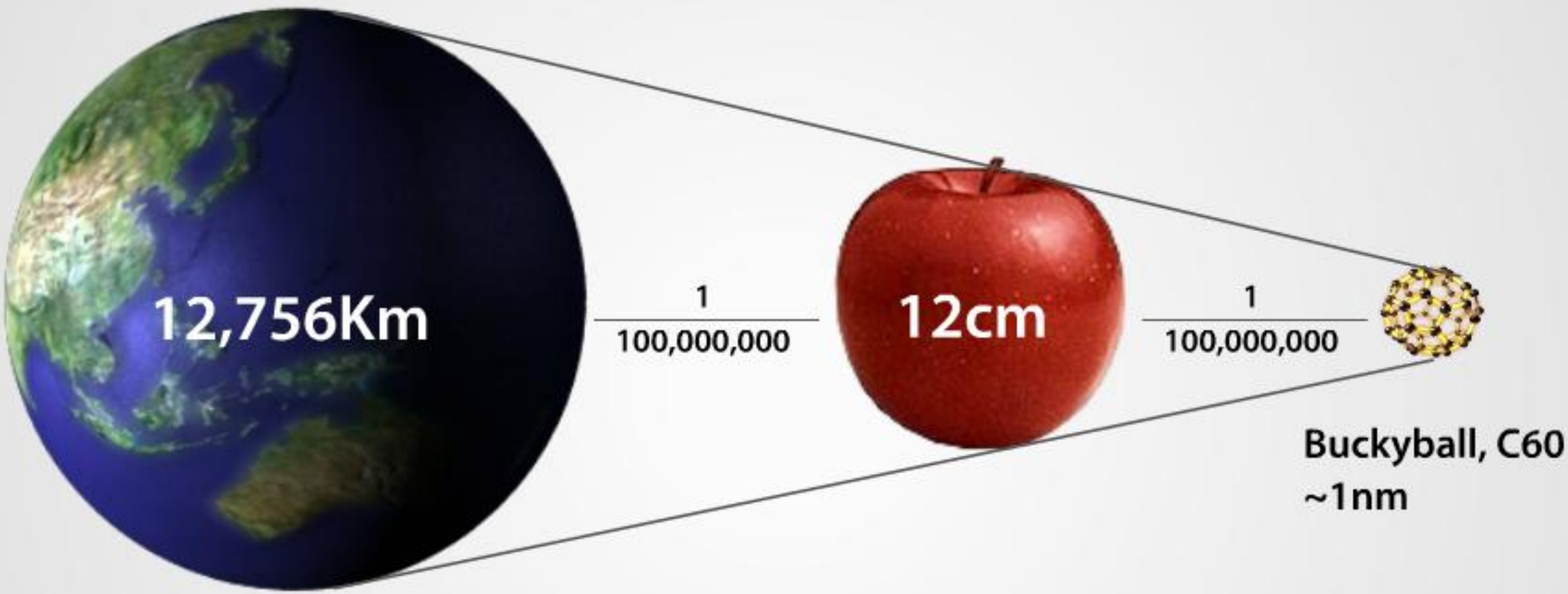
The versatile tools in surface and inner morphology characterization and manipulation : TEM, SEM & AFM

_____Abu Zafar Al Munsur



www.parksystems.com

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History of Microscopy

Human eye cells

Paint on concrete

Mikros (small) + Skopeo (look at)

Greek Origin

Historic Figures in Microscopy

Antony van Leeuwenhoek
(1632-1723)

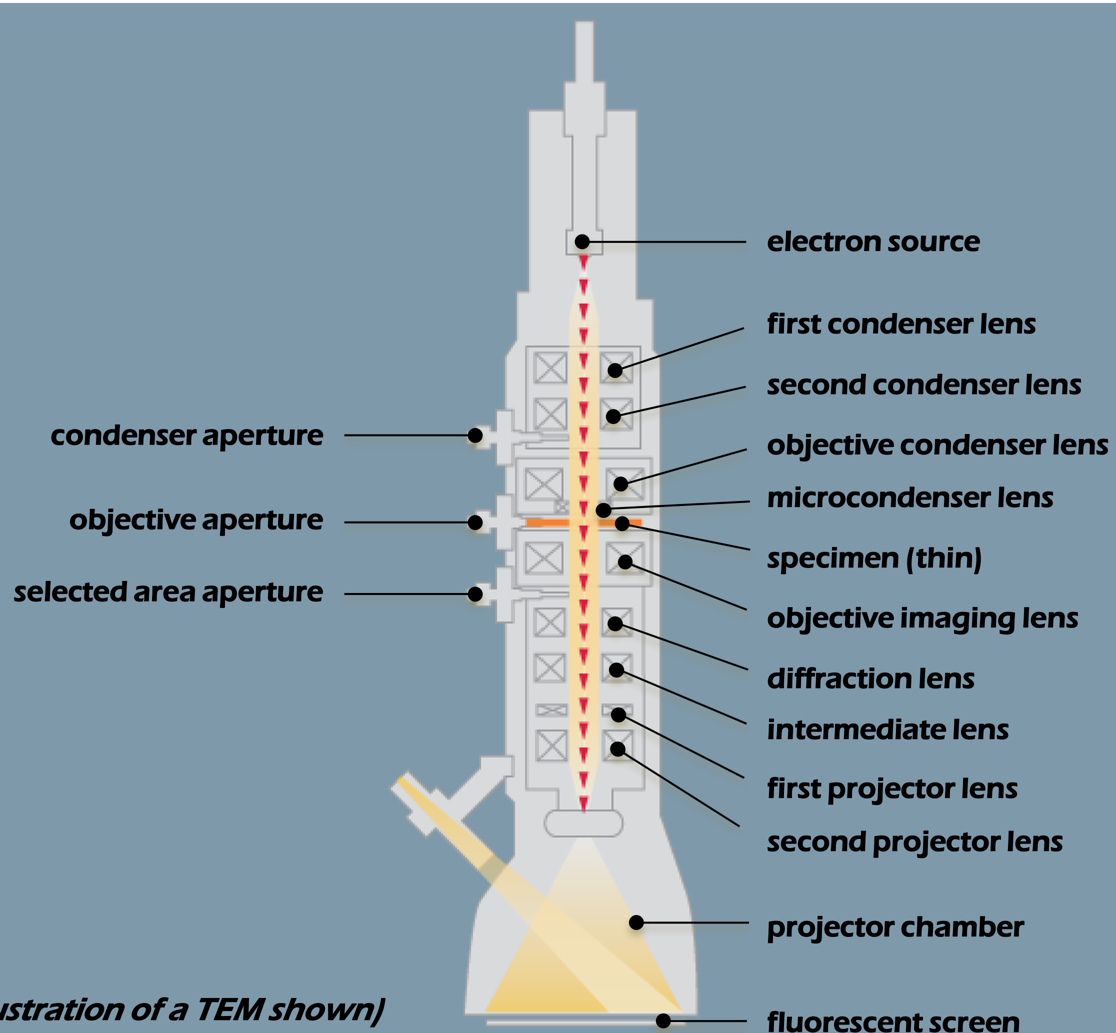
Robert Hooke
(1635-1703)

Ernst Abbe
(1840-1905)

Ernst Ruska
(1906-1988)

Richard Feynman
(1918-1988)

Basic Microscope Classifications



(Illustration of a TEM shown)

Charged particle microscope

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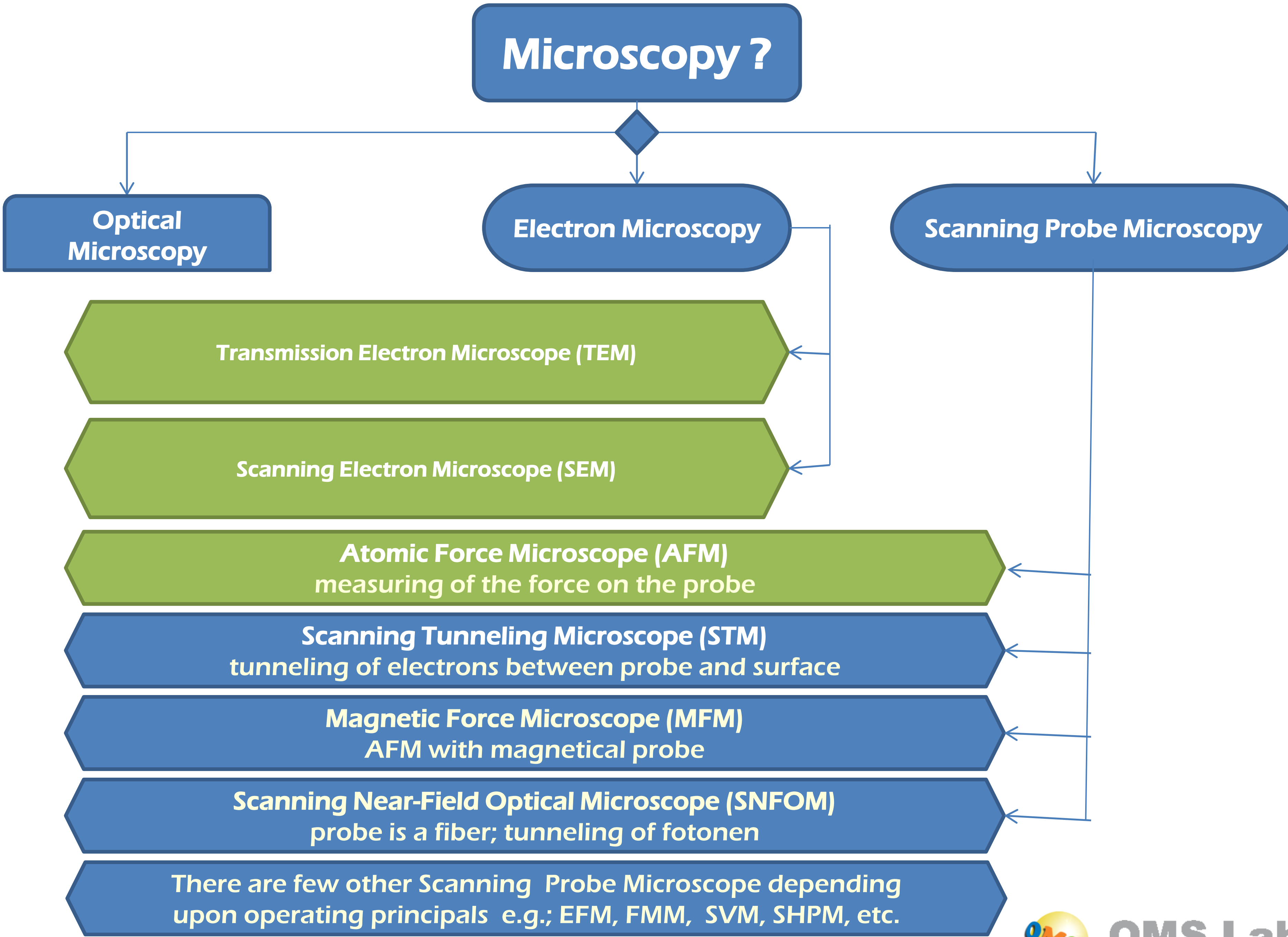

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KEY CONCEPTS IN MICROSCOPY

- What is resolution and resolving power?
- What is an electron?
  - The electron gun
- Electromagnetic lenses
- The importance of vacuum technology

KEY CONCEPT: Resolution

Resolution

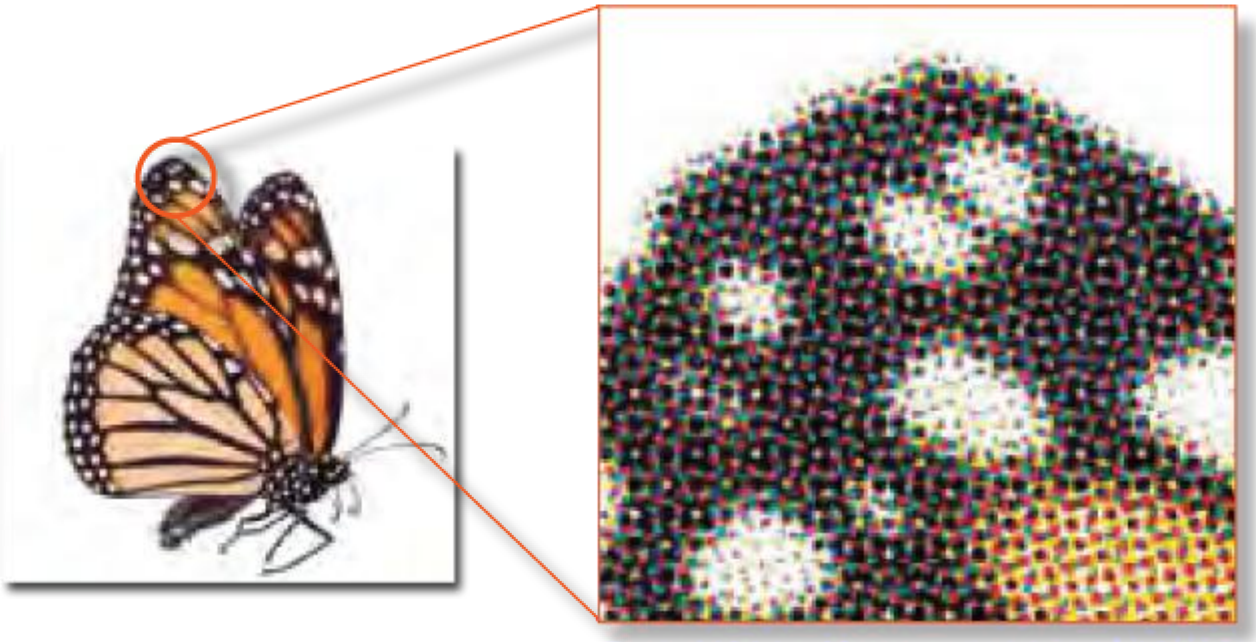
is defined as the act, process, or capability of distinguis hing between two separate, but adjacent objects or sou rces of light, or between two nearly equal wavelengths.

Resolving Power

is the ability to make points or lines which are closely adjacent in an object distinguishable in an image.

Resolving Power of the Human Eye

What can we see?



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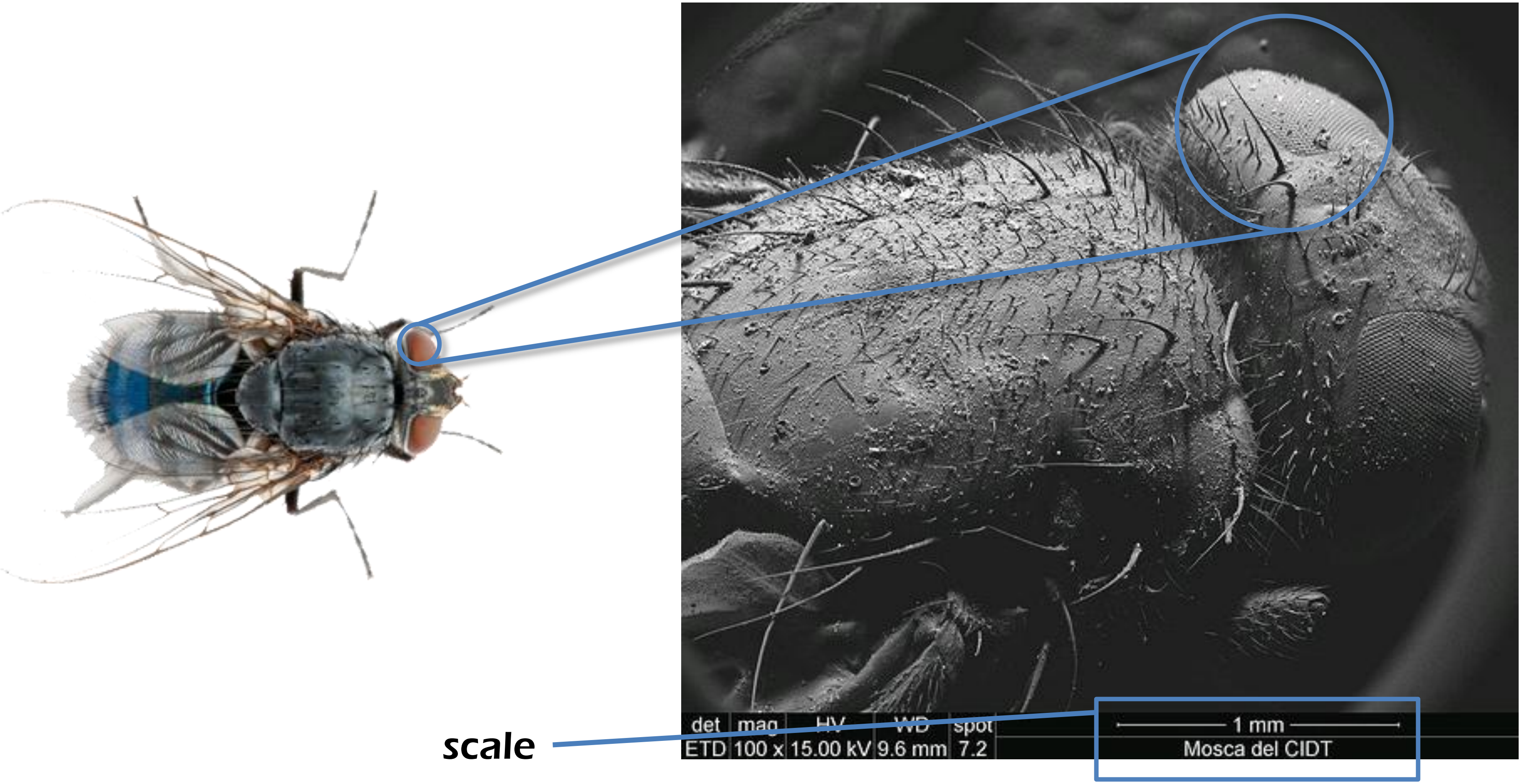
Resolution & Magnification



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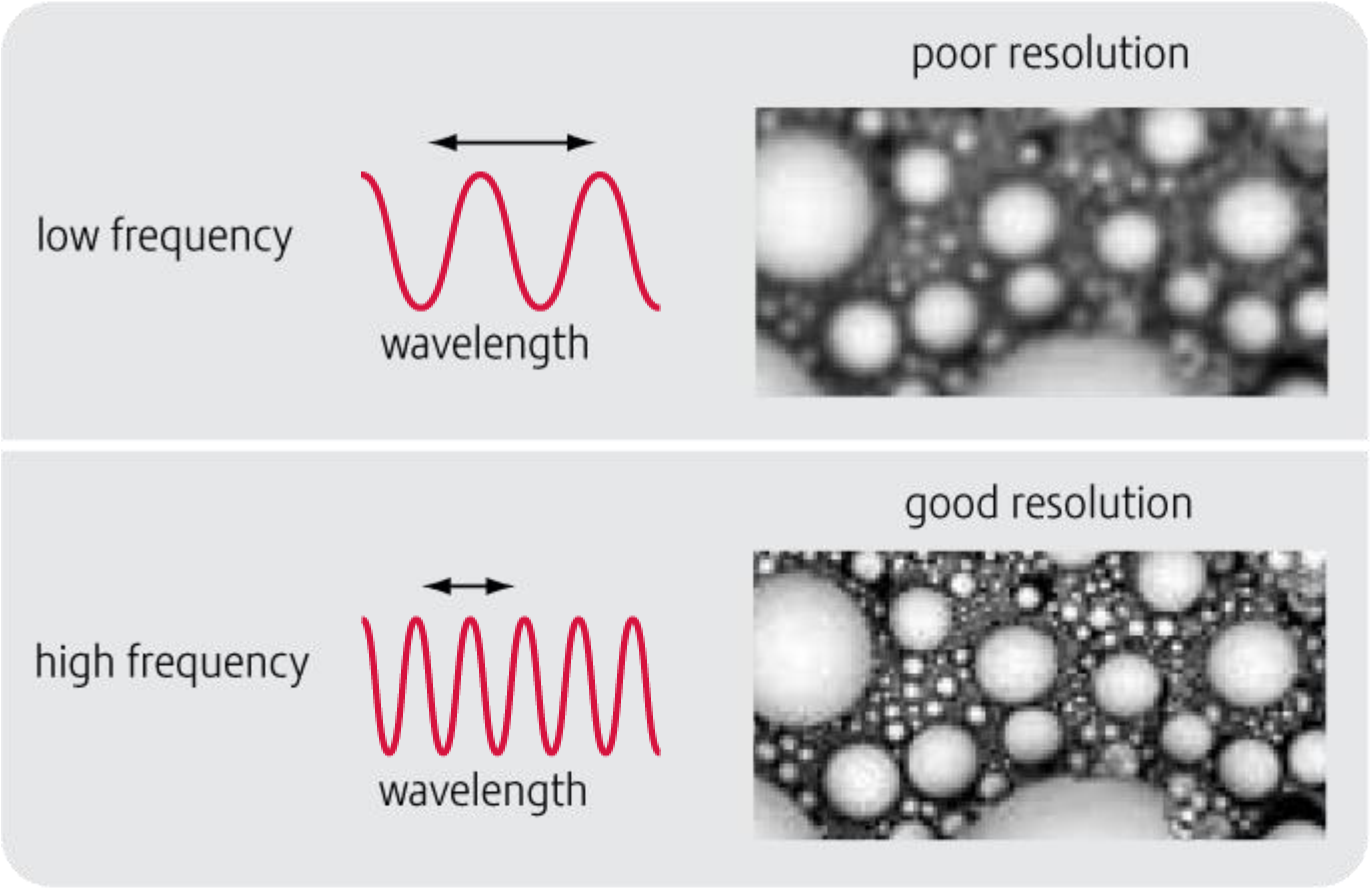
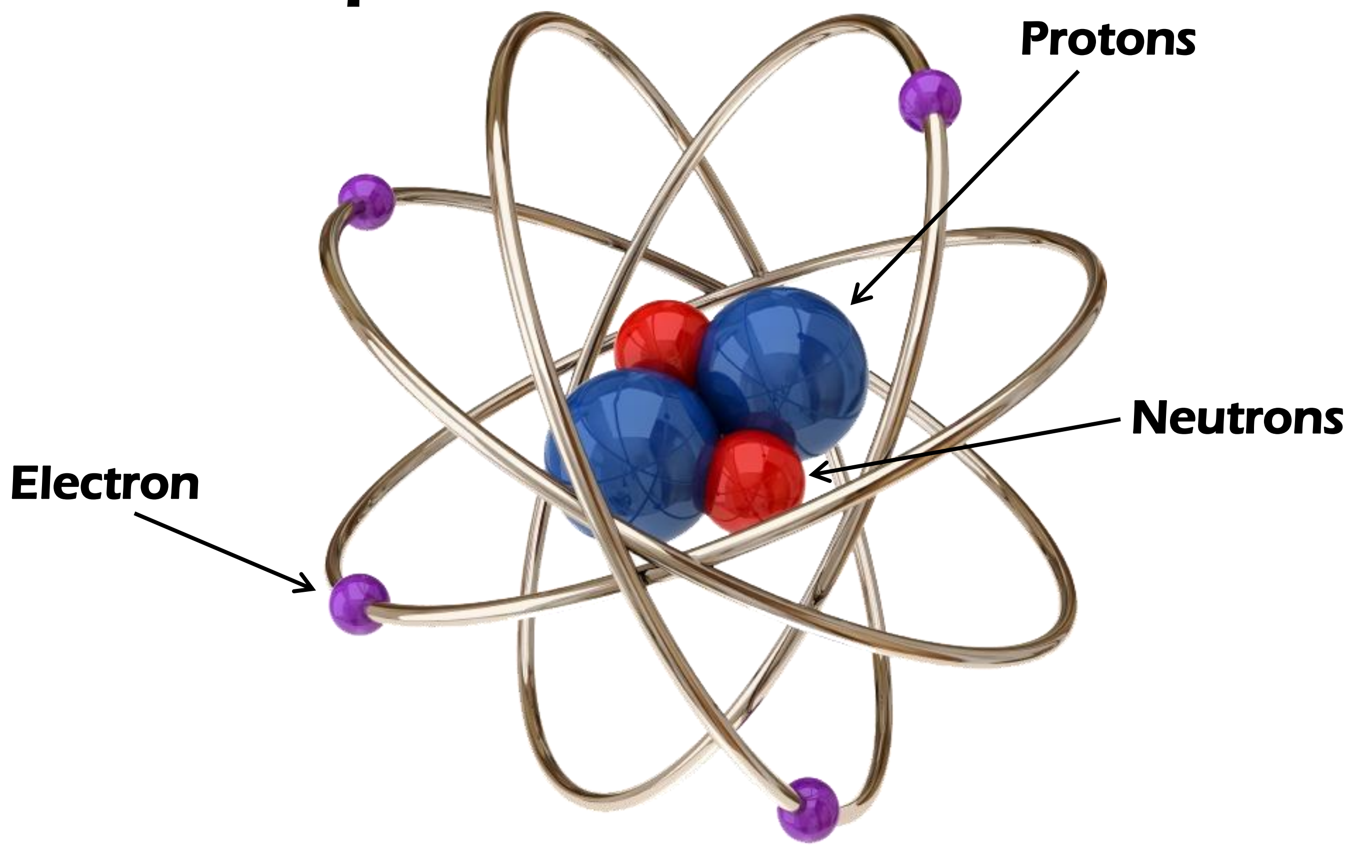
How is Resolution Affected by Wavelength?



