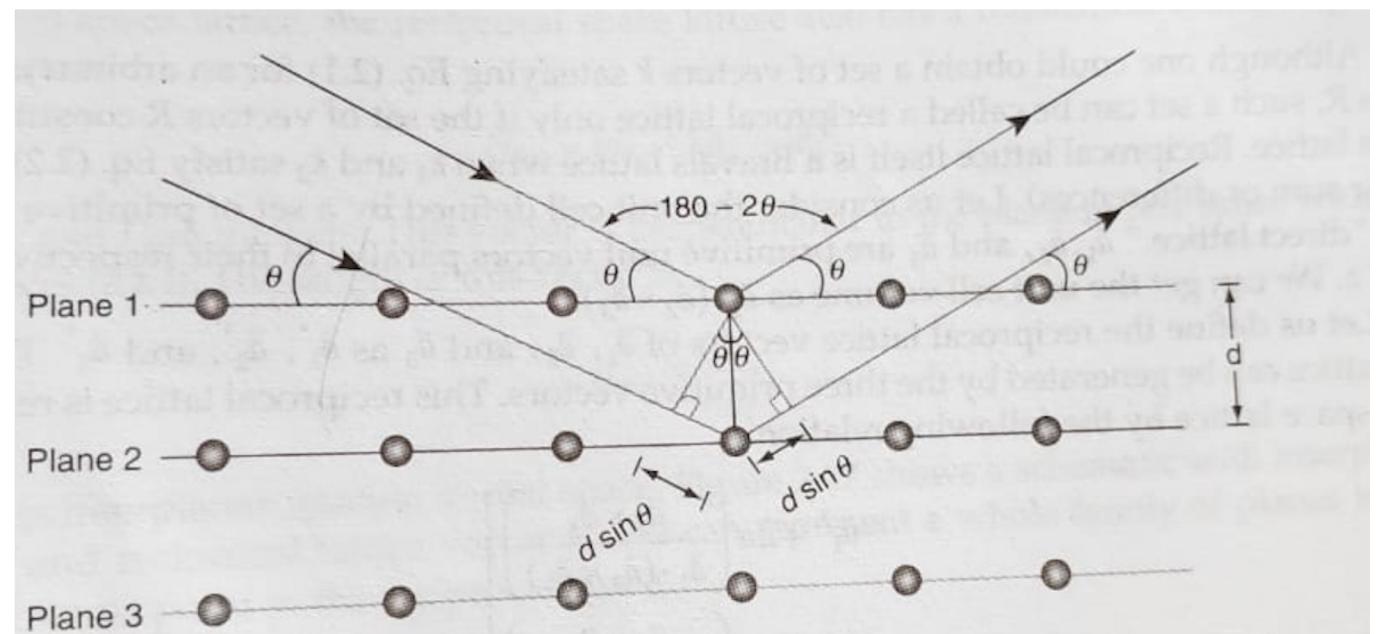
**“Bragg’s Law”**  
 $2d \sin\theta = n\lambda$