KEY CONCEPT: The Electron

An atom is made up of:



Motivation for EM

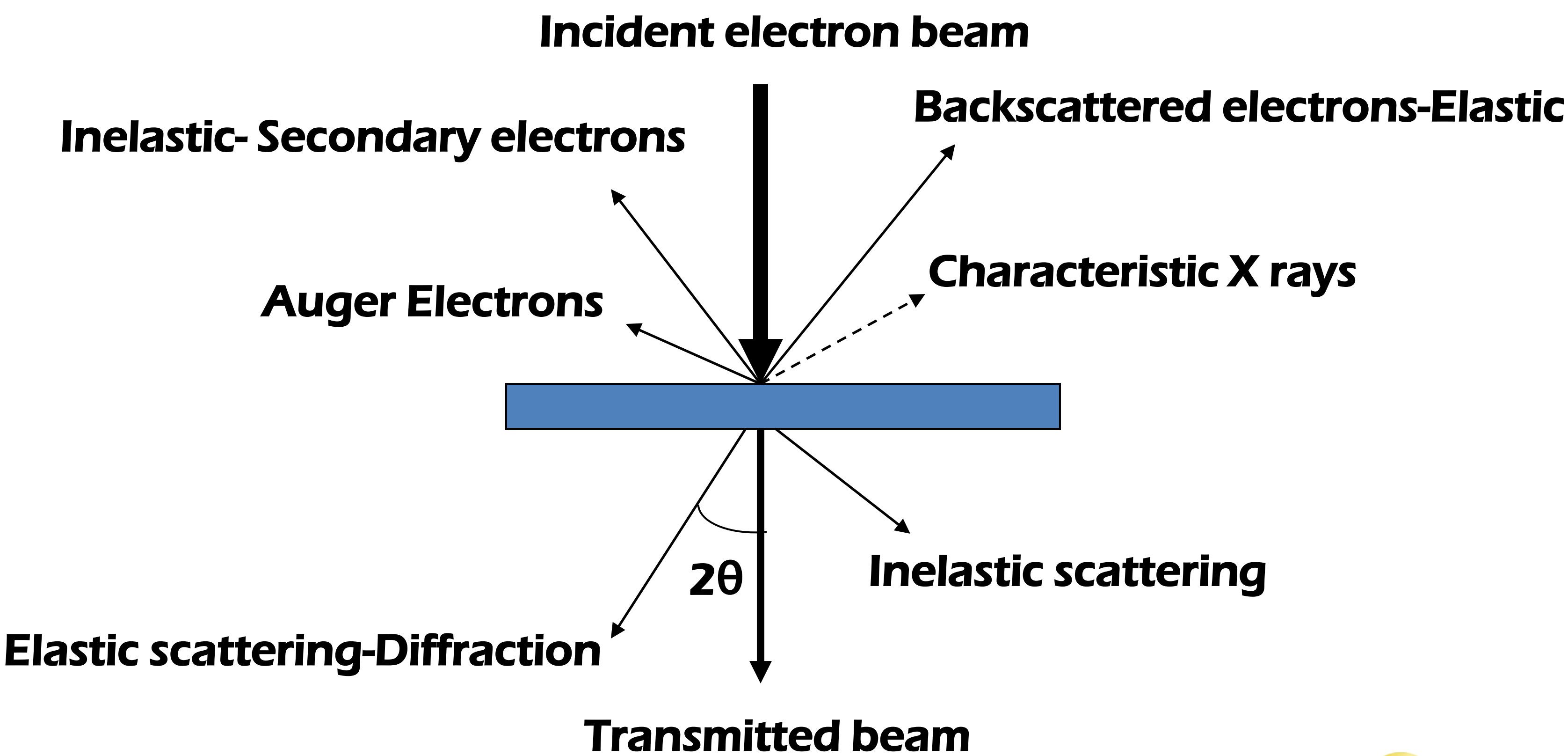
- Resolution of light microscope is limited:
  wavelength of visible light, $\sin\theta = 1.22 * \lambda / D$
- less diffraction for smaller wavelengths
- possible magnification: ~ 2 000

- Different approach: use electrons instead of light

Access to much smaller wavelengths
  $\lambda = h/p$, (3.7 pm for 100 keV)
- Electrostatic/ electromagnetic lenses
  instead of glass lenses
- possible magnification: ~ 2 000 000

Interaction with matter

Why do we use electrons as probe?



Interaction with matter

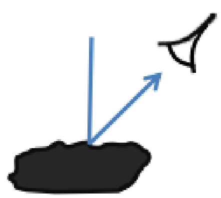
1. Easy to produce high brightness electron beams
   - ➢ High coherence beams allow us to generate diffraction patterns and high spatial resolution images
2. Easily manipulated
   - ➢ Electron lenses and deflectors can used to easily change focal lengths and beam directions which is a necessary operating condition for flexible imaging devices
3. High energy electrons have a short wavelength
   - ➢ Shorter wavelengths means higher spatial resolution (Raleigh Criterion)
4. Electrons interact strongly with matter
   - ➢ Secondary signals have information specific to the material
   - ➢ Bragg diffracted electrons –structure, orientation, phase distribution, defect content and structures, etc.

Interaction with matter

Backscattered electrons	→	**Topography and**
Secondary electrons	→	**composition**
Auger electrons		**Topography**
Transmitted electrons	→	
X-Rays	→	**Structure and composition**
phonons		**Composition**

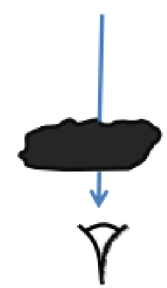
2 different approaches:

Backscattered and secondary electrons



SEM

Transmitted electrons



TEM

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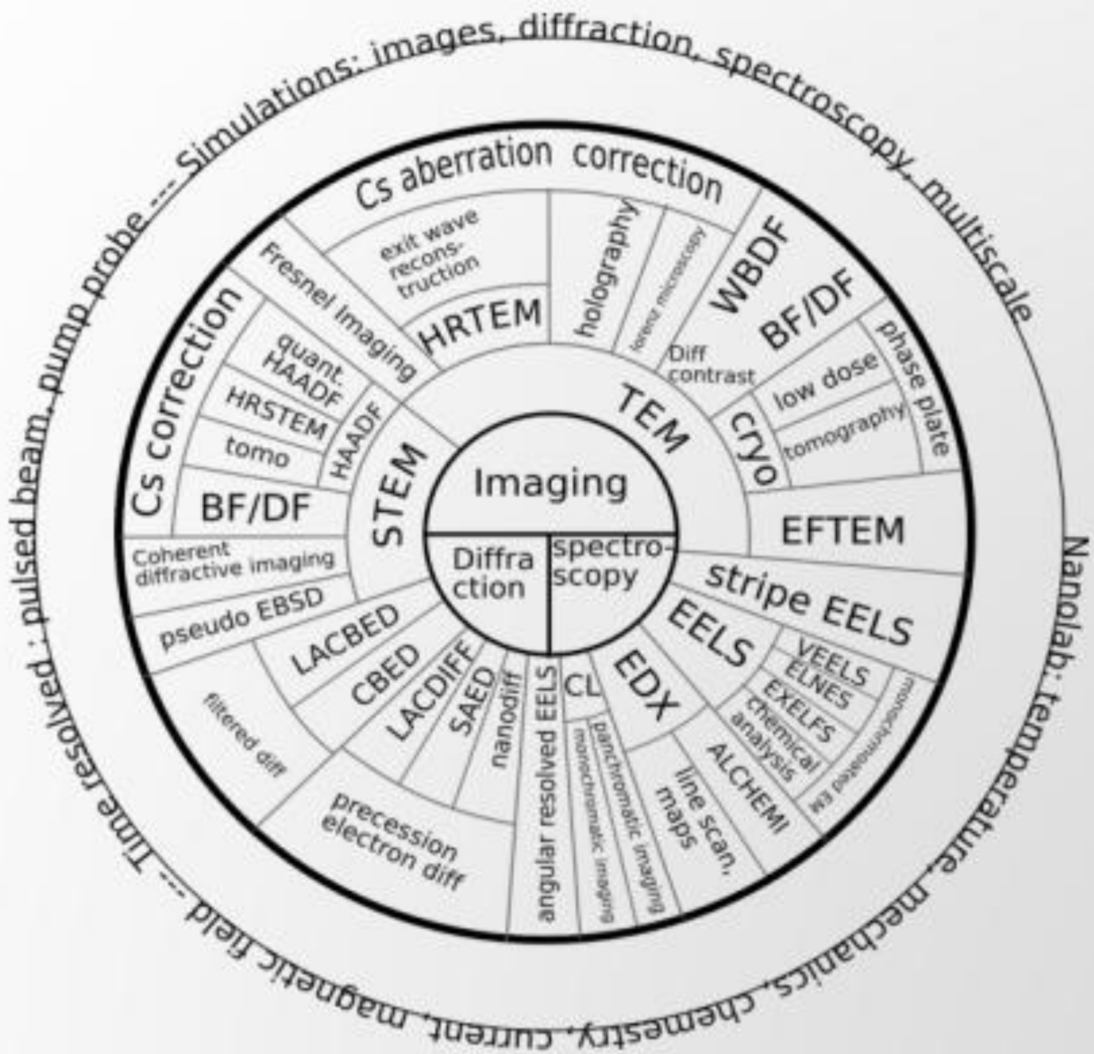
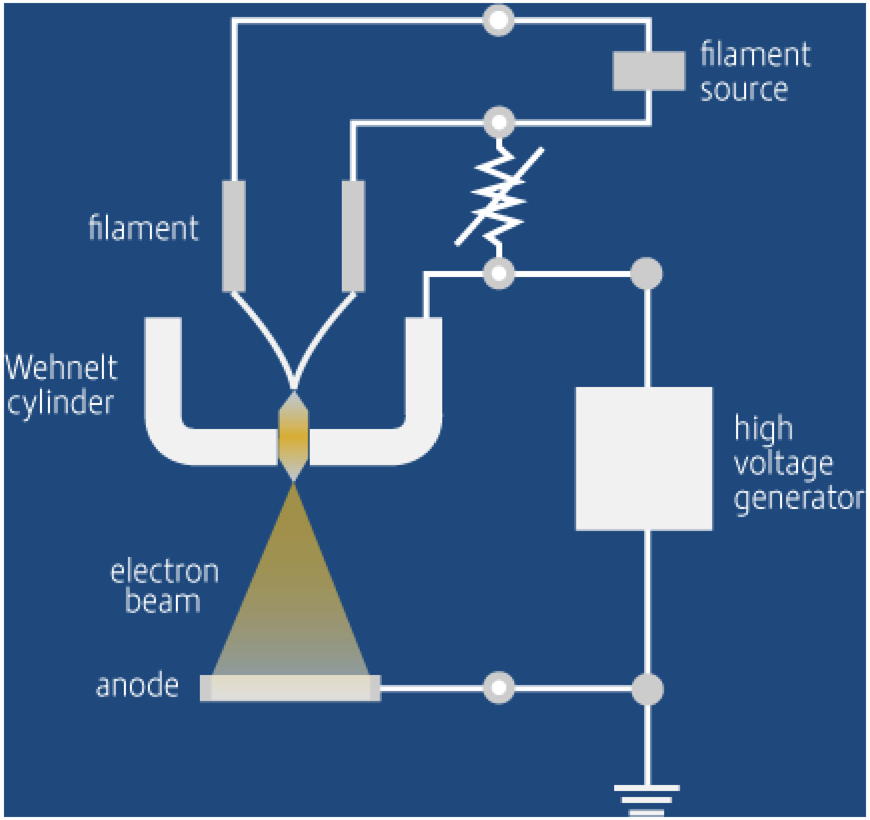
TEM imaging modes



thomas.lagrange@epfl.ch • www.epfl.ch• cime.epfl.ch• +41 (0)21 6934430

CORE TECHNOLOGY: The Electron Gun

- Three main sources of electrons:
  - Tungsten
  - LaB_6 (lanthanum hexaboride)
  - Field Emission Gun (FEG)
- Different costs and benefits of each
- Each selected primarily for their brightness



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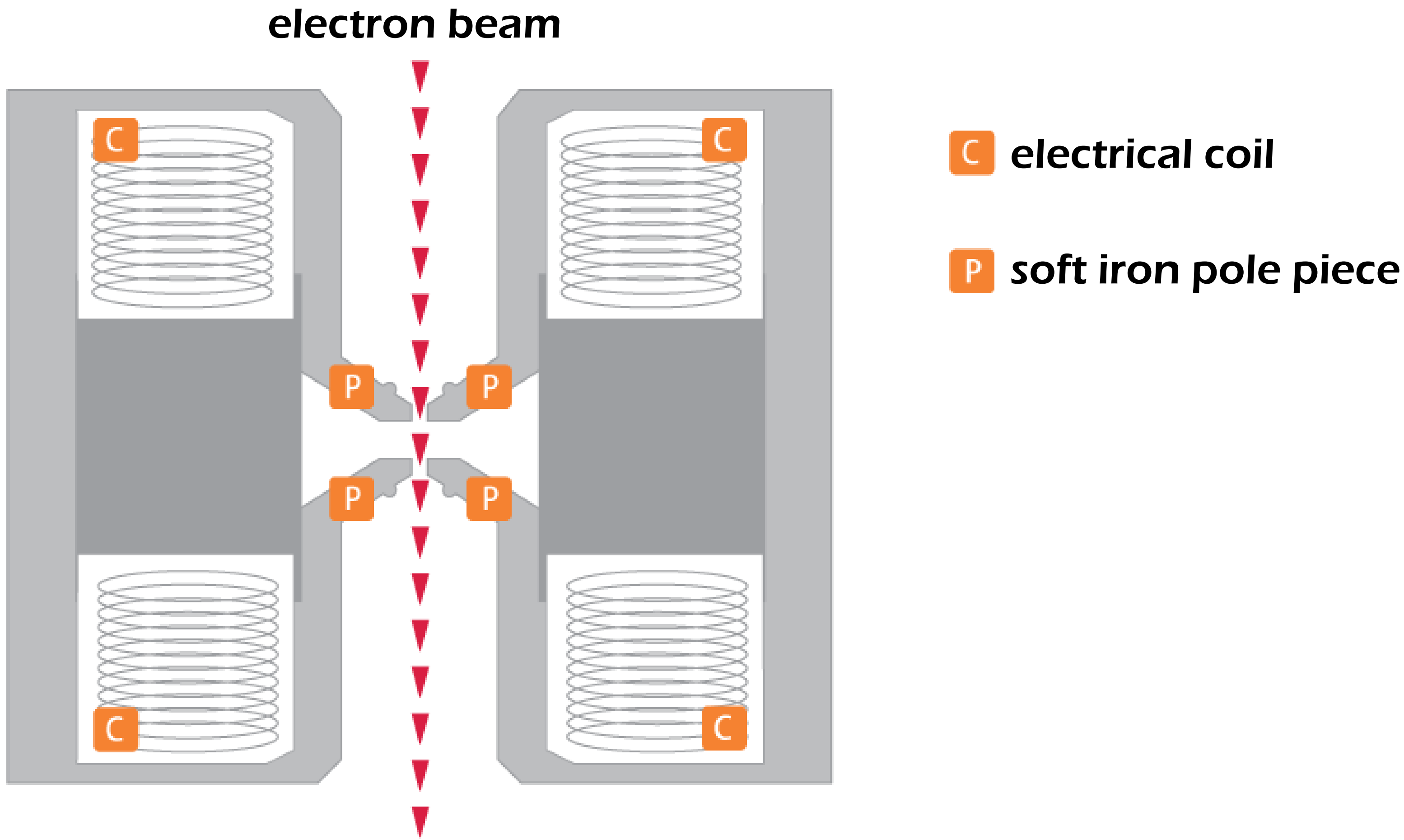
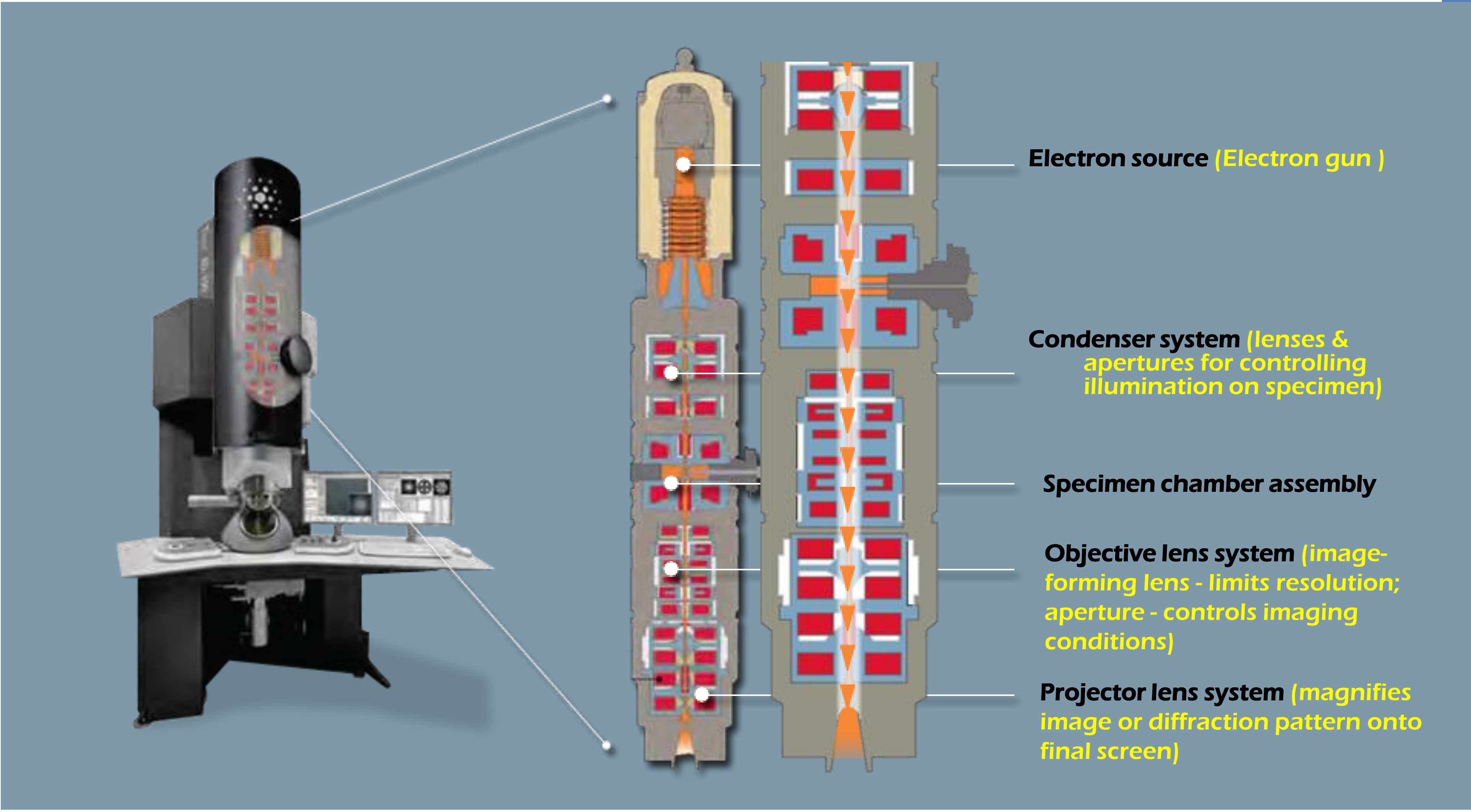
CORE TECHNOLOGY: Electromagnetic Lenses



CORE TECHNOLOGY: The Vacuum

- Mean free path of electron in air is short.
- Tungsten filament burn out in air.
- A vacuum is a region of reduced gas pressure.
- Electron microscopes use a vacuum to make electrons behave like light.

What is a Transmission Electron Microscope?