where,

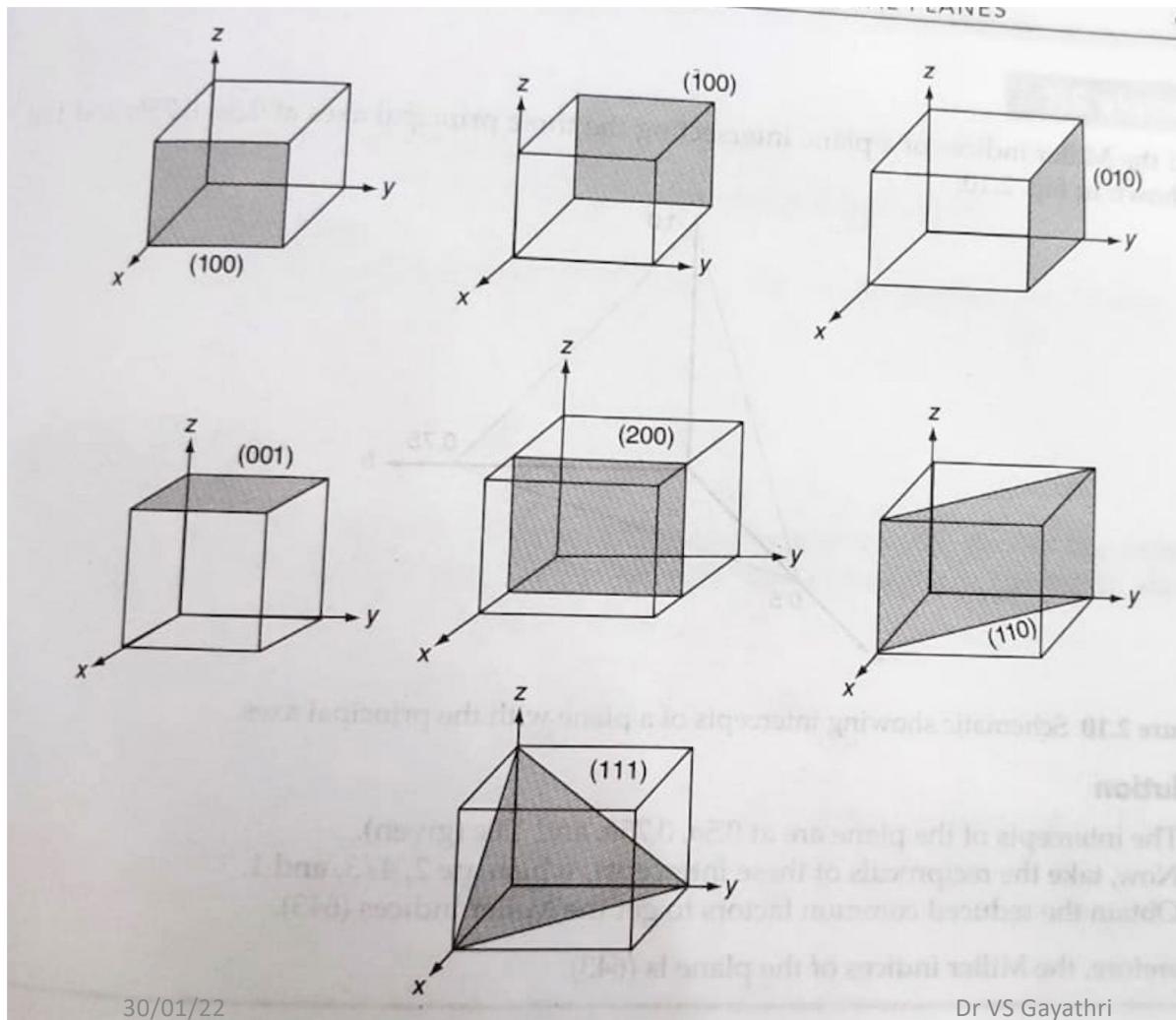
$\theta$  : angle of incidence.

n :order of reflection(integer)