TEM is based on three possible set of techniqes

Diffraction

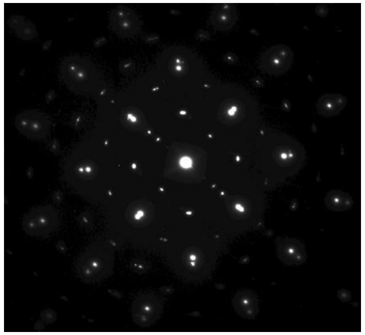
From regions down to a few nm (CBED).

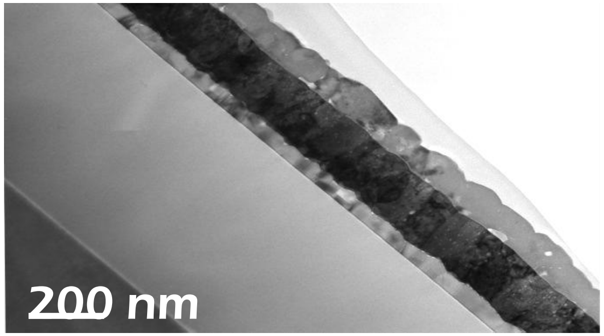
Imaging

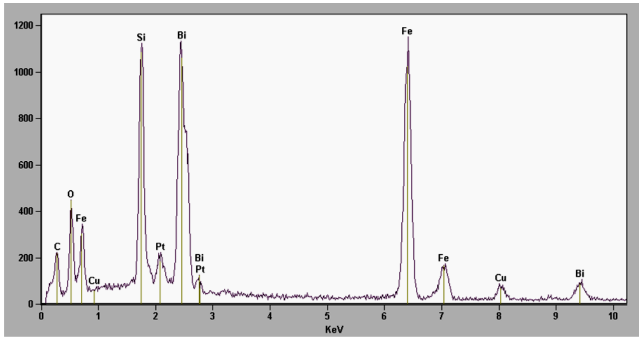
With spatial resolution down to the atomic level (HREM and STEM)

Spectroscopy

Chemistry and elecronic states (EDS and EELS). Spatial and energy resolution down to the atomic level and ~0.1 eV.







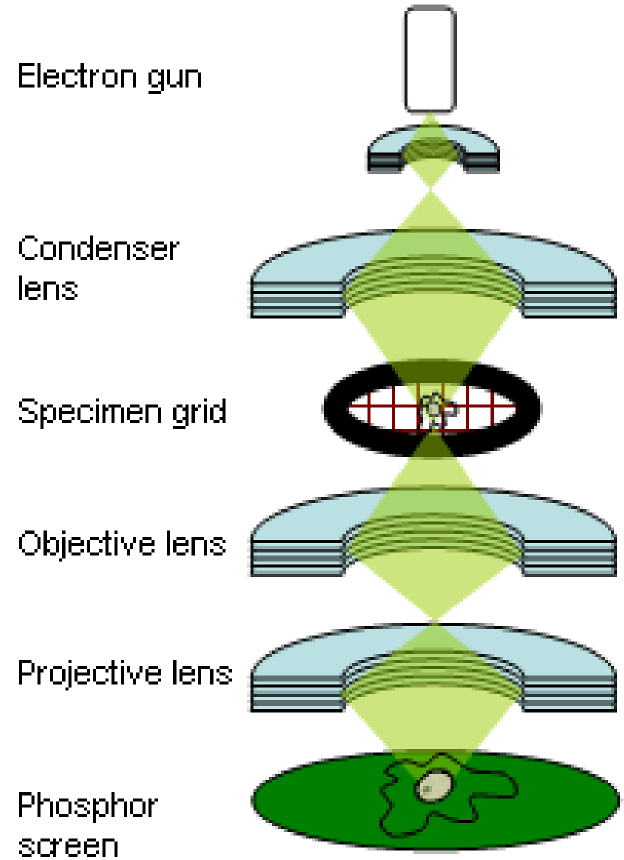
Analytical Transmissions Electron Microscopy (TEM)

- **Basic principles**
- **Operational modes**
  - **Diffraction**
  - **Imaging**
- **Sample preparation**
- **Spectroscopy**

http://www.matter.org.uk/tem/default.htm

Transmission Electron Microscope (TEM) Working Concept

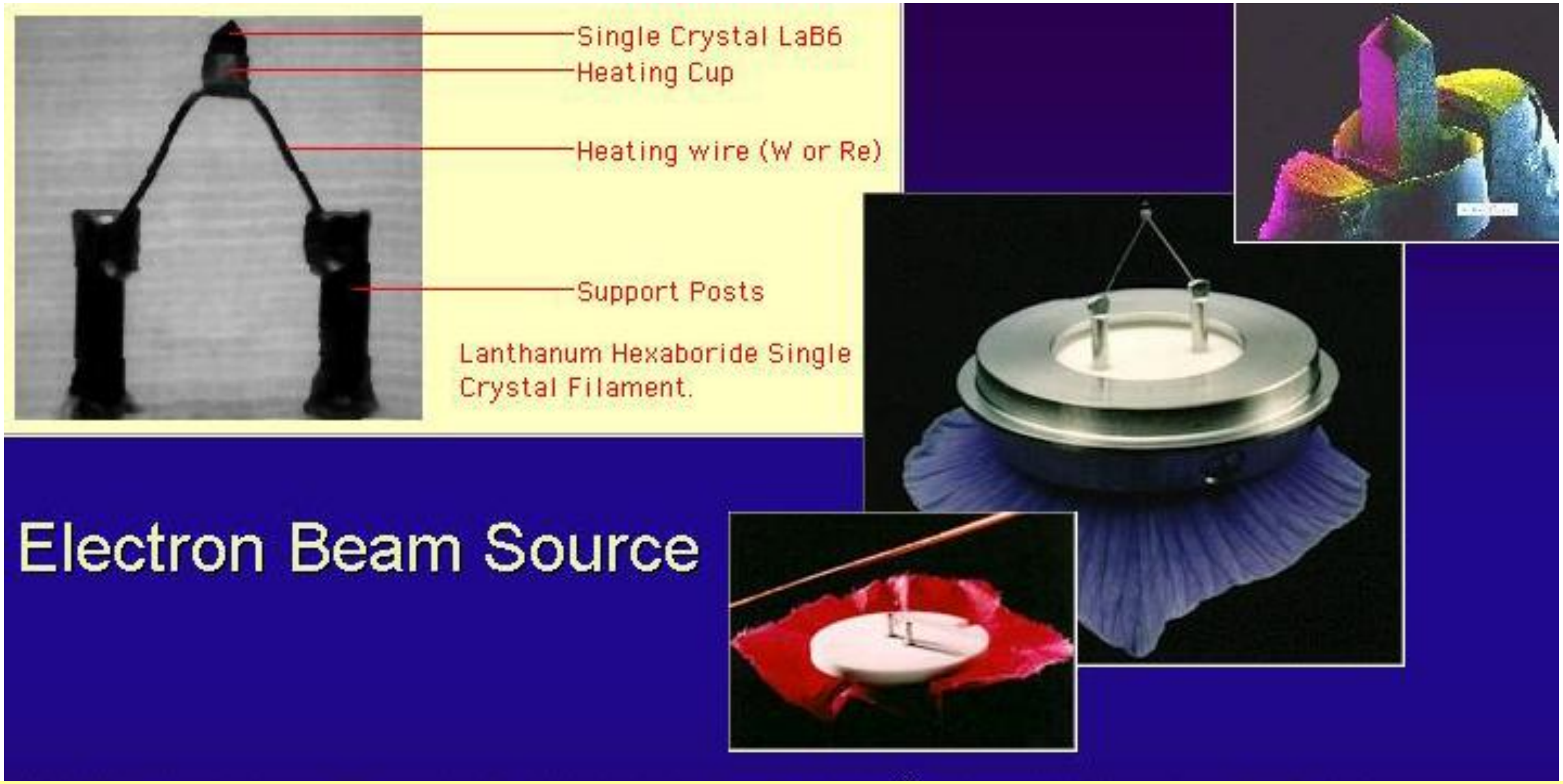
✓Works like a slide projector.
✓A projector shines a beam of light through (transmits) the slide, as the light passes through it is affected by the structures and objects on the slide.
✓These effects result in only certain parts of the light beam being transmitted through certain parts of the slide.
✓This transmitted beam is then projected onto the viewing screen, forming an enlarged image of the slide.
✓TEMs work the same way except that they shine a beam of electrons (like the light) through the specimen (like the slide)
✓Whatever part is transmitted is projected onto a phosphor screen for the user to see
✓A more technical explanation of typical TEMs workings is as follows



How an Electron Beam is Produced?

- Electron guns are used to produce a fine, controlled beam of electrons which are then focused at the specimen surface.
- The electron guns may either be thermionic gun or field-emission gun

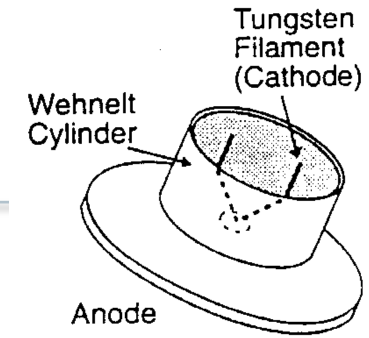
Electron beam Source



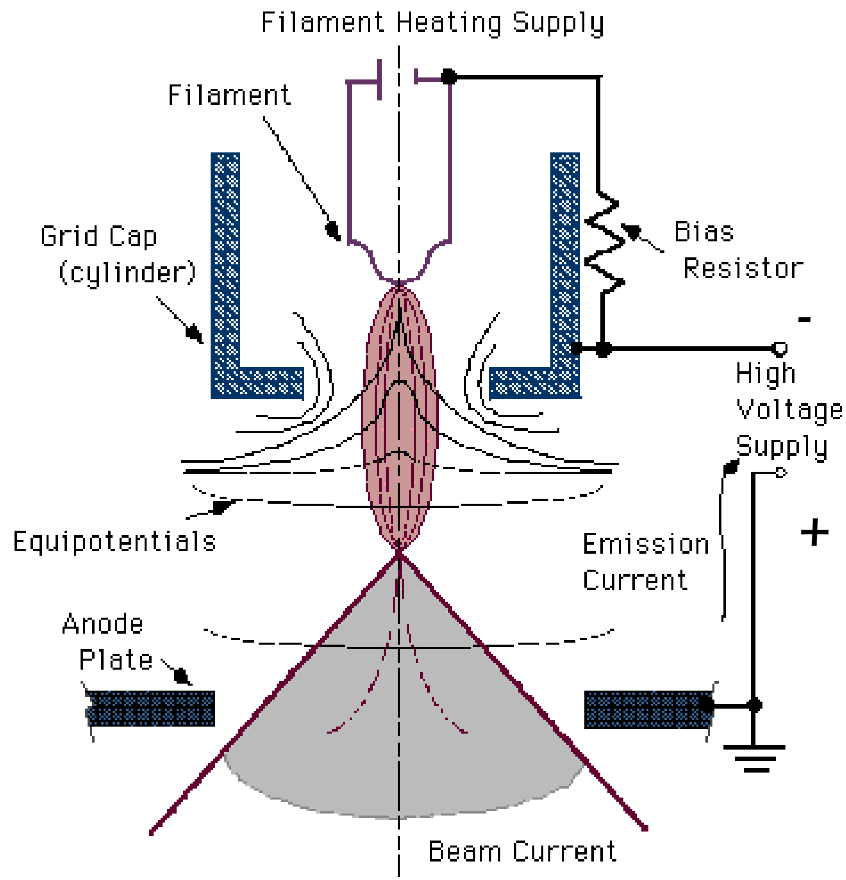
W or LaB_6 Filament

Thermionic or Field Emission Gun

Thermionic Emission Gun



- A tungsten filament heated by DC to approximately 2700K or LaB_6 rod heated to around 2000K
- A vacuum of 10^{-3} Pa (10^{-4} Pa for LaB_6) is needed to prevent oxidation of the filament
- Electrons "boil off" from the tip of the filament
- Electrons are accelerated by an acceleration voltage of 1-50kV



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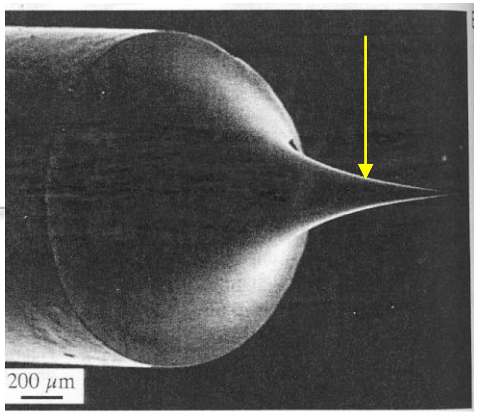
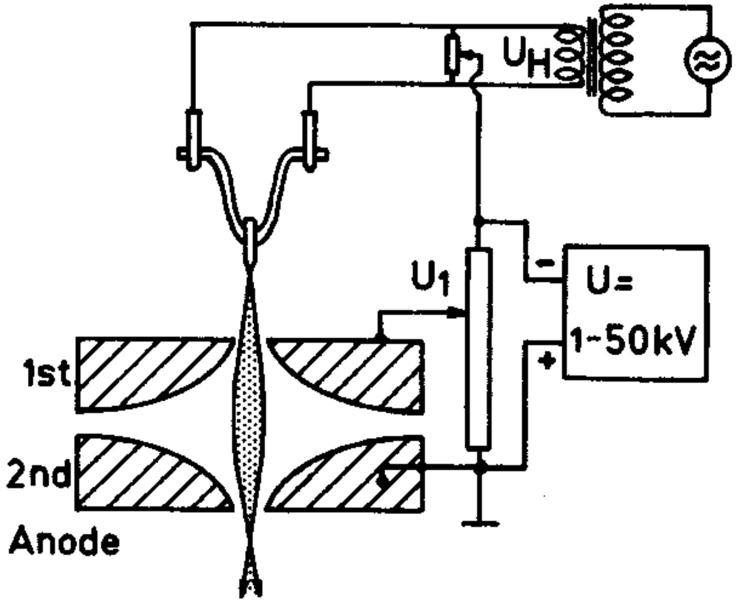
Field Emission Gun



- The tip of a tungsten needle is made very sharp (radius < 0.1 μm)
- The electric field at the tip is very strong (> 10^7 V/cm) due to the sharp point effect
- Electrons are pulled out from the tip by the strong electric field
- Ultra-high vacuum (better than 10^{-6} Pa) is needed to avoid ion bombardment to the tip from the residual gas.
- Electron probe diameter < 1 nm is possible



Field-emission gun

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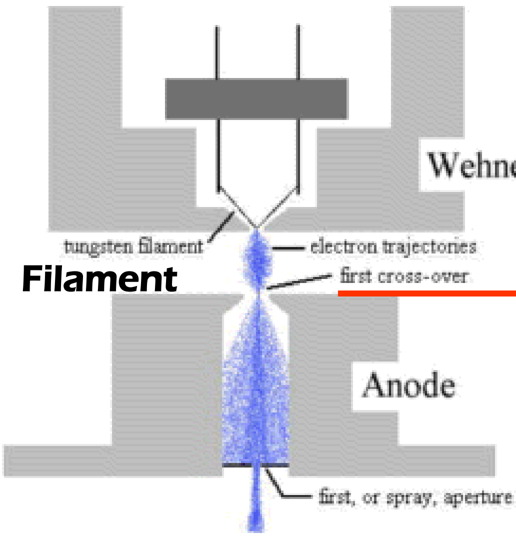
Source of Electrons

Thermionic Gun

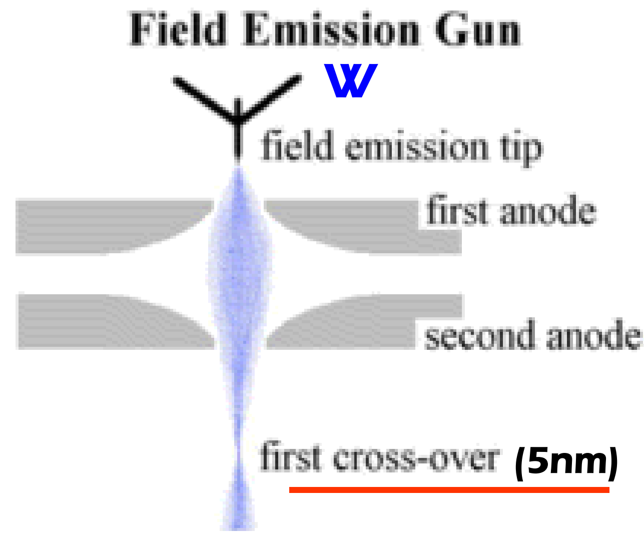
T: ~1500°C



Filament

(5-50mm)

E: >10MV/cm



(5nm)

W and LaB_6

Cold- and thermal FEG

Electron Gun Properties

Source	Brightness	Stability(%)	Size	Energy spread	Vacuum
W	$3X10^5$	~1	50mm	3.0(eV)	10^{-5} (t)
LaB_6	$3x10^6$	~2	5mm	1.5	10^{-6}
C-FEG	10^9	~5	5nm	0.3	10^{-10}
T-FEG	10^9	<1	20nm	0.7	10^{-9}

Brightness – beam current density per unit solid angle

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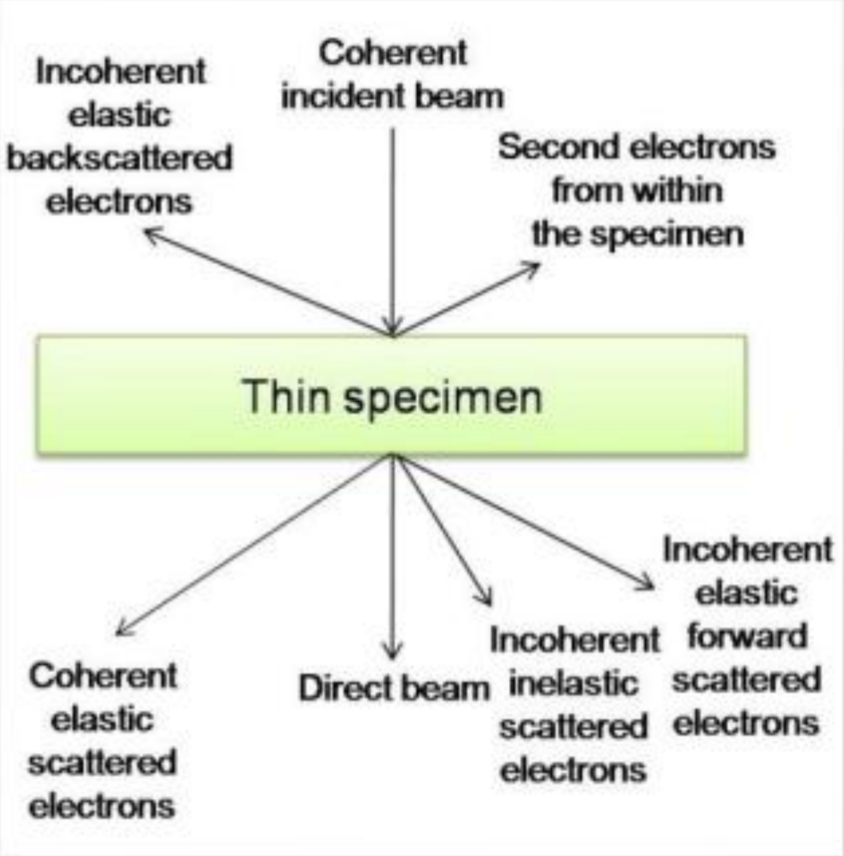
Operational mode: Interaction with matter

Two Categories of electrons

1. Elastically scattered
   - Coherent
     - ➢ Bragg diffracted electrons (selected area electron diffraction, bright-field, dark-field, weak beam)
     - ➢ Phase Contrast imaging (HRTEM)
   - Incoherent
     - ➢ Mass-thickness contrast imaging
     - ➢ Z-Contrast imaging (HAADF STEM)
     - ➢ Backscattered electrons
2. Inelastically scattered
   - Secondary signals
     - ➢ Characteristic X-rays and Bremsstrahlung
     - ➢ Visible light (CL)
     - ➢ Auger electrons
   - Incoherent
     - ➢ Secondary Electrons
     - ➢ Electron Energy Loss Spectroscopy (EELS)

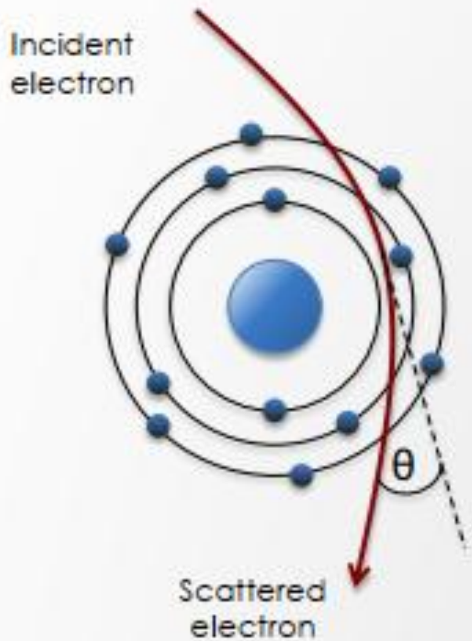


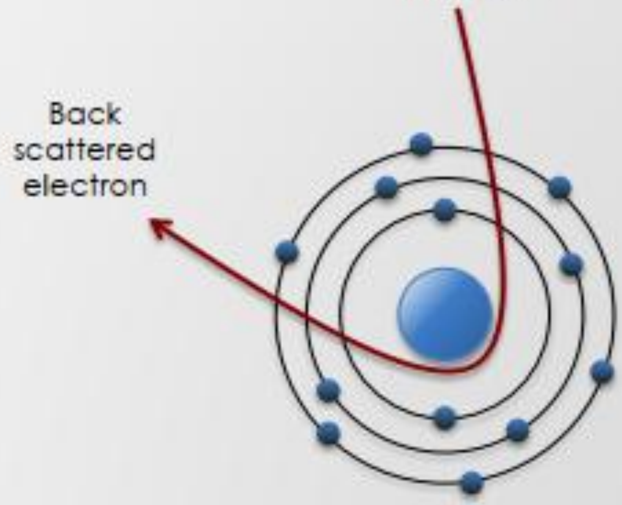
Operational mode: Interaction with matter

Elastic scattering

No energy transfer

- ❑ Low angle diffusion: Coulomb interaction with the electron cloud.
- ❑ High angle diffusion, or back scattering: Coulomb interaction with nucleus.
- ❑ Atom is not ionized.



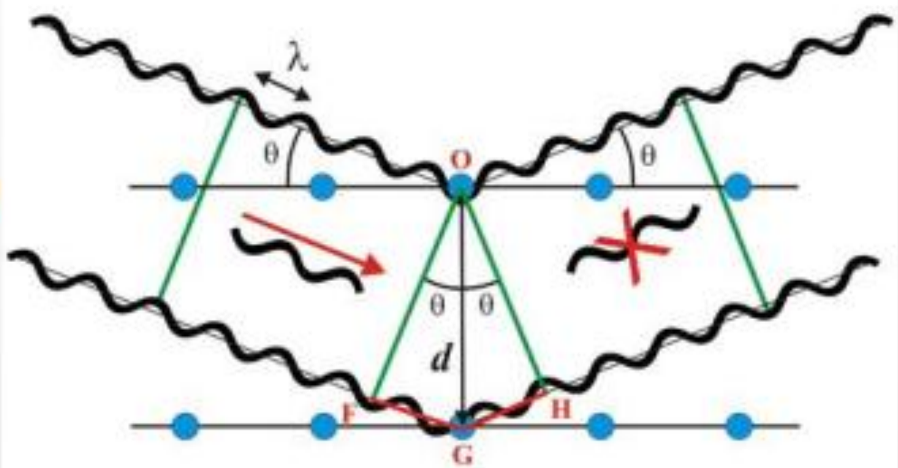


Rutherford scatter
Z-contrast

Electron-matter interactions in a thin sample: Electron Diffraction

The Bragg's law

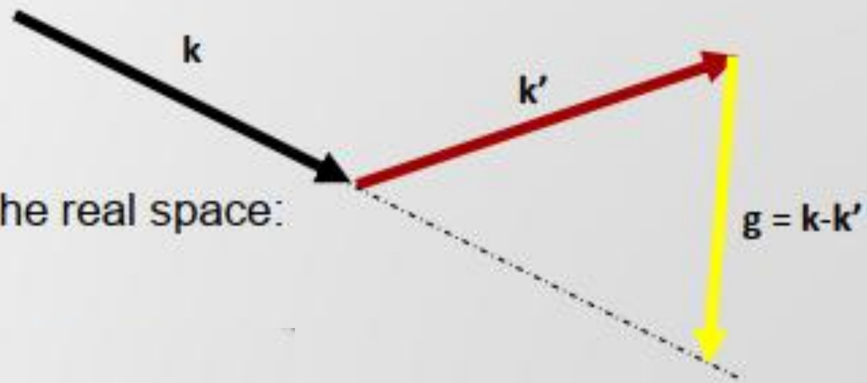
Bragg diffraction occurs when radiation, with a wavelength comparable to the atomic spacing, is scattered by the atom centers and undergoes constructive interference. The path difference between two waves undergoing interference is given by $2d\sin\theta$, where θ is the scattering angle



$2\sin\theta\, d_{hkl} = n\lambda$ $d_{hkl} = n\lambda/2\sin\theta$

Elastic diffraction

$|\mathbf{k}| = |\mathbf{k}'|$



Periodic arrangement of atoms in the real space:
g : vector in the reciprocal space

Operational mode

Convergent beam **Parallel beam**

Can be scanned
(STEM mode)

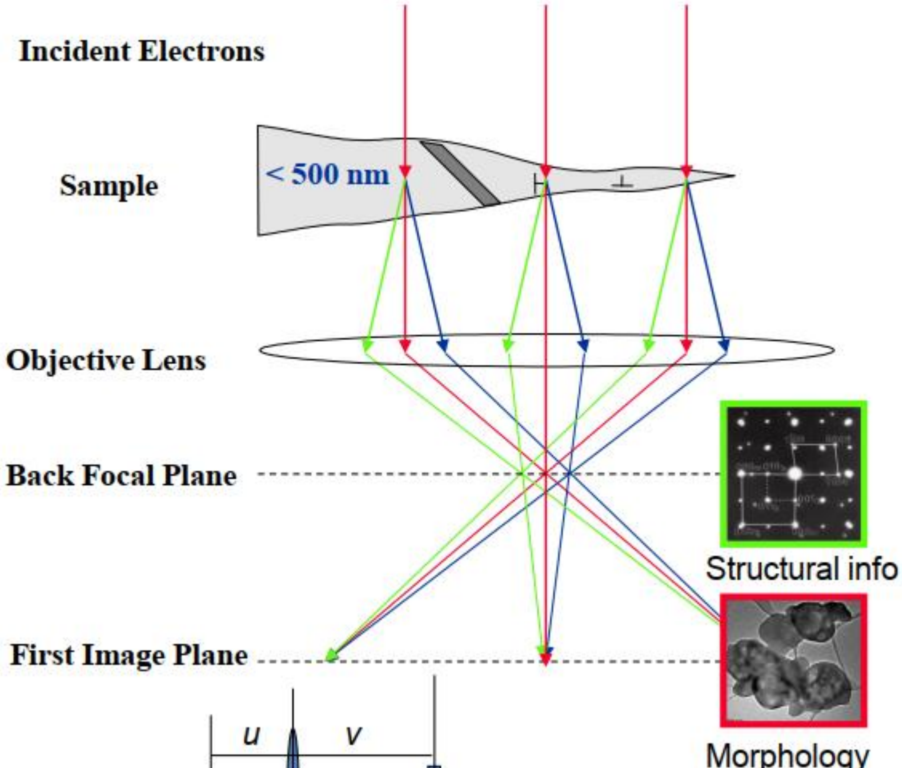
Spectroscopy and
mapping
(EDS and EELS)

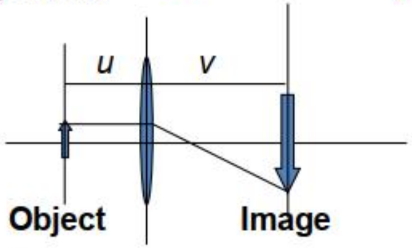
Diffraction mode

Or

Imaging mode

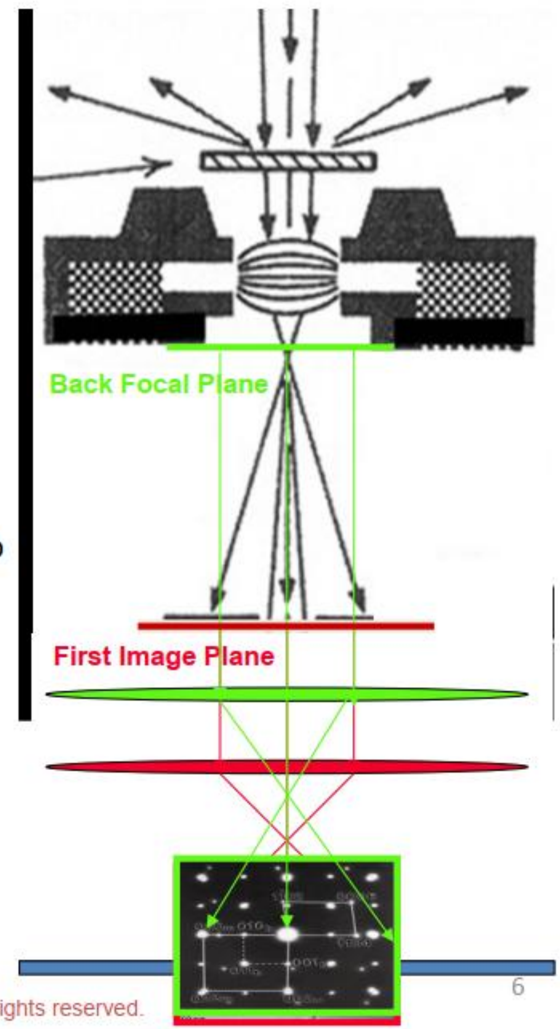
How does a TEM Obtain Image and Diffraction?



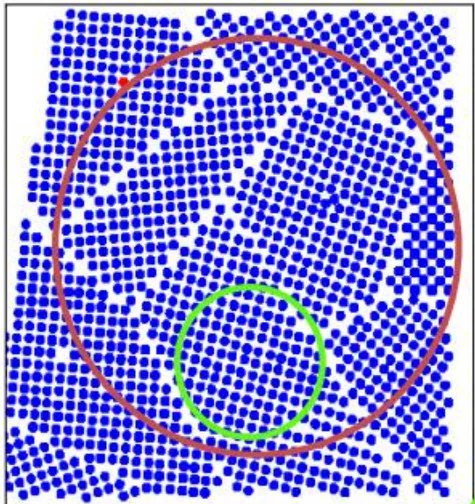


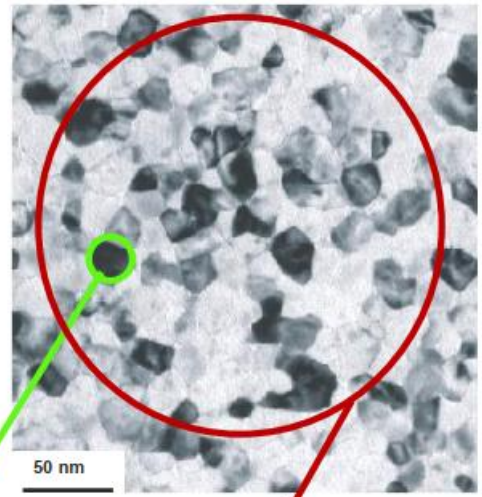
$$\frac{1}{u}+\frac{1}{v}=\frac{1}{f}$$

Conjugate planes



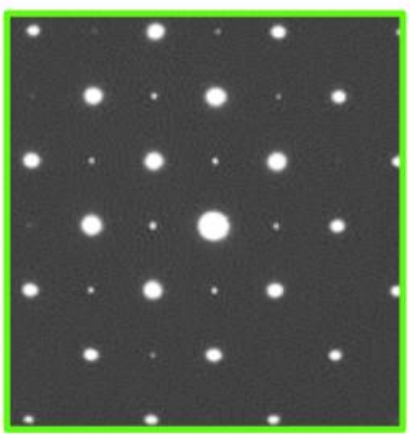
Electron Diffraction



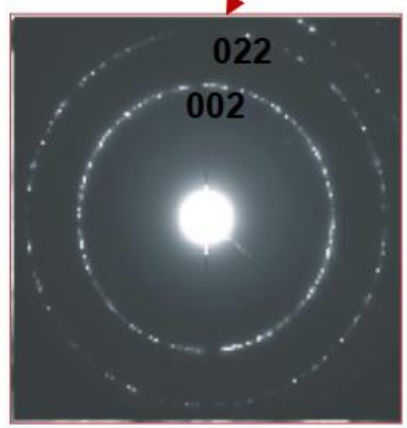


Diffraction patterns from single grain or multiple grains

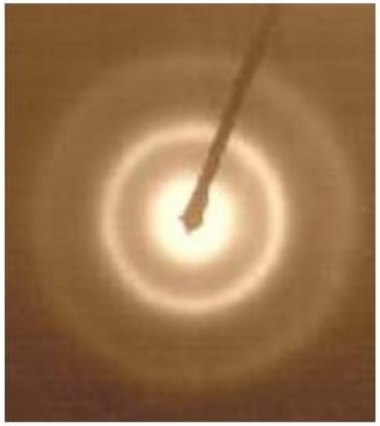
1) Selected-Area Electron Diffraction
2) NanoArea Electron Diffraction
3) Convergent Beam Electron diffraction



Single crystal

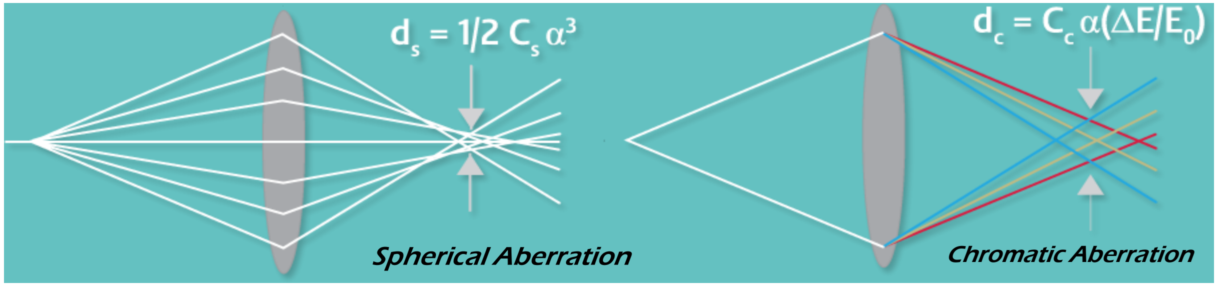


Polycrystal



Amorphous

TEM Aberration Correction

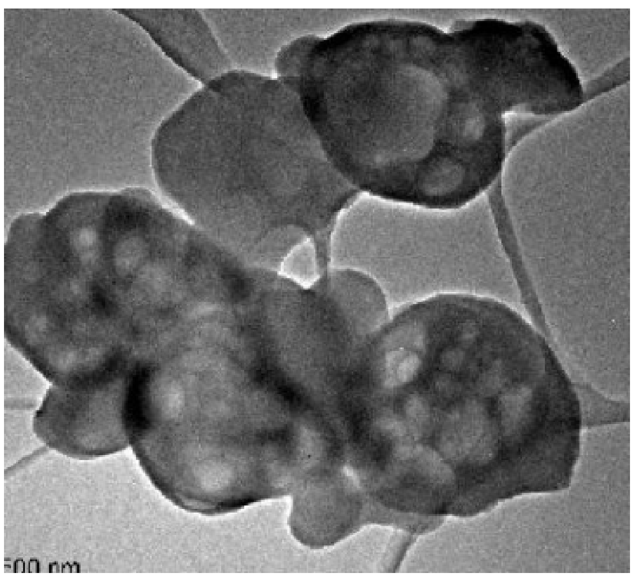


- Chromatic aberration is distortion that occurs when there is a failure of a lens to focus all colors (wavelengths) to the same convergence point.
  - Correcting the aberration is necessary, otherwise the resulting image would be blurry and delocalized, a form of aberration where periodic structures appear to extend beyond their physical boundaries.
  - Recent improvements in aberration correction have resulted in significantly-improved image quality and sample information.
- Spherical aberration occurs when parallel light rays that pass through the central region of the lens focus farther away than the light rays that pass through the edges of the lens.
  - Result is multiple focal points and a blurred image.

Major Imaging Techniques

Major Imaging Contrast Mechanisms:

1. Mass-thickness contrast
2. Diffraction contrast
3. Phase contrast
4. Z-contrast



Mass-thickness contrast

1) Imaging techniques in **TEM** mode
   a) Bright-Field TEM (Diff. contrast)
   b) Dark-Field TEM (Diff. contrast)
   c) Weak-beam imaging
      hollow-cone dark-field imaging
   d) Lattice image (Phase)
   e) High-resolution Electron Microscopy (Phase)
      Simulation and interpretation
2) Imaging techniques in **scanning** transmission electron microscope (**STEM**) mode
   1) Z-contrast imaging (Dark-Field)
   2) Bright-Field STEM imaging
   3) High-resolution Z-contrast imaging (Bright- & Dark-Field)
3) Spectrum imaging
   1) Energy-Filtered TEM (**TEM** mode)
   2) EELS mapping (**STEM** mode)
   3) EDS mapping (**STEM** mode)

Technology of Sectioning & specimen preparation

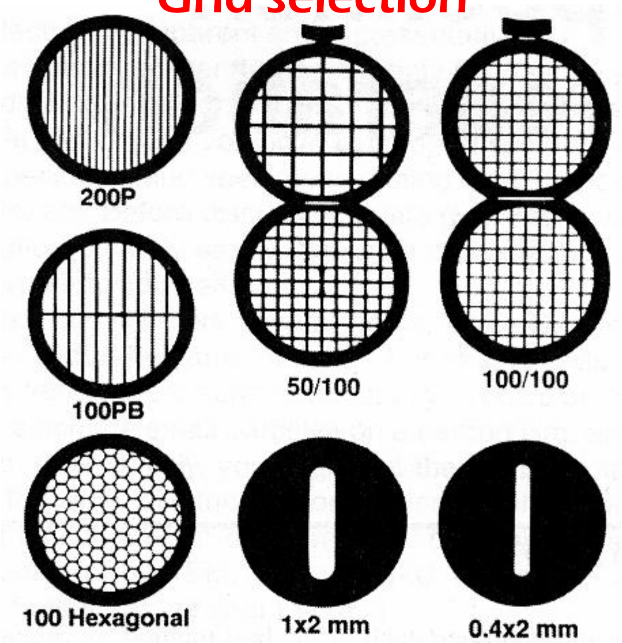
- Ultramicrotome
- Knife Selection
- Specimen Preparation
- Sectioning
- Mounting Grids
- Staining
- A Few Sectioning Artifacts

Technology of Sectioning & specimen preparation

Reichert Ultracut Ultramicrotome

Knives

Grid selection



Technology of specimen preparation

- Coarse preparation of samples:
  - Small objects (mounted on grids):
    - Strew
    - Spray
    - Cleave
    - Crush
  - Disc cutter (optionally mounted on grids)
  - Grinding device
- Intermediate preparation:
  - Dimple grinder
- Fine preparation:
  - Chemical polisher
  - Electropolisher
  - Ion thinning mill
    - PIMS: precision milling (using SEM on very small areas (1 X 1 μm^2)
    - PIPS: precision ion polishing (at 4° angle) removes surface roughness wi th minimum surface damage
    - Beam blockers may be needed to mask epoxy or easily etched areas
- Each technique has its own disadvantages and potential artifact

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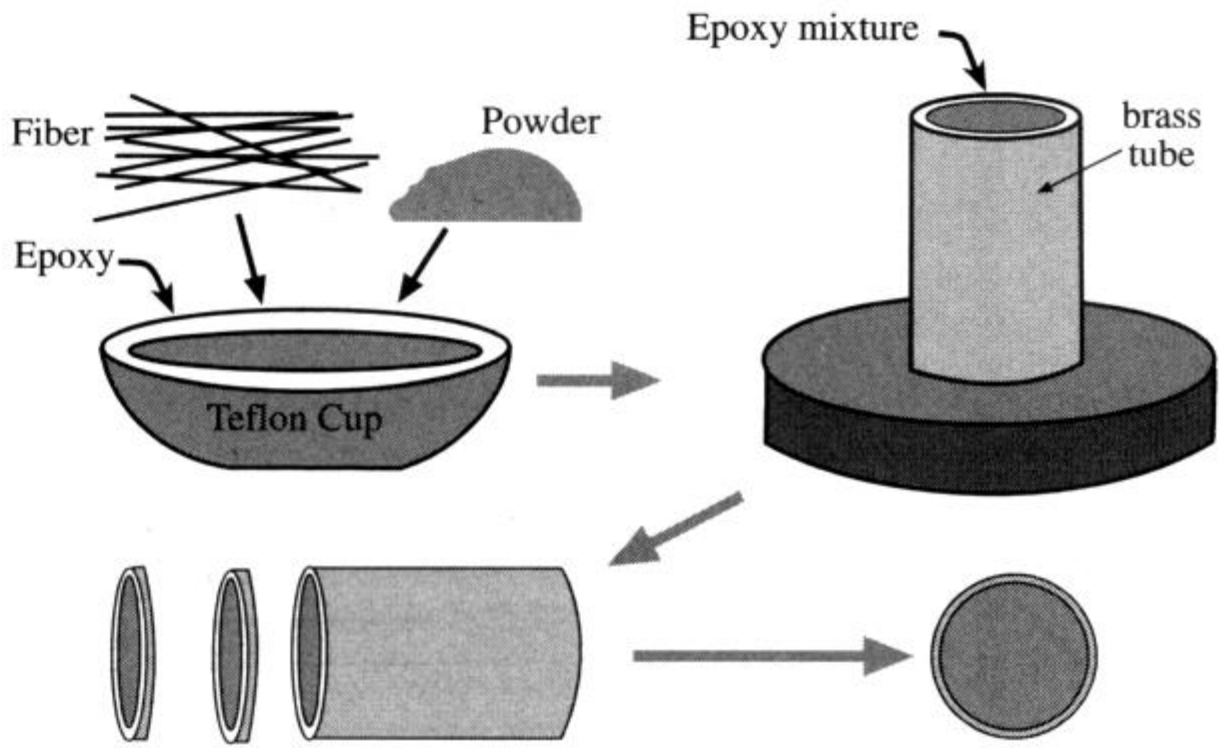
Epoxy mounting

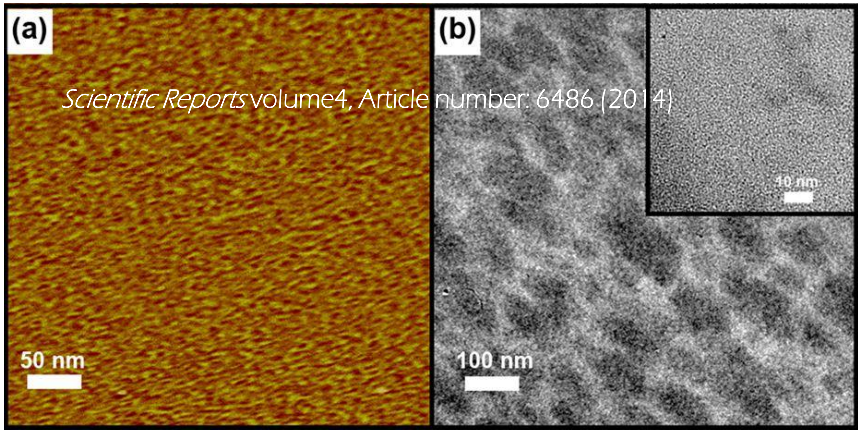


Epoxy mounting of sectioned specimens prepared by thinning:

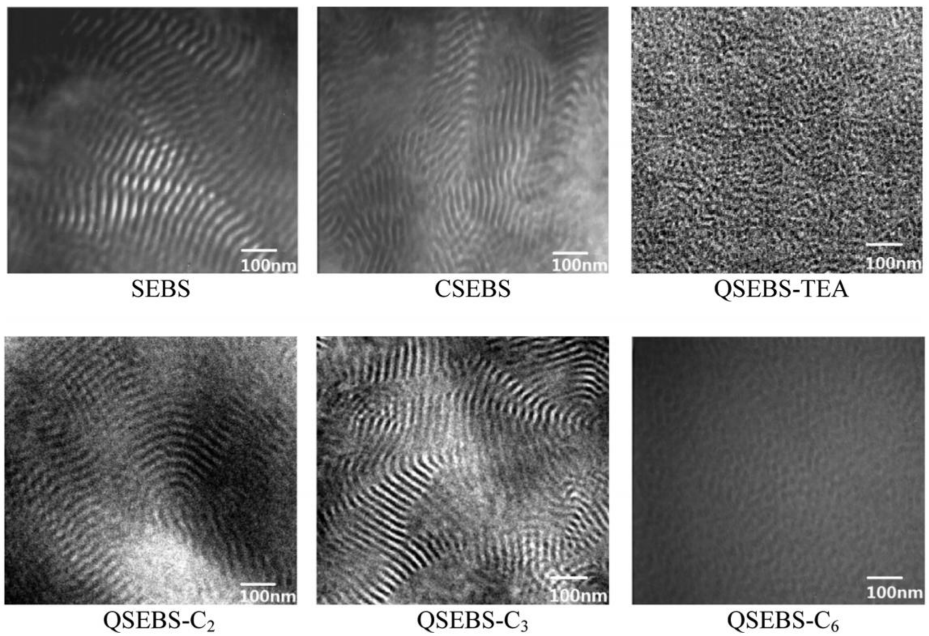
- Sequence of steps for thinning particles and fibers.
- Materials are first embedding them in epoxy
- 3 mm outside diameter brass tube is filled with epoxy prior to curing
- Tube and epoxy are sectioned into disks with diamond saw
- Specimens are then dimple ground and ion milled to transparency