d :spacing between planes



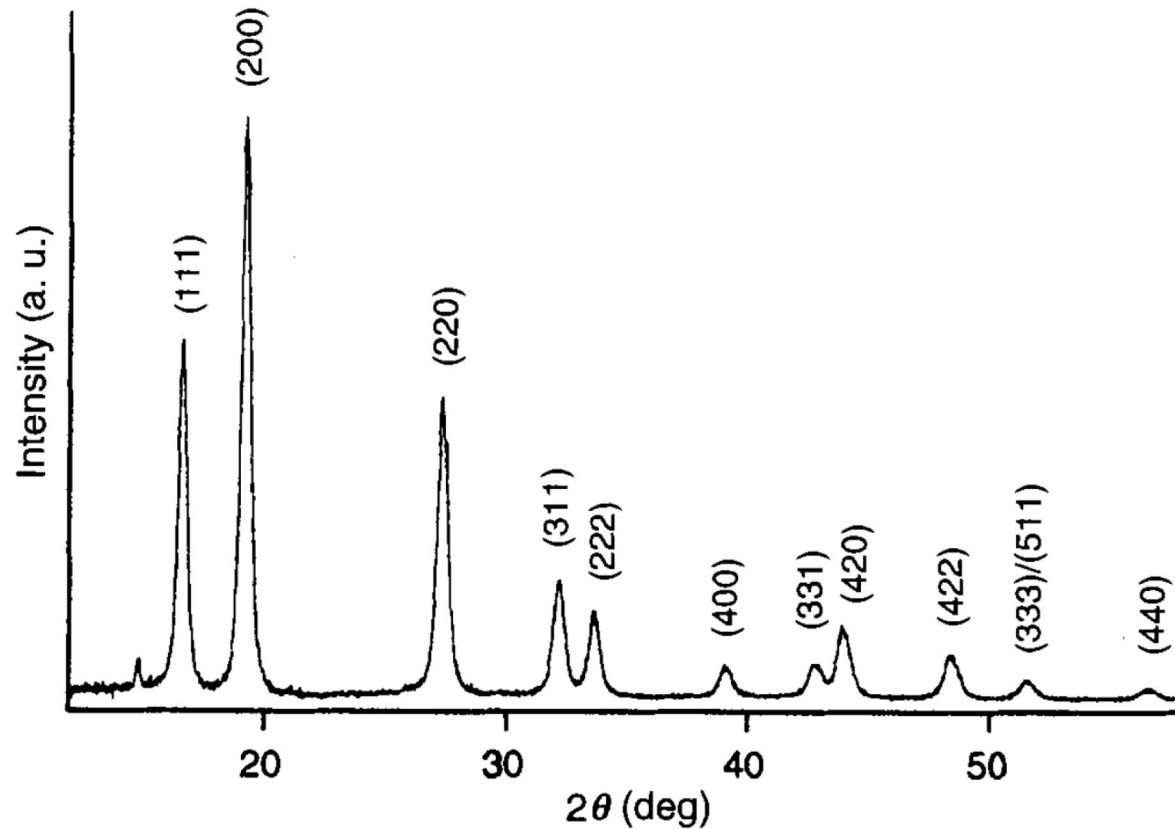
## Miller indices of some important planes in a cubic crystal



The distance between parallel crystallographic planes with indices  $hkl$  for a simple cubic lattice of lattice constant  $a$  has the form:

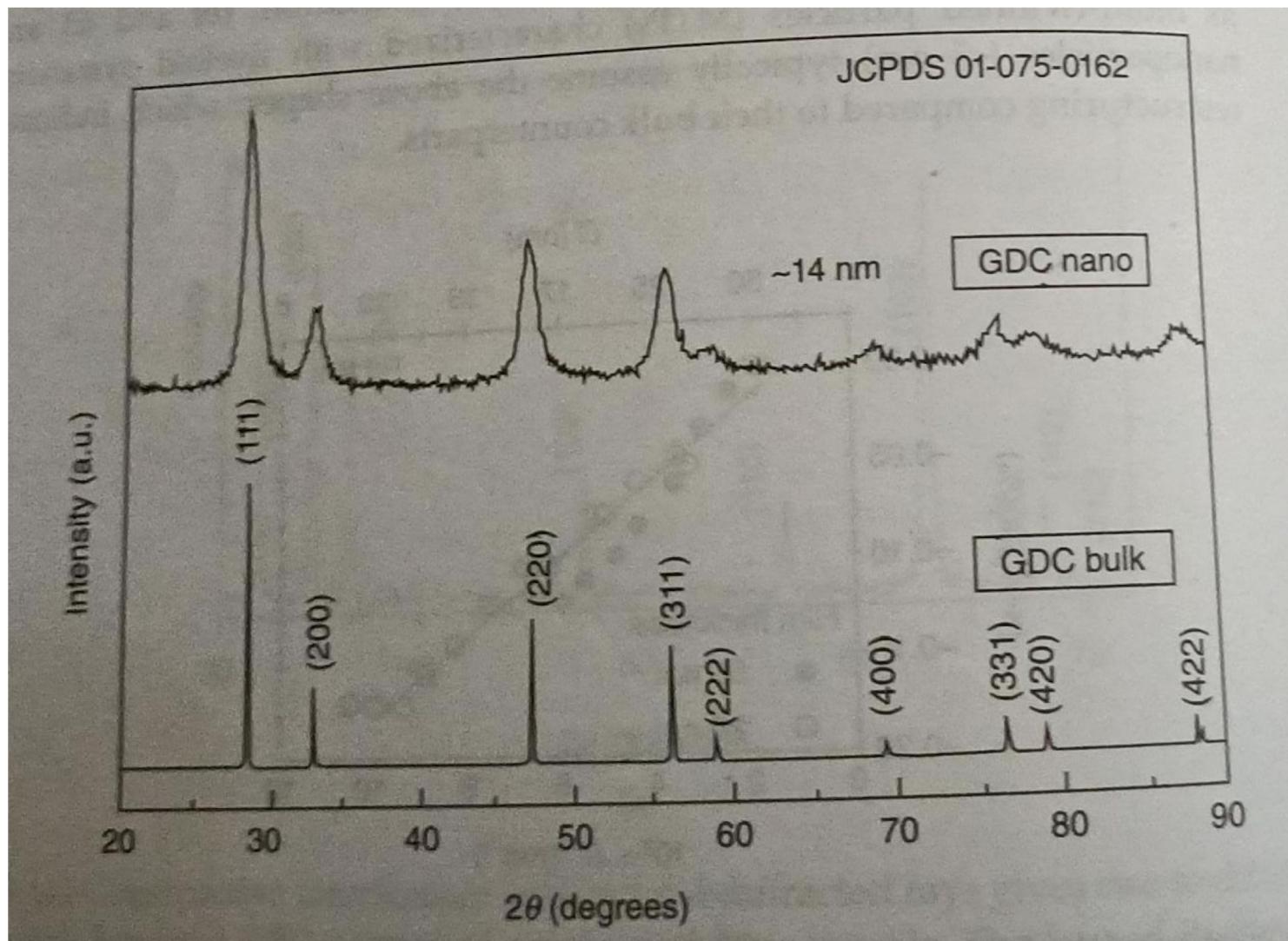
$$d_{hkl} = \frac{a}{(h^2+k^2+l^2)^{1/2}}$$