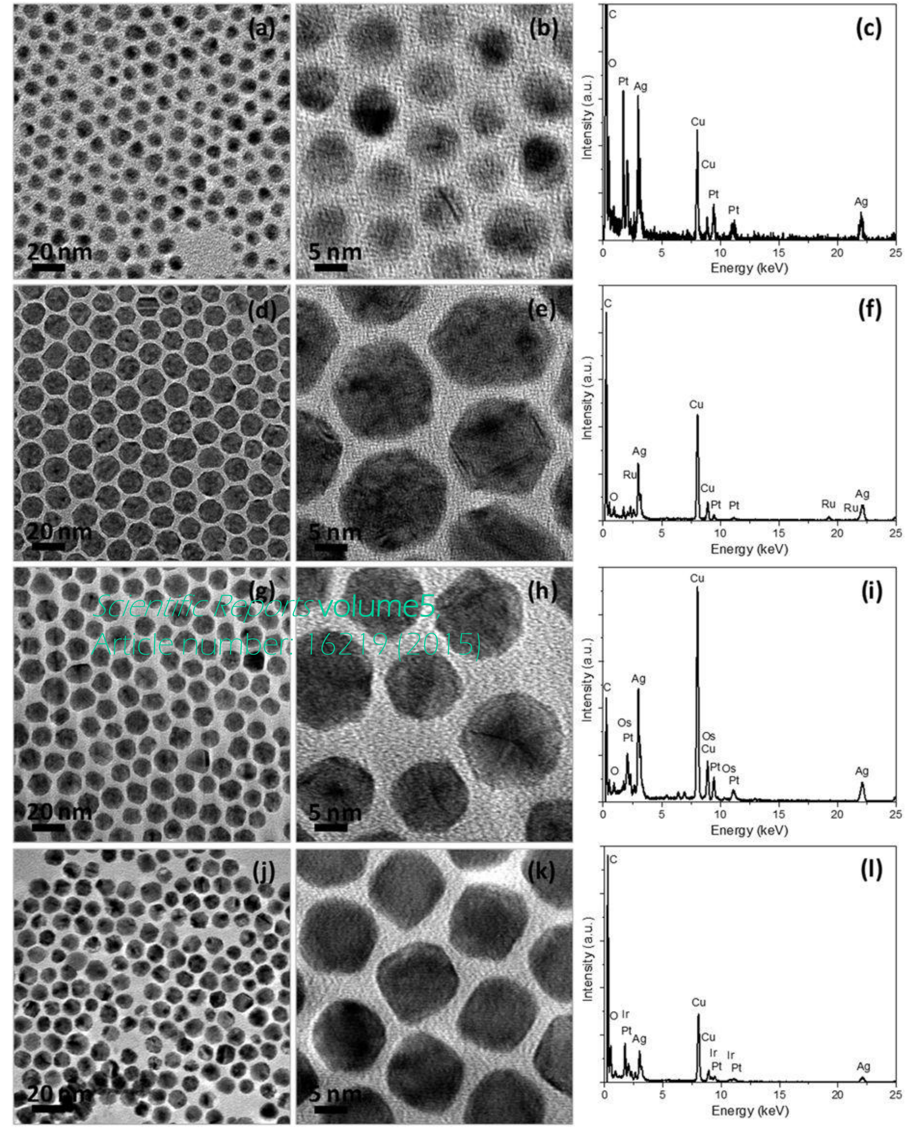
Williams & Carter, 1996, Fig. 10-10

Spectroscopy



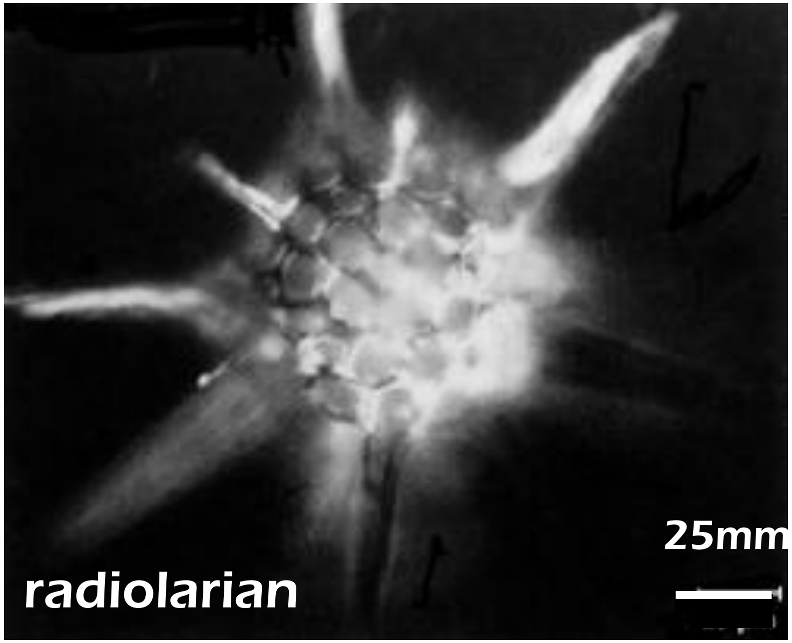
Scientific Reports volume4, Article number: 6486 (2014)





Scientific Reports volume5, Article number: 16219 (2015)

Scanning Electron Microscope (SEM)



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SEM

Small depth of field
Low resolution

Large depth of field
High resolution

http://www.mse.iastate.edu/microscopy/

Scanning Electron Microscope (SEM)

What is SEM?

Working principles of SEM

Major components and their functions

Electron beam - specimen interactions

Interaction volume and escape volume

Magnification, resolution, depth of field and image contrast

Energy Dispersive X-ray Spectroscopy (EDS)

Wavelength Dispersive X-ray Spectroscopy (WDS)

Orientation Imaging Microscopy (OIM)

X-ray Fluorescence (XRF)

Scanning Electron Microscope

– a Totally Different Imaging Concept

Instead of using the full-field image, a point-to-point measurement strategy is used.

High energy electron beam is used to excite the specimen and the signals are collected and analyzed so that an image can be constructed.

The signals carry topological, chemical and crystallographic information, respectively, of the samples surface.

https://www.youtube.com/watch?v=VWxYsZPtTsI at~4:18-4:38
http://www.youtube.com/watch?v=lrXMIghANbg at~4:16-4:42
https://www.youtube.com/watch?v=nPskvGJKtDI

Main Applications

- **Topography**

  The surface features of an object and its texture (hardness, ref lectivity… etc.)

- **Morphology**

  The shape and size of the particles making up the object (stre ngth, defects in IC and chips…etc.)

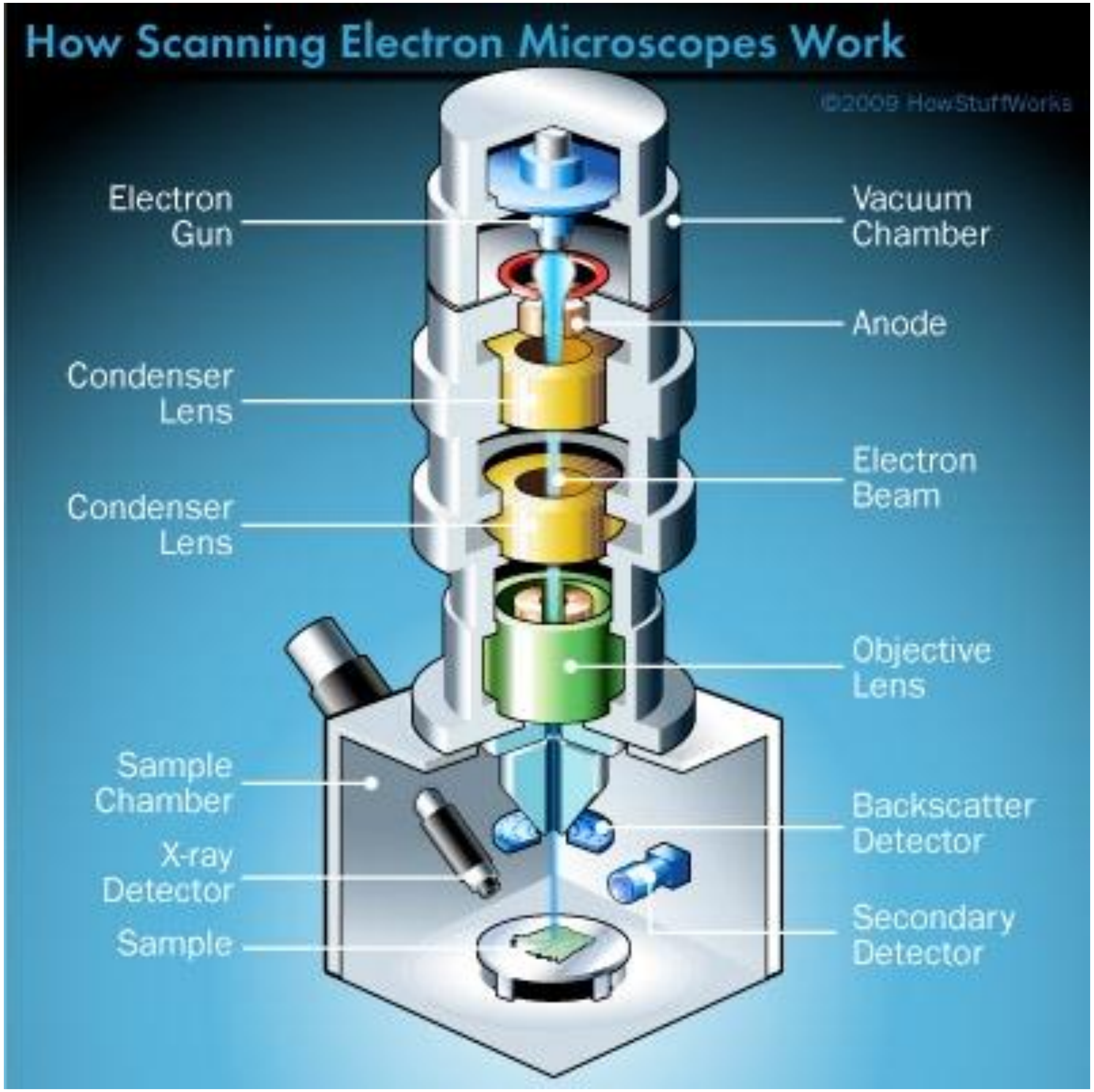
- **Composition**

  The elements and compounds that the object is composed of and the relative amounts of them (melting point, reactivity, h ardness…etc.)

- **Crystallographic Information**

  How the grains are arranged in the object (conductivity, elect rical properties, strength…etc.)

- **What is SEM?**
- **Working principles of SEM**
- **Major components and their functions**



1. e- beam strikes sample and electron penetrate surface
2. Interactions occur between electrons and sample
3. Electrons and photons emitted from sample
4. Emitted e- or photons detected

A more detailed look inside

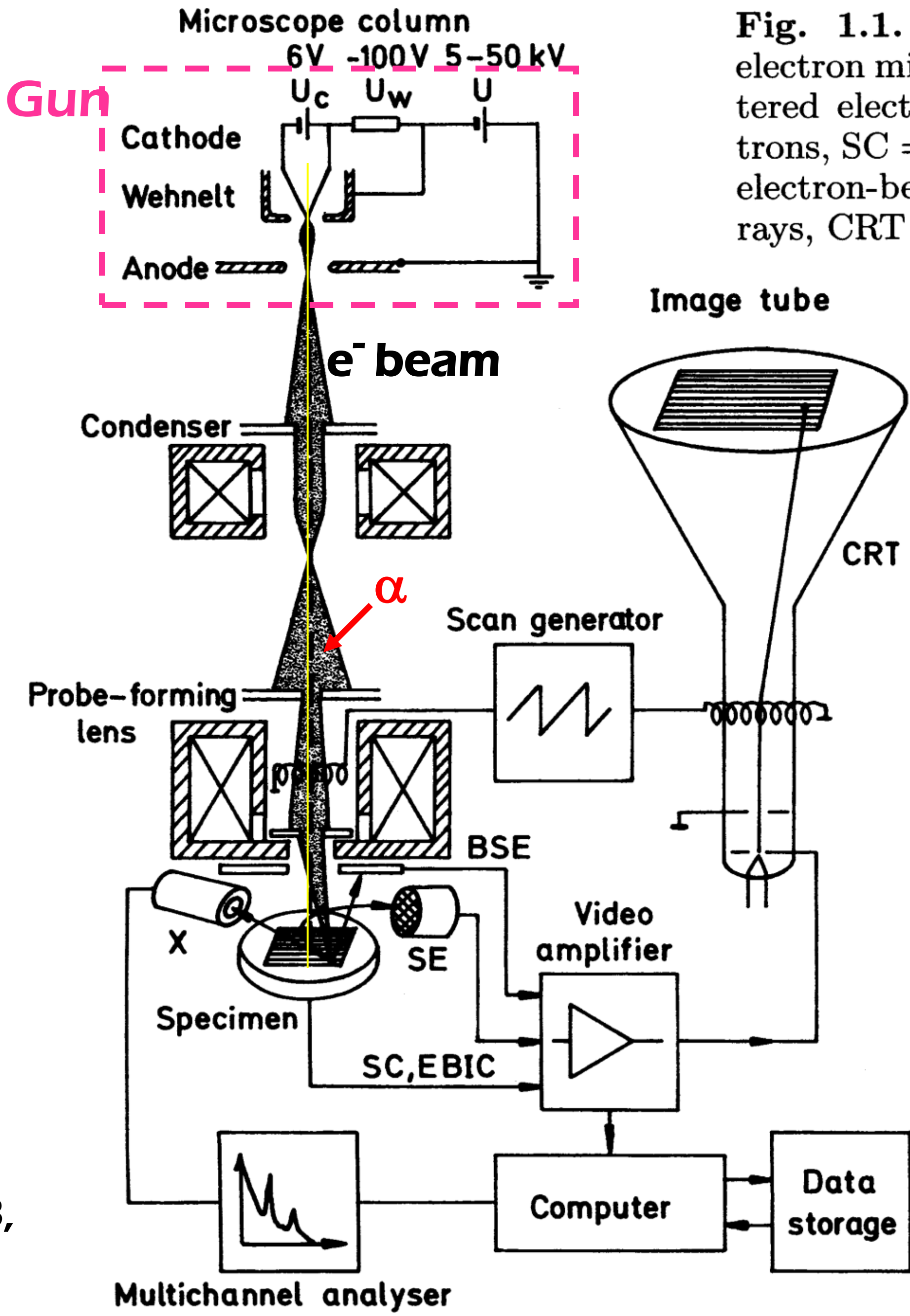
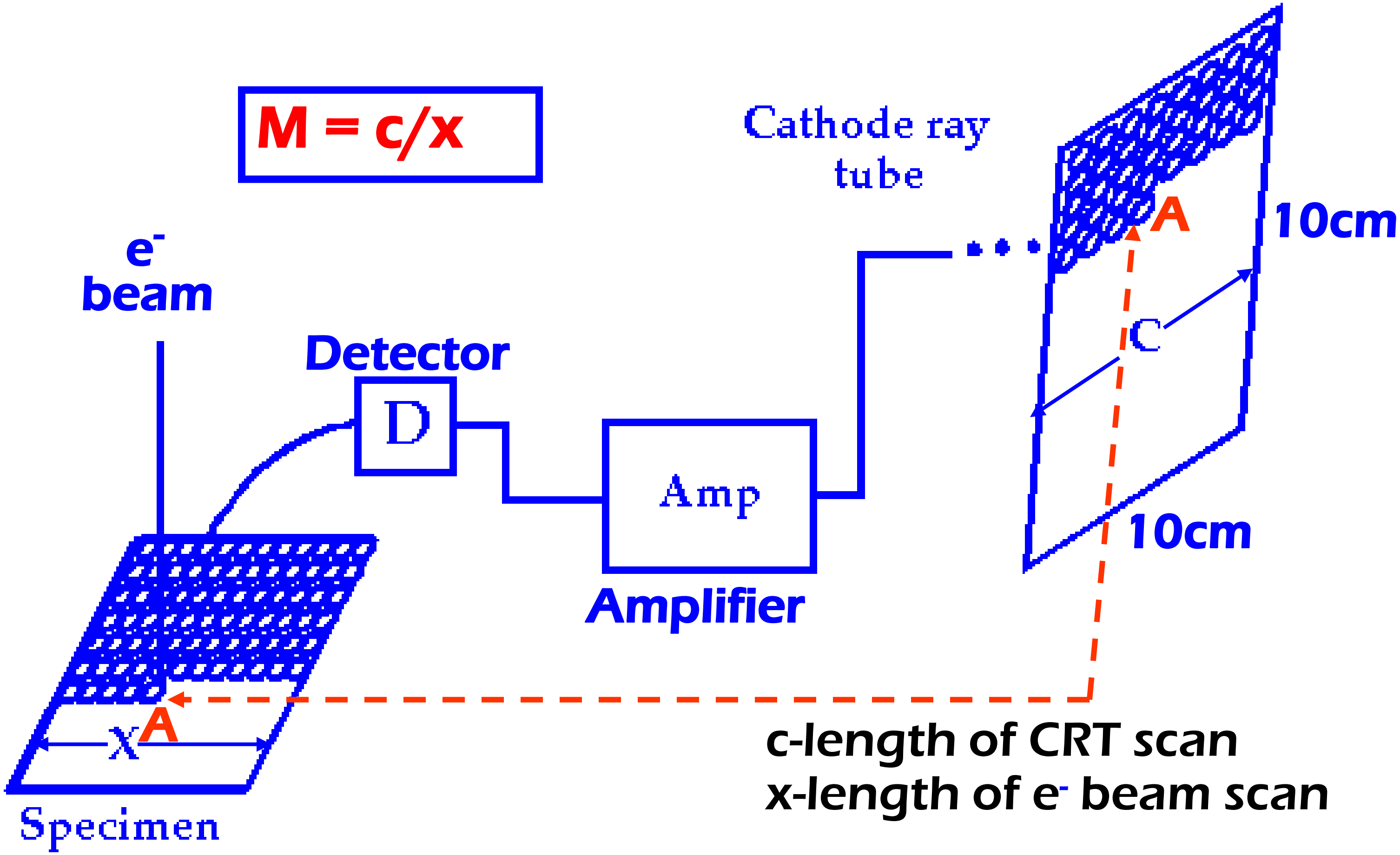


Fig. 1.1. Principle of the scanning electron microscopoe (BSE = backscattered electrons, SE = secondary electrons, SC = specimen current, EBIC = electron-beam-induced current, X = x-rays, CRT = cathode-ray tube)

Source: L. Reimer, "Scanning Electron Microscope", 2nd Ed., Springer-Verlag, 1998, p.2

Image Formation in SEM

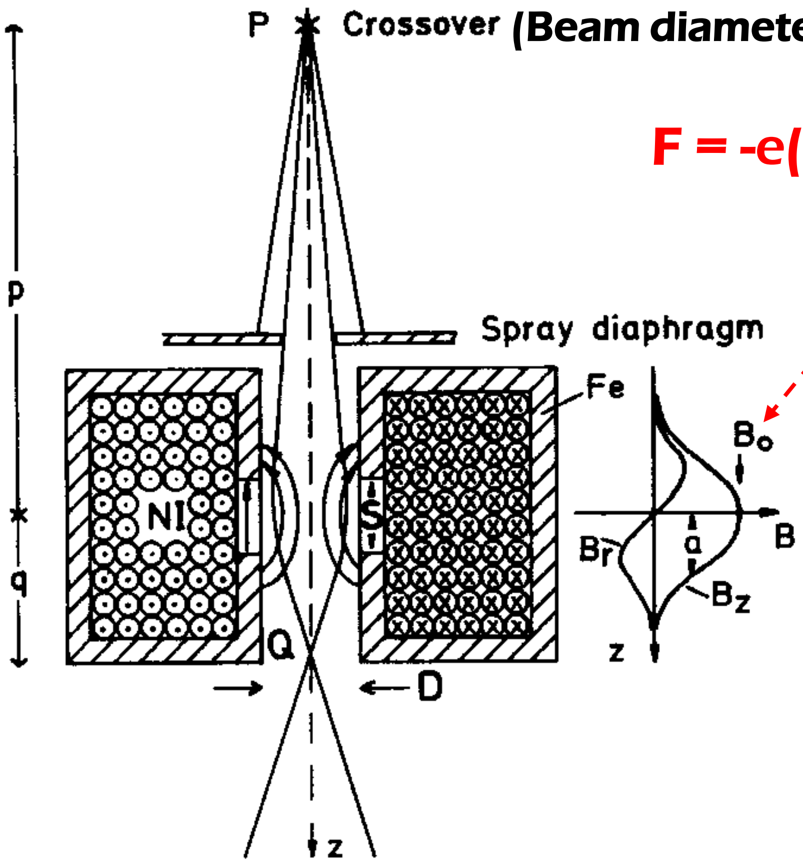


c-length of CRT scan
x-length of e^- beam scan

Beam is scanned over specimen in a raster pattern in synchronization with beam in CRT. Intensity at A on CRT is proportional to signal detected from A on specimen and signal is modulated by amplifier.

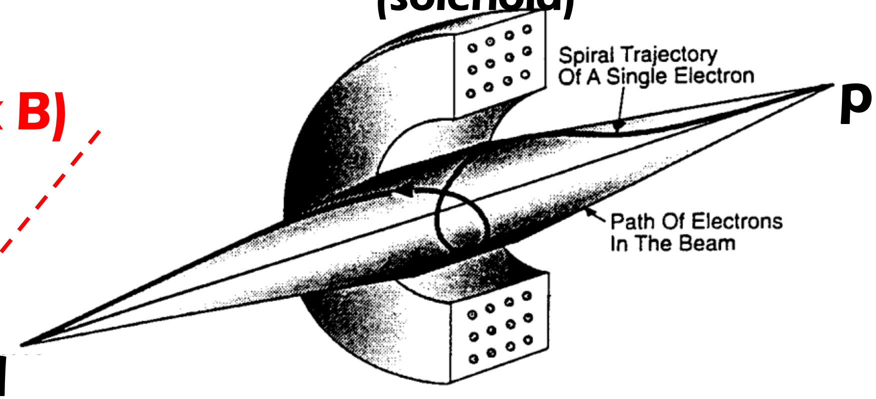
How Is Electron Beam Focused?

A magnetic lens is a solenoid designed to produce a specific magnetic flux distribution.



$F = -e(v \times B)$

Magnetic lens (solenoid)



Lens formula: $1/f = 1/p + 1/q$

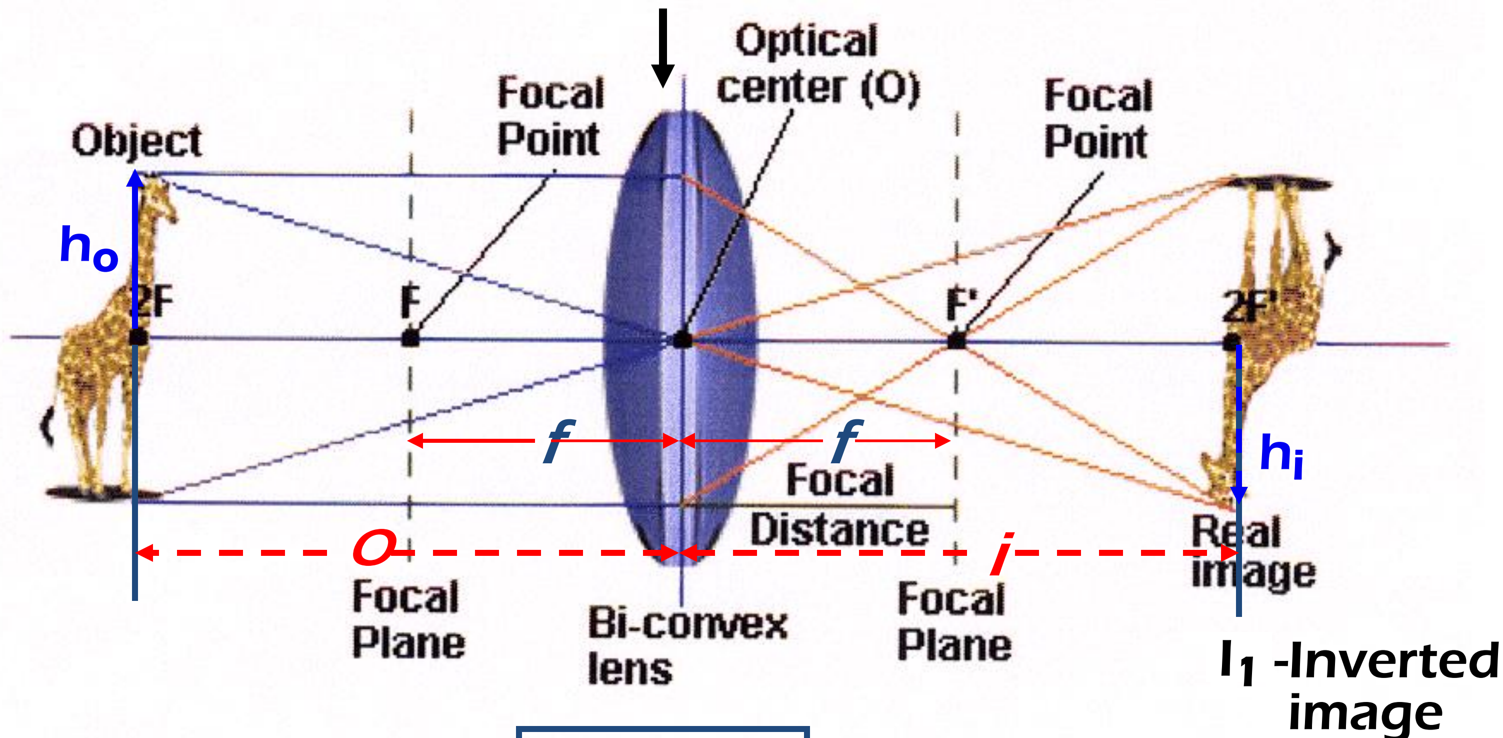
Demagnification: $M = q/p$

$f \propto B_o^2$

f can be adjusted by changing B_o, i.e., changing the current through coil.

Lens formula and magnification

Objective lens



Lens Formula

$$\frac{1}{f} = \frac{1}{O} + \frac{1}{i}$$

Magnification by objective

$$m_o = \frac{h_i}{h_o} = \frac{i}{O}$$

f-focal length (distance)

O-distance of object from lens

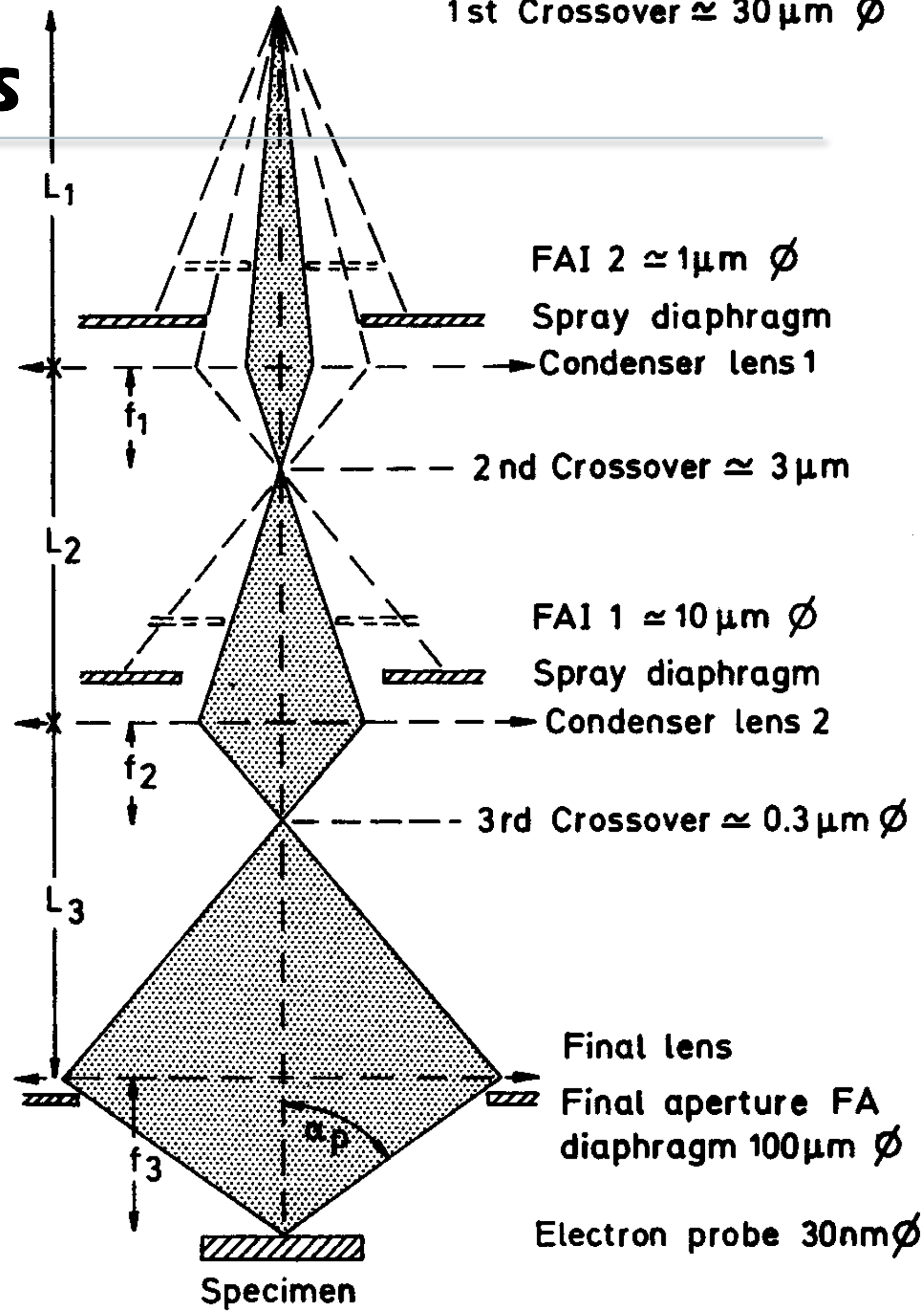
i-distance of image from lens

http://www.youtube.com/watch?v=-k1NNIOzjFo&feature=related at~3:00-3:40

http://micro.magnet.fsu.edu/primer/java/lenses/converginglenses/index.html http://www.matter.org.uk/tem/lenses/simulation_of_condenser_system.htm change of f

The Condenser Lens

For a thermionic gun, the diameter of the first **cross-over point** ~20-50μm
If we want to focus the beam to a size **< 10 nm** on the specimen surface, the magnification should be ~1/5000, which is not easily attained with one lens (say, the objective lens) only.
Therefore, condenser lenses are added to **demagnify** the cross-over points.

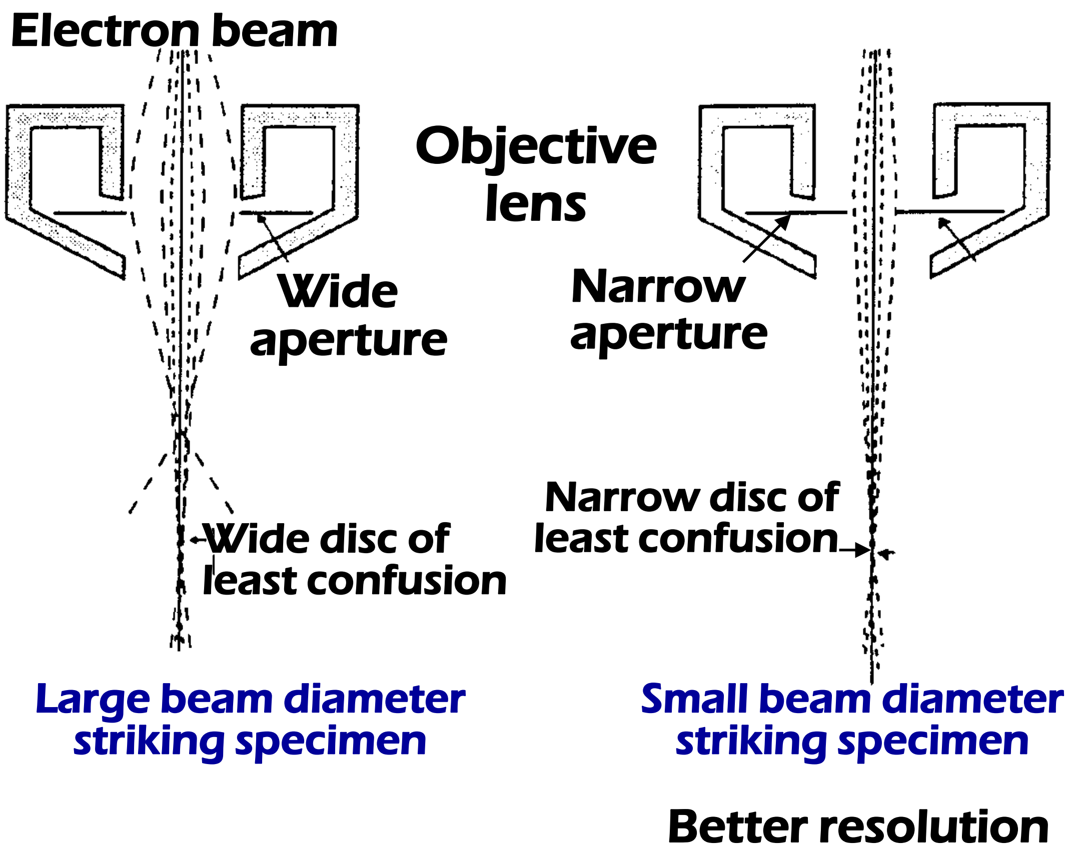


Demagnification:

$$M = f/L$$

The Objective Lens – Aperture

- Since the electron s coming from the electron gun have spread in kinetic energies and directions of movement, they may not be focused to the same plane to form a sharp spot.
- By inserting an aperture, the stray electrons are blocked and the remaining narrow beam will come to a narrow



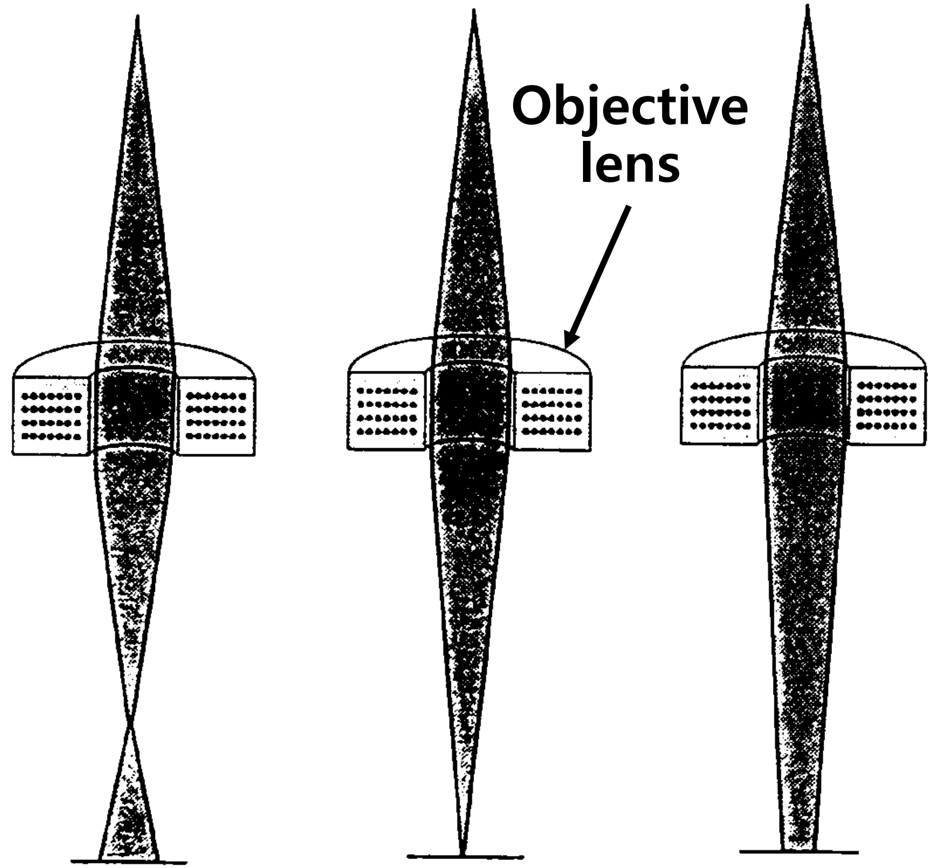
"Disc of Least Confusion"

https://www.youtube.com/watch?v=E85FZ7WLvao

http://www.matter.org.uk/tem/lenses/simulation_of_condenser_system.htm aperture http://www.matter.org.uk/tem/lenses/second_condenser_lens.htm

The Objective Lens - Focusing

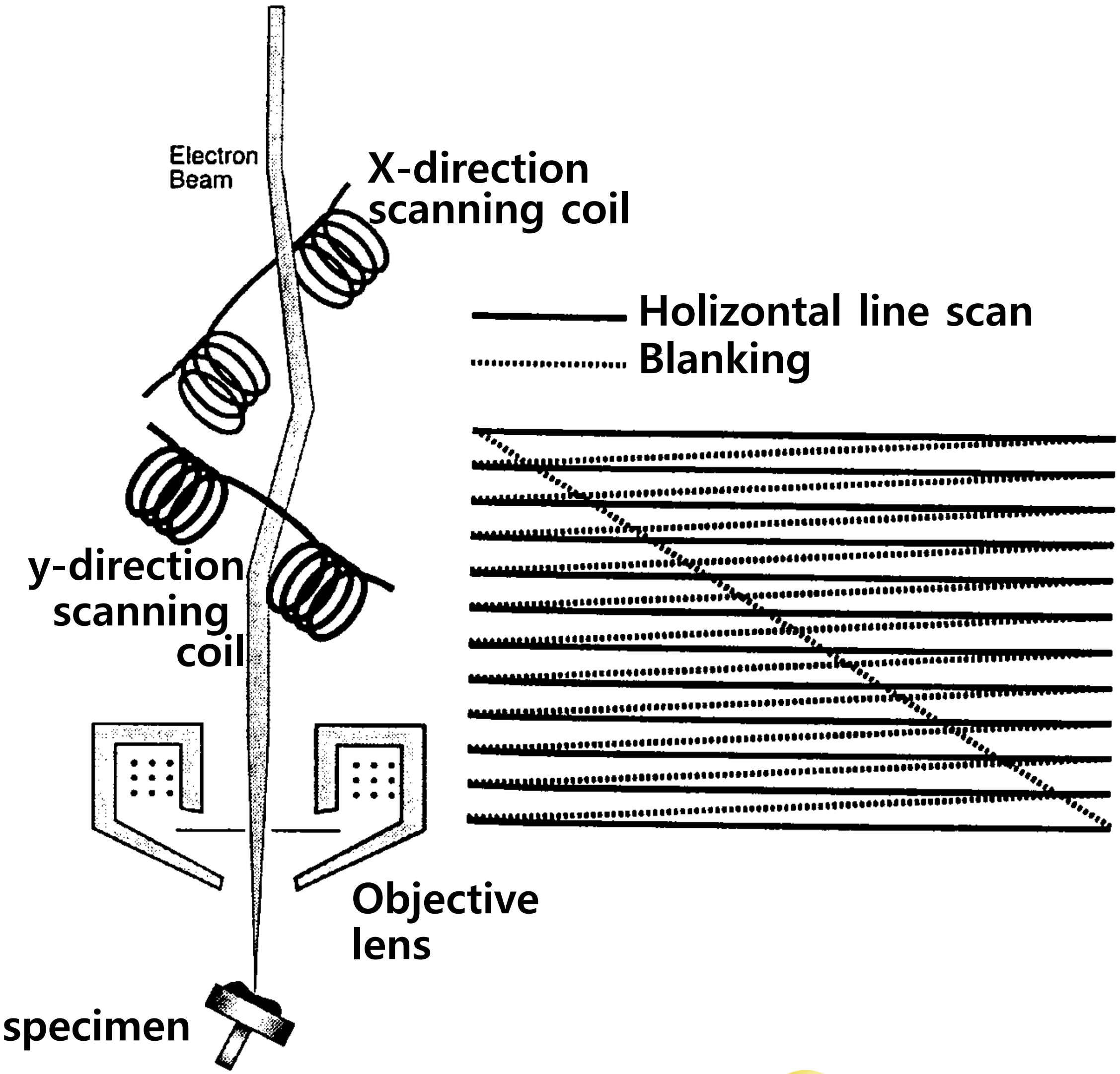
- By changing the current in the objective lens, the magnetic field strength changes and therefore the **focal length** of the objective lens is changed.



Out of focus lens current too strong	in focus lens current optimized	out of focus lens current too weak
Over-focused	Focused	Under-focused

The Scan Coil and Raster Pattern

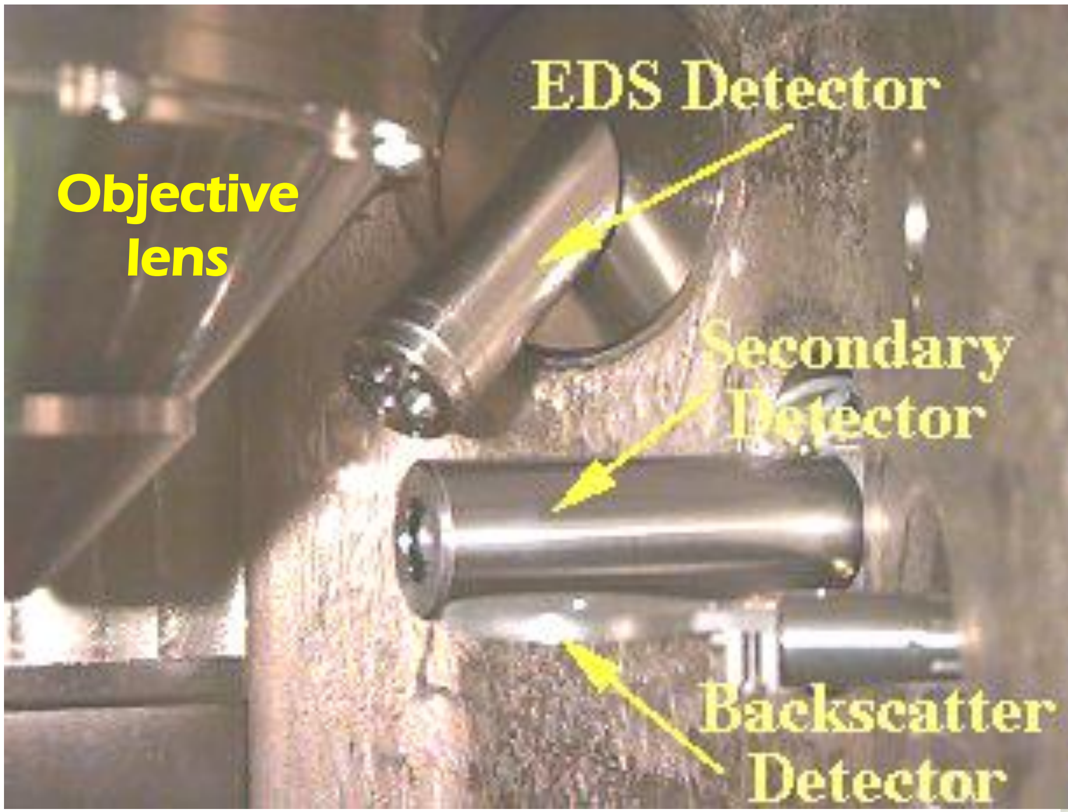
- Two sets of coils are used for scanning the electron beam across the specimen surface in a **raster** pattern similar to that on a TV screen.
- This effectively samples the specimen surface **point by point** over the scanned area.



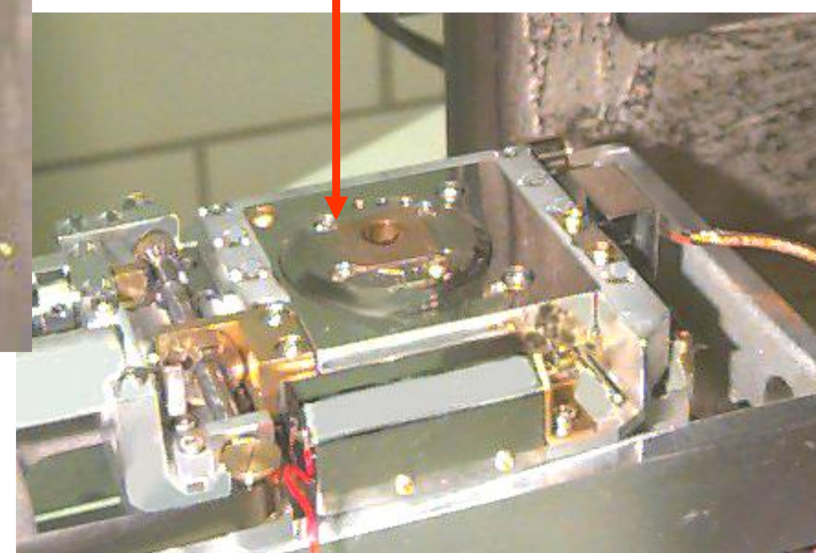
http://www.youtube.com/watch?v=lrXMIghANbg at ~4:12

http://www.youtube.com/watch?v=VWxYsZPtTsI at~4:45
http://virtual.itg.uiuc.edu/training/EM_tutorial internal

Electron Detectors and Sample Stage



Sample stage

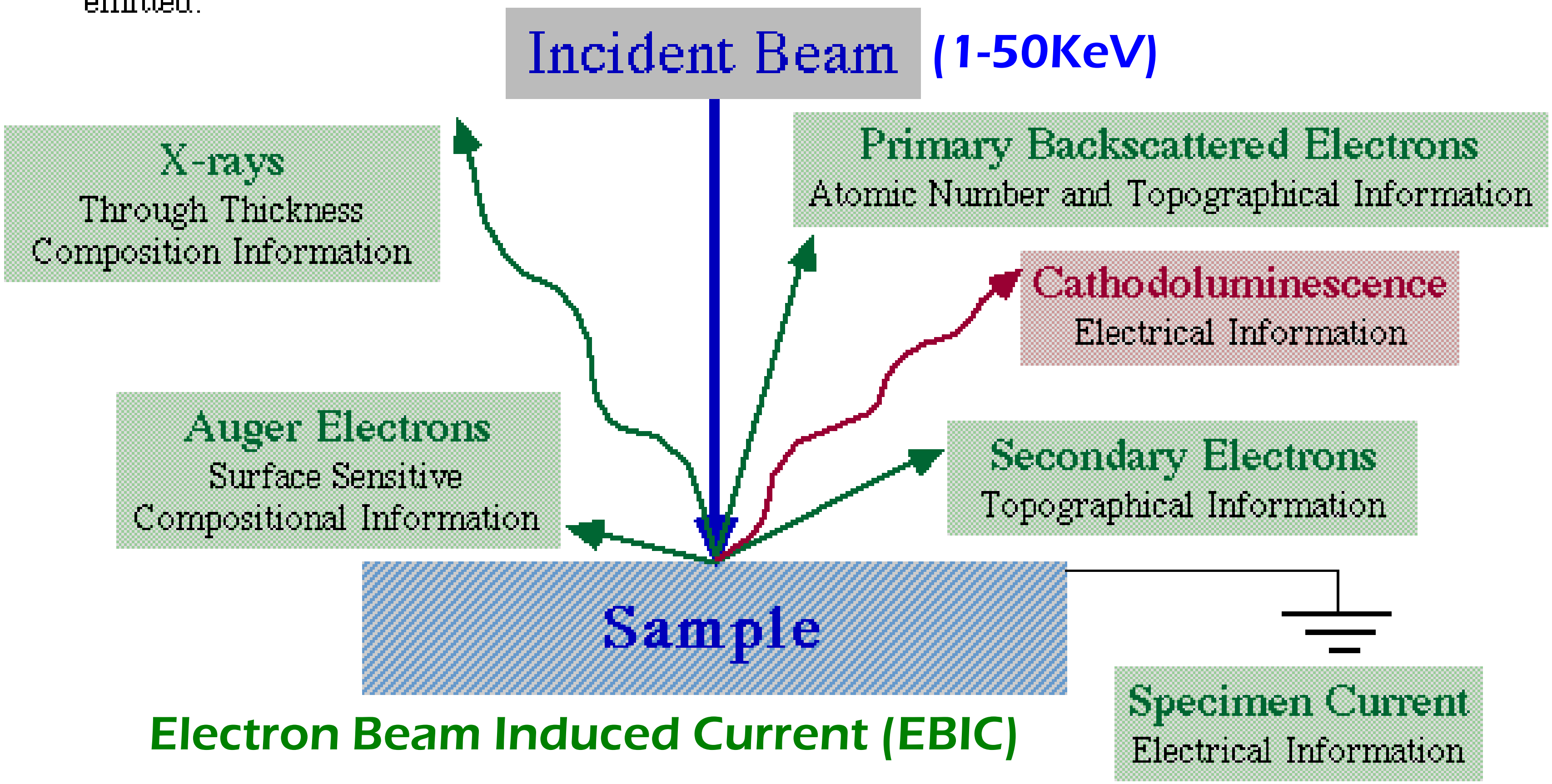


https://www.youtube.com/watch?v=Mr9-1Sz_CK0 at~2:20-2:30

Electron Beam and Specimen Interactions

Sources of Image Information

When the electron beam strikes the sample, both **photon** and **electron** signals are emitted.



https://www.youtube.com/watch?v=F9qwfYwwCRM at~0.58-1:38
http://www.youtube.com/watch?v=Mr9-1Sz_CK0 at~2:30-2:42

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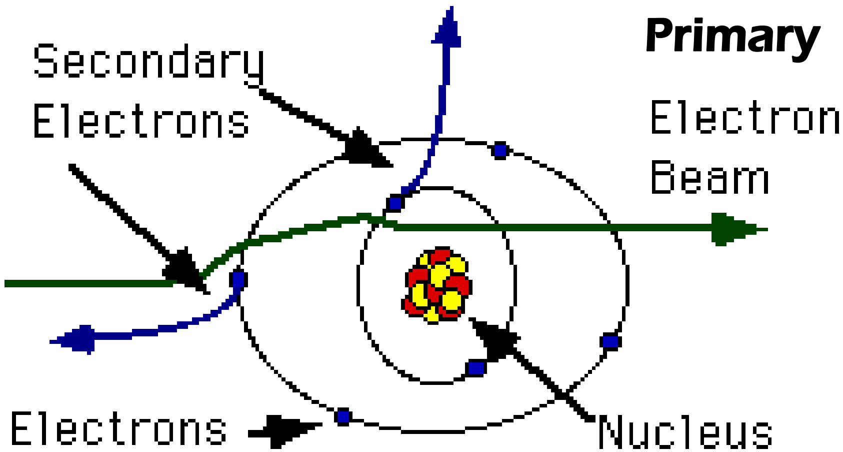
http://www.youtube.com/watch?v=Mr9-1Sz_CK0 at~2:52-3:52
https://www.youtube.com/watch?v=F9qwfYwwCRM at~0:58-1:14

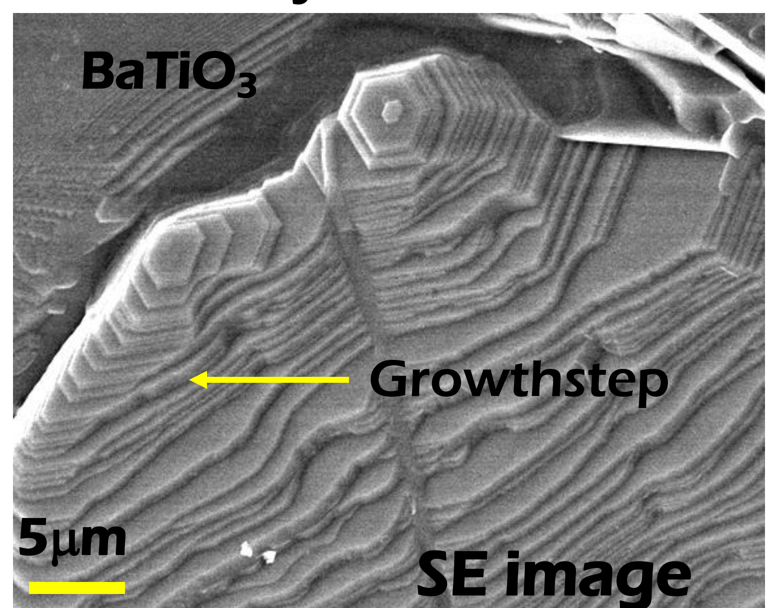
Secondary Electrons (SE)



Produced by **inelastic** interactions of high energy electrons with valence (or conduction) electrons of atoms in the specimen, causing the ejection of the electrons from the atoms. These ejected electrons with energy less than **50eV** are termed "secondary electrons".
Each incident electron can produce several secondary electrons.

SE yield: $d = n_{SE}/n_B$ independent of **Z**
d decreases with increasing beam energy and increases with decreasing glancing angle of incident beam

Production of SE is very **topography** related. Due to their low energy, only SE that are very near the surface (**<10nm**) can exit the sample and be examined (**small escape depth**).



Z – atomic number

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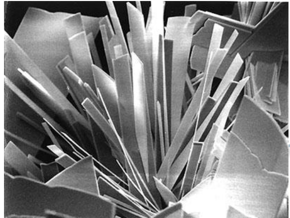
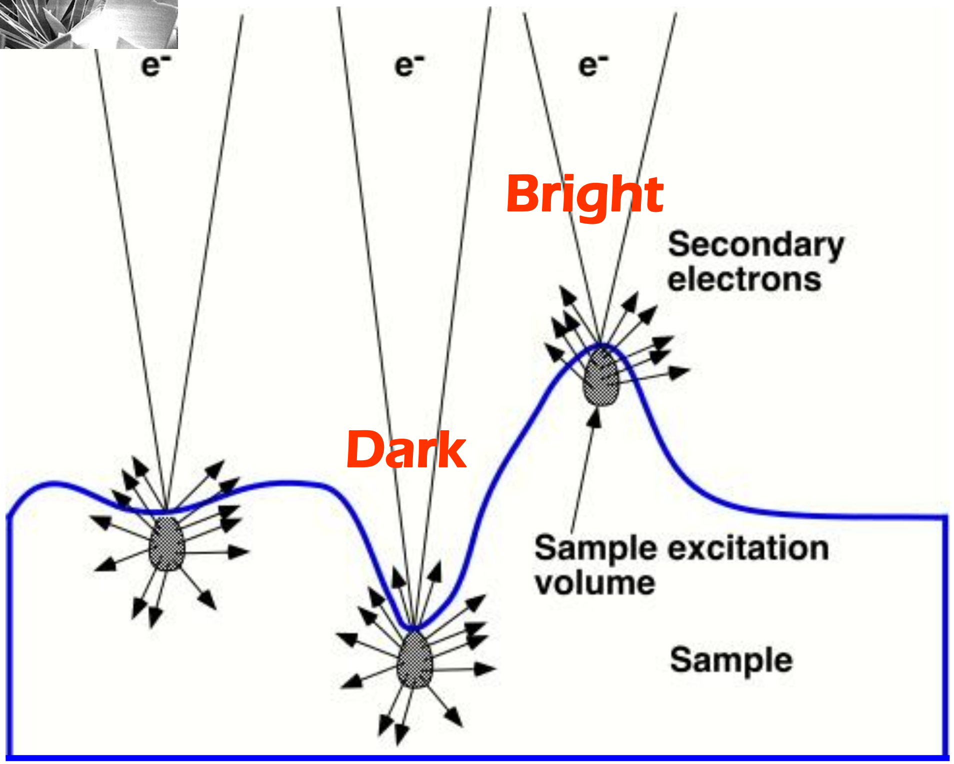
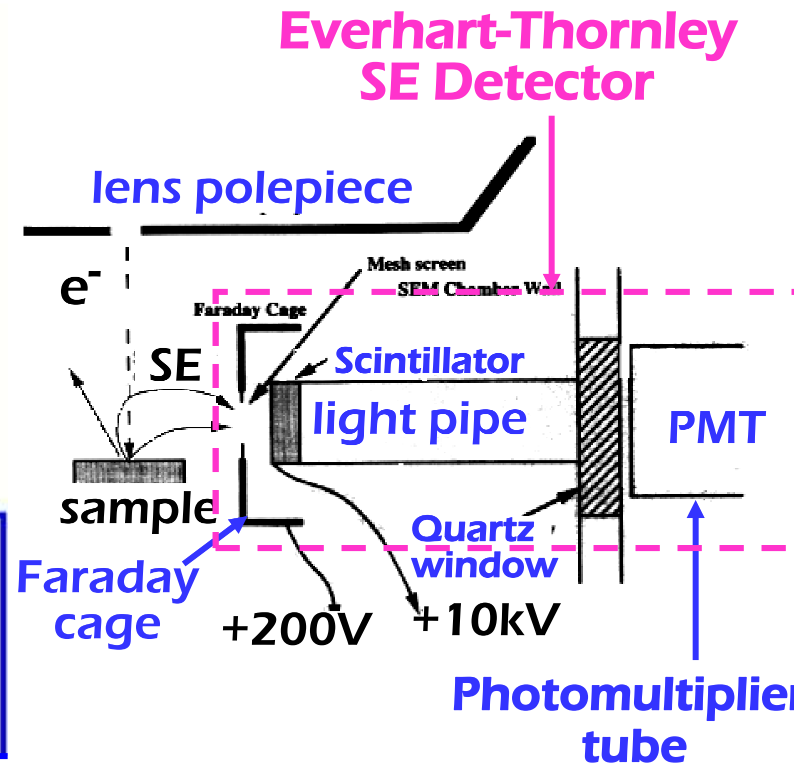
Topographical Contrast





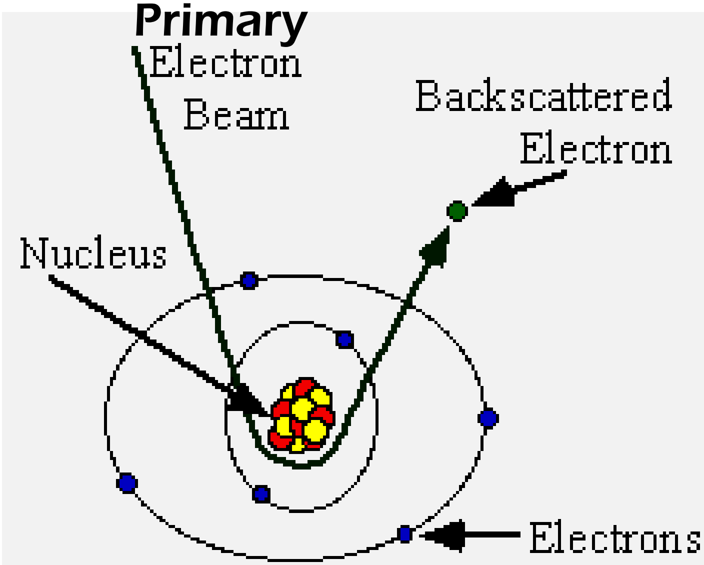


Topographic contrast arises because **SE generation** depend on the **angle of incidence** between the beam and sample. Thus local variations in the angle of the surface to the beam (**roughness**) affects the numbers of electrons leaving from point to point. The resulting "**topographic contrast**" is a function of the **physical shape** of the specimen.

http://www.youtube.com/watch?v=IrXMIghANbg at ~2:10-3:30 (3:09~3:18)
https://www.youtube.com/watch?v=GY9IfO-tVfE at~4:35-6:00
http://www.youtube.com/watch?v=VWxYsZPtTsI at~3:00-3:20

http://www.youtube.com/watch?v=Mr9-1Sz_CK0 at~3:52-4:26

Backscattered Electrons (BSE)



BSE image from flat surface of an Al (Z=13) and Cu (Z=29) alloy

BSE are produced by **elastic interactions** of beam electrons with nuclei of atoms in the specimen and they have **high energy** and **large escape depth.**

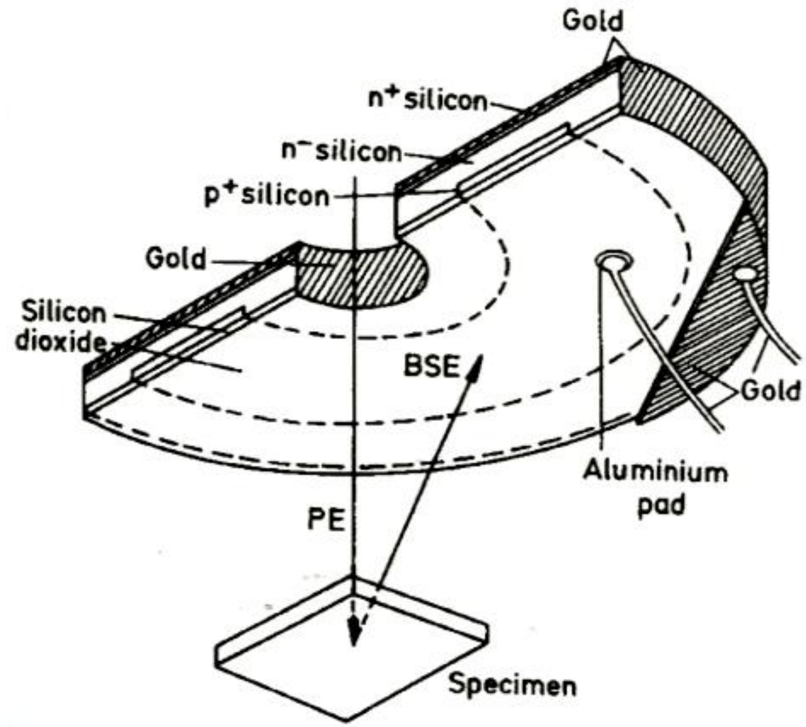
BSE yield: $h = n_{BS}/n_B$ ~ function of atomic number, **Z**

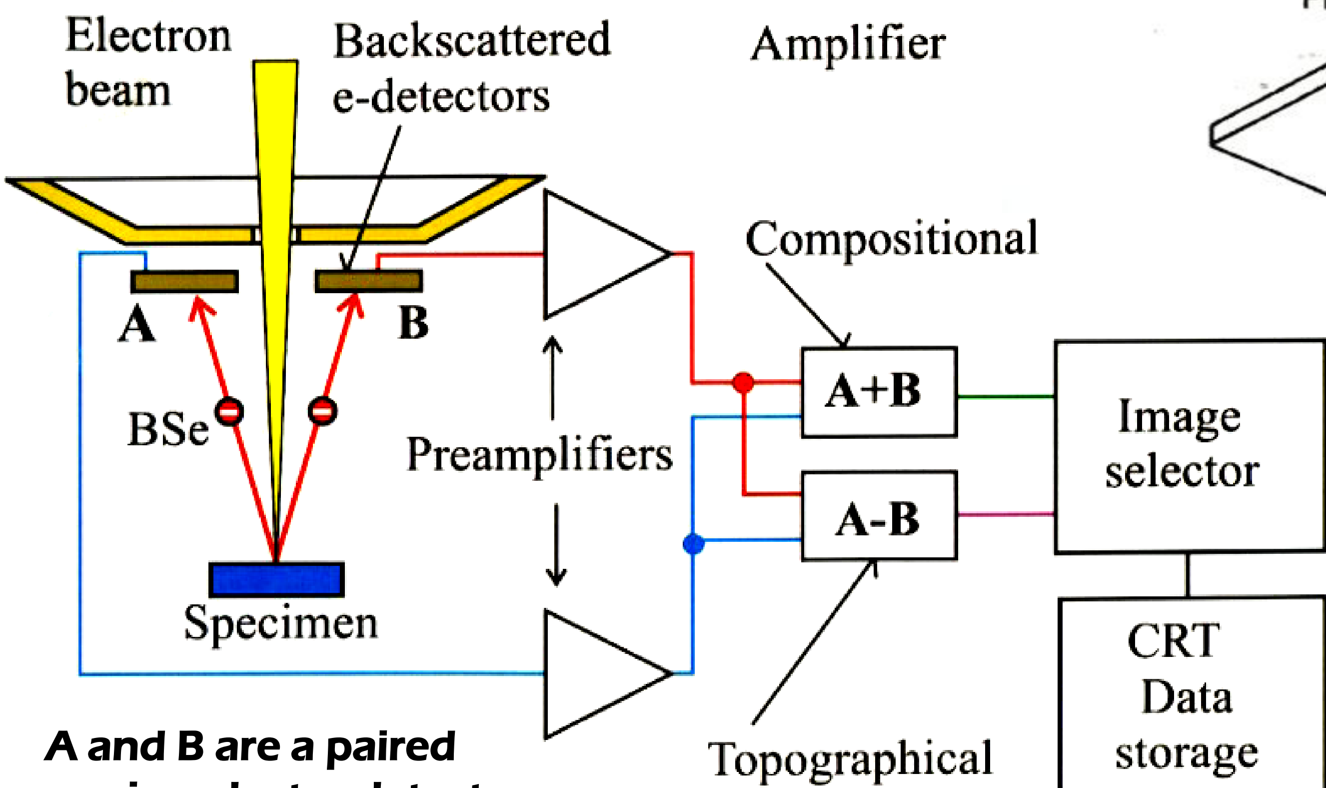
BSE images show characteristics of **atomic number contrast**, i.e., high average Z appear brighter than those of low average Z. **h** increases with **tilt.**

http://www.youtube.com/watch?v=VWxYsZPtTsI at ~3:20-3:35
https://www.youtube.com/watch?v=F9qwfYwwCRM at~1:14-1:34

Semiconductor Detector for Backscattered Electrons

High energy electrons produce electron-hole pairs (charge carriers) in the semiconductor, and generate a current pulse under an applied potential.





A and B are a paired semiconductor detectors

https://www.youtube.com/watch?v=F9qwfYwwCRM at~4:25-4:50

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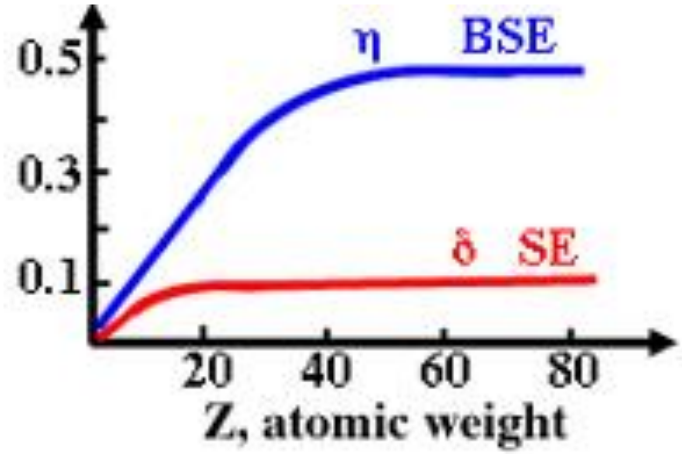
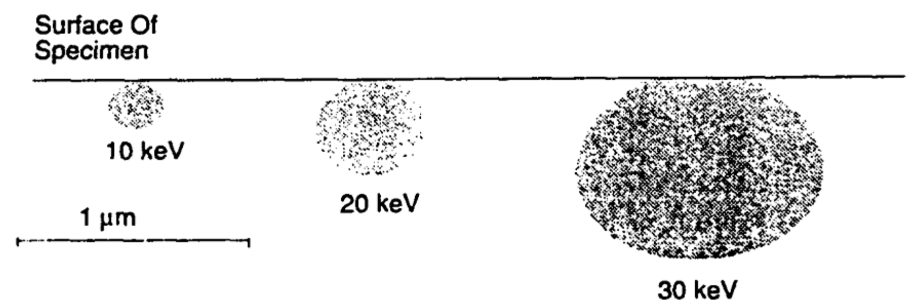
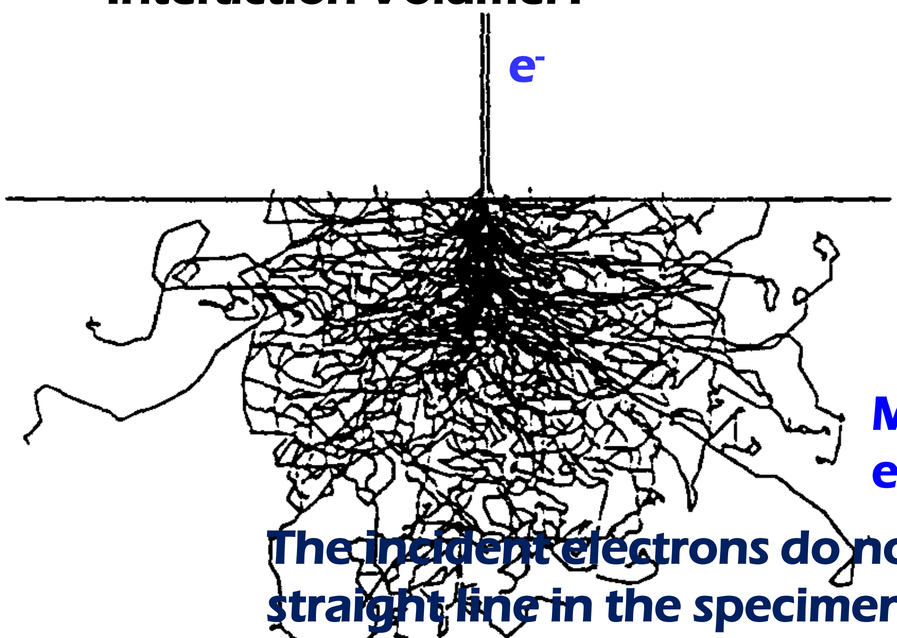
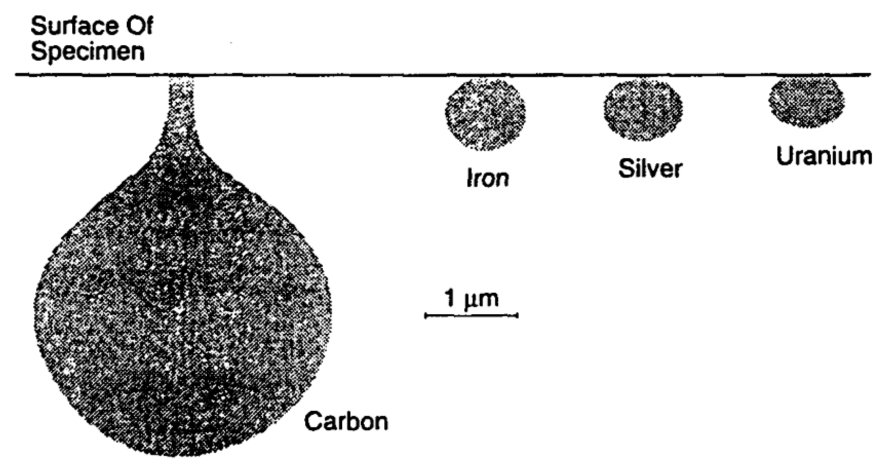
Effect of Atomic Number, Z, on BSE and SE Yield





Interaction Volume: I





Monte Carlo simulations of 100 electron trajectories

The incident electrons do not go along a straight line in the specimen, but a zig-zag path instead.

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Escape Volume of Various Signals

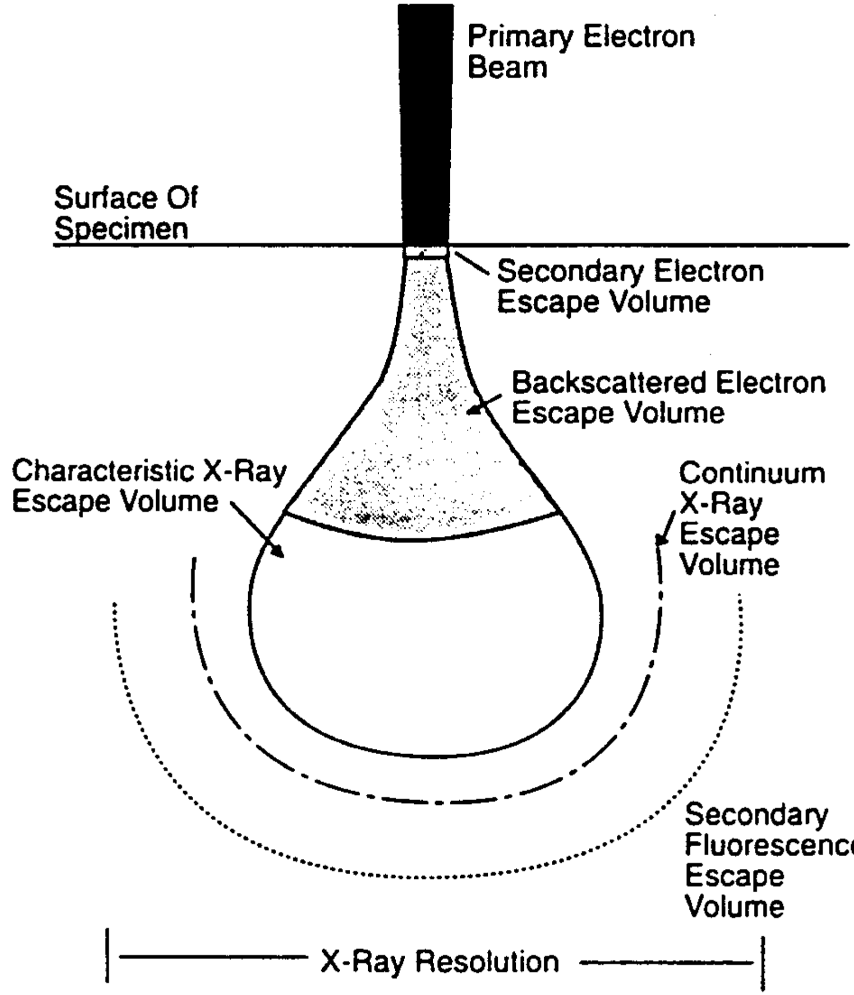
- The incident electrons interact with specimen atoms along their path in the specimen and generate various signals.
- Owing to the **difference in energy** of these signals, their **'penetration depths'** are different
- Therefore **different signal** observable on the specimen surface comes from **different parts of the interaction volume**
- **The volume responsible for the respective signal** is called the **escape volume of that signal**.

Escape Volumes of Various Signals

If the diameter of primary electron beam is ~5nm

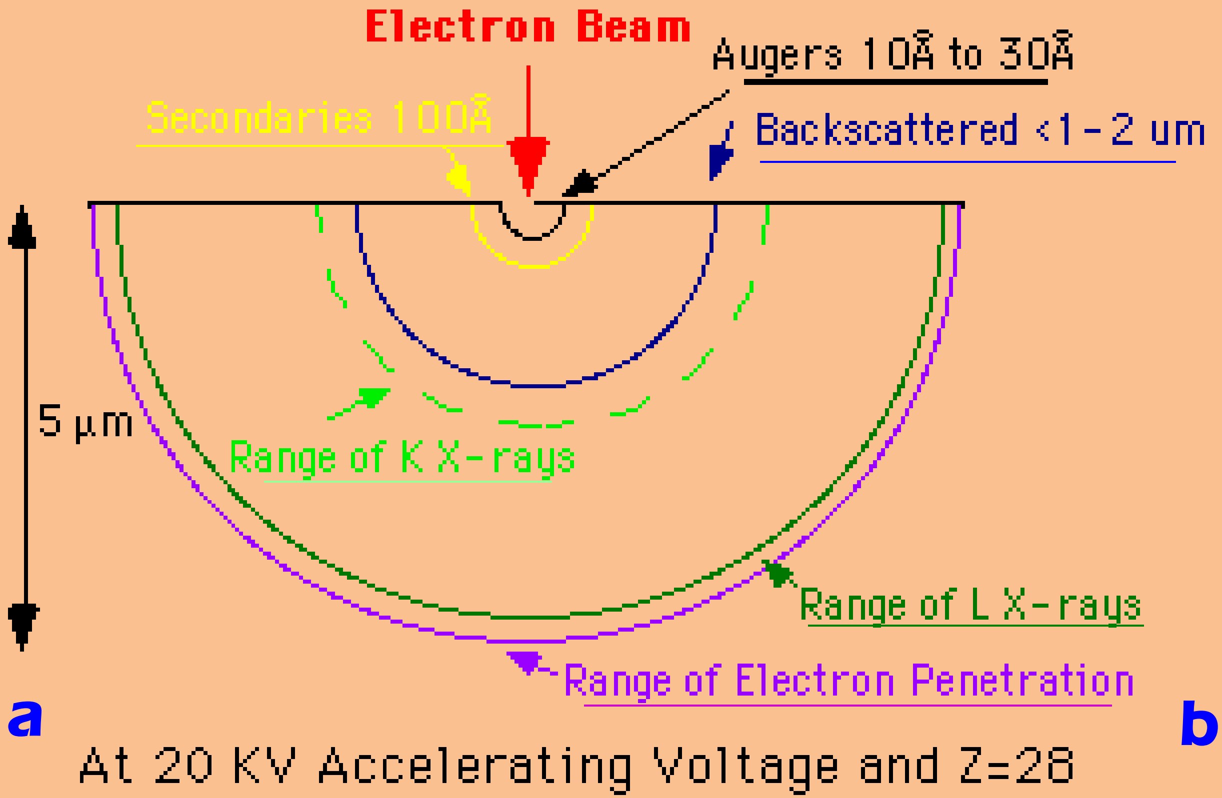
- **Dimensions of escape zone of**

- **Secondary electron:** diameter~**10nm**; depth~**10nm**
- **Backscattered electron:** diameter~**1μm**; depth~**1μm**
- **X-ray**: from the whole interaction volume, i.e., ~**5μm** in diameter and depth

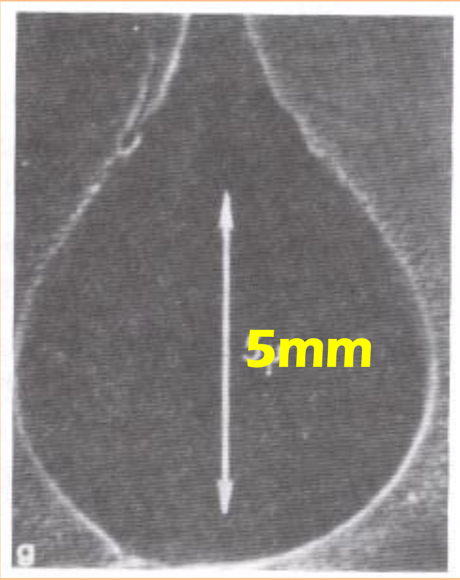


http://www.youtube.com/watch?v=VWxYsZPtTsI ~3:38-4:10

Electron Interaction Volume



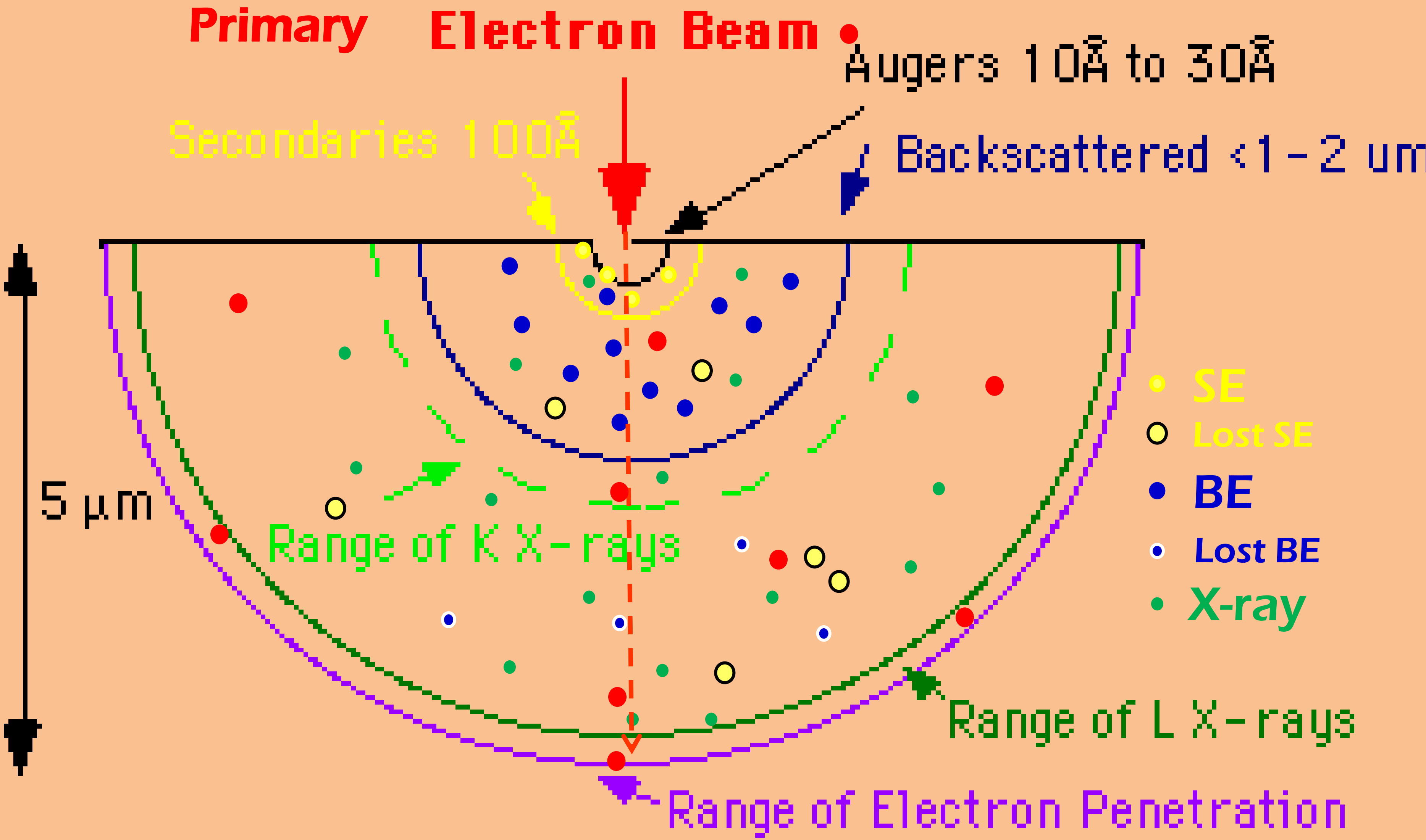
Pear shape



a. Schematic illustration of electron beam interaction in Ni

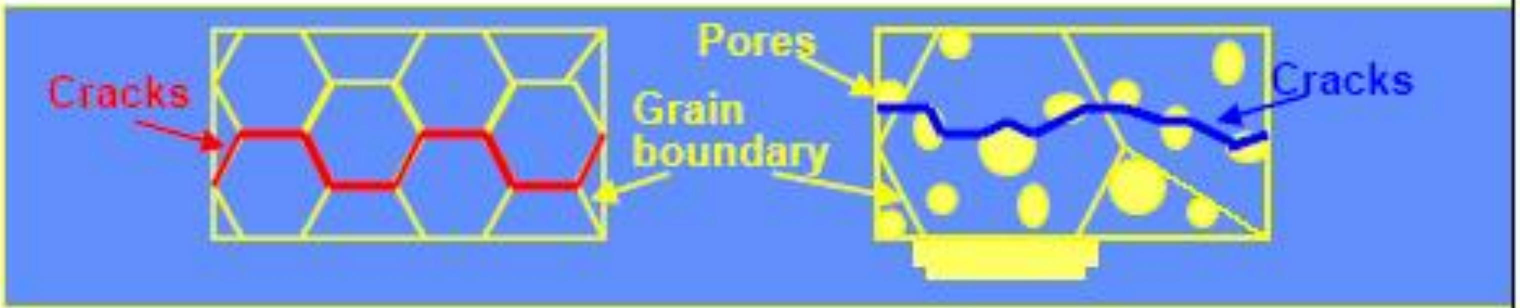
b. Electron interaction volume in polymethylmethacrylate (plastic-a low Z matrix) is indirectly revealed by etching

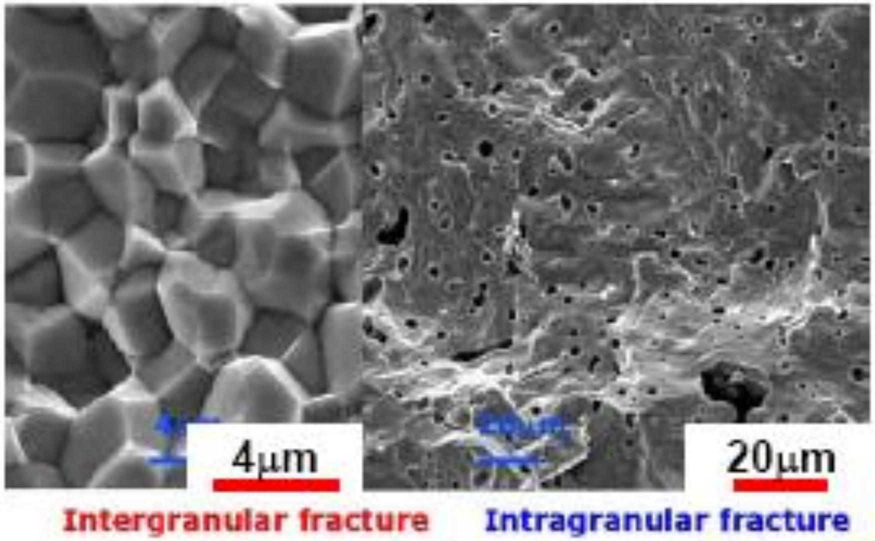
Escape Volumes of Various Signals



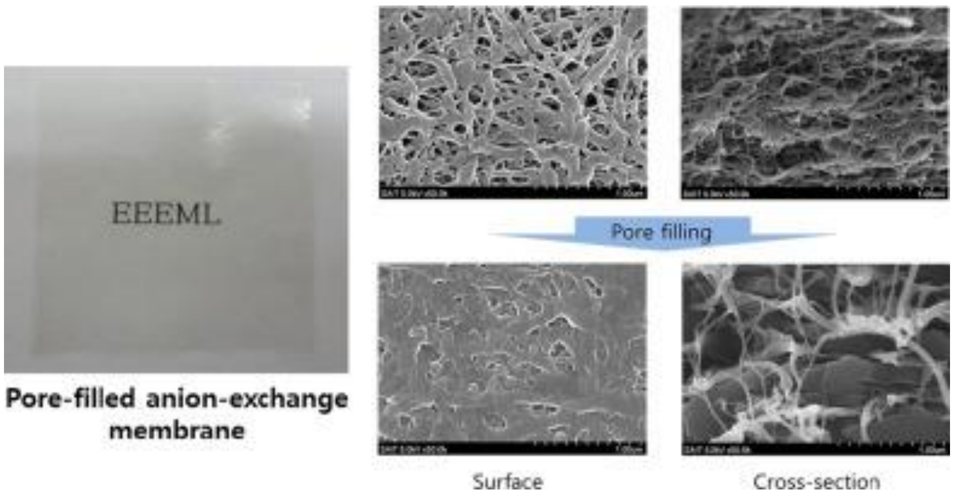
At 20 KV Accelerating Voltage and Z=28

e.g. Identification of Fracture Mode





SEM micrographs of fractured surface of two $BaTiO_3$ samples.



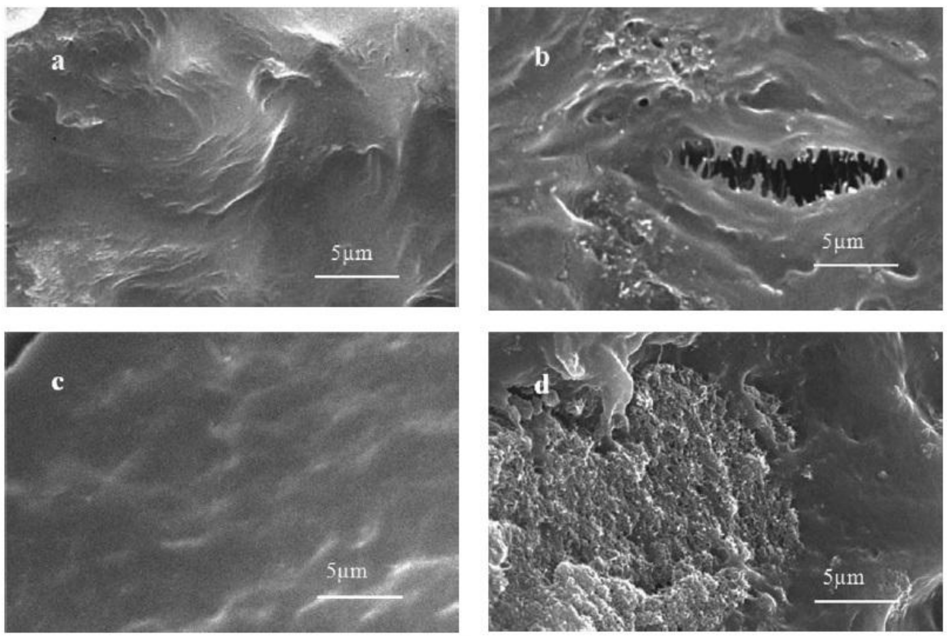