## X-ray diffraction scan of nanocrystalline TiN

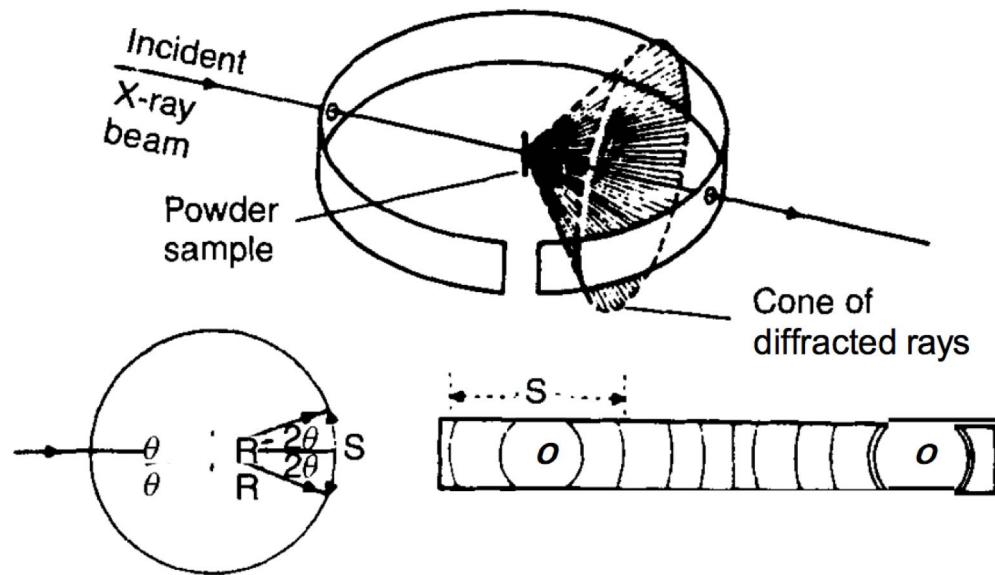


Labels are the  
crystallographic planes

## Diffraction pattern for nanoparticles of Gd-doped ceria



## Debye-Scherrer powder diffraction technique



- ❖ Widely used to obtain structures of powders of nanoparticles.

- ❖ This is an alternative approach for obtaining  $\theta$  that satisfy the Bragg condition in a powdered sample.
- ❖ Often this technique is used for sample identification.

## Debye-Scherrer powder diffraction technique

- ❖ Employs a monochromatic X-ray beam incident on a powder sample.
- ❖ The conical pattern of X-rays emerging for each angle  $2\theta$  is incident on the film strip in arcs.

$$\diamond \text{ Bragg angle } \theta = \frac{S}{4R}$$

Where,

S: distance between two corresponding reflections on the film

R: radius of the film cylinder

- ❖ A single exposure of the powder to the X-ray beam provides all the Bragg angles at the same time.

## Determination of Crystal size: The Scherrer equation

- The *Scherrer equation*, in X-ray diffraction is a formula that relates the crystal size to the broadening of a peak in a diffraction pattern.
- It is named after *Paul Scherrer*.
- It is used in the *determination of size of particles* of crystals in the form of powder.

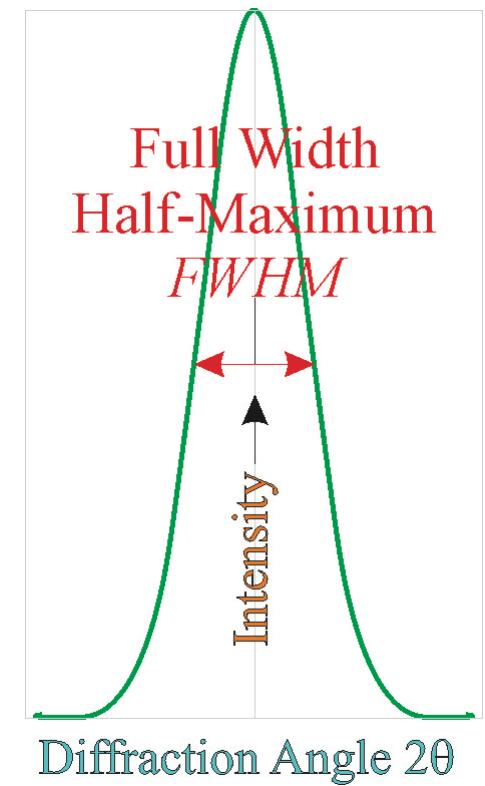
In the absence of inhomogeneous strains, the crystal size,  $D$ , can be estimated from the peak broadening using Scherrer's formula :

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

where,

- $\lambda$  is the wavelength
- $D$  is average crystalline size
- $B$  is the line broadening of diffraction peak measured at FWHM (in radians).

Full Width at Half-Maximum (FWHM) is typically used as a measure of the broadening of peak.



- The Scherrer's formula is used for the determination of grain size from broadened peaks.
- This works best for Gaussian line profiles.
- The formula is not expected to be valid for very small grain sizes (<10 nm). At very large grain sizes also the accuracy of the method suffers (as the broadening is small).
- Instrumental broadening has to be subtracted first.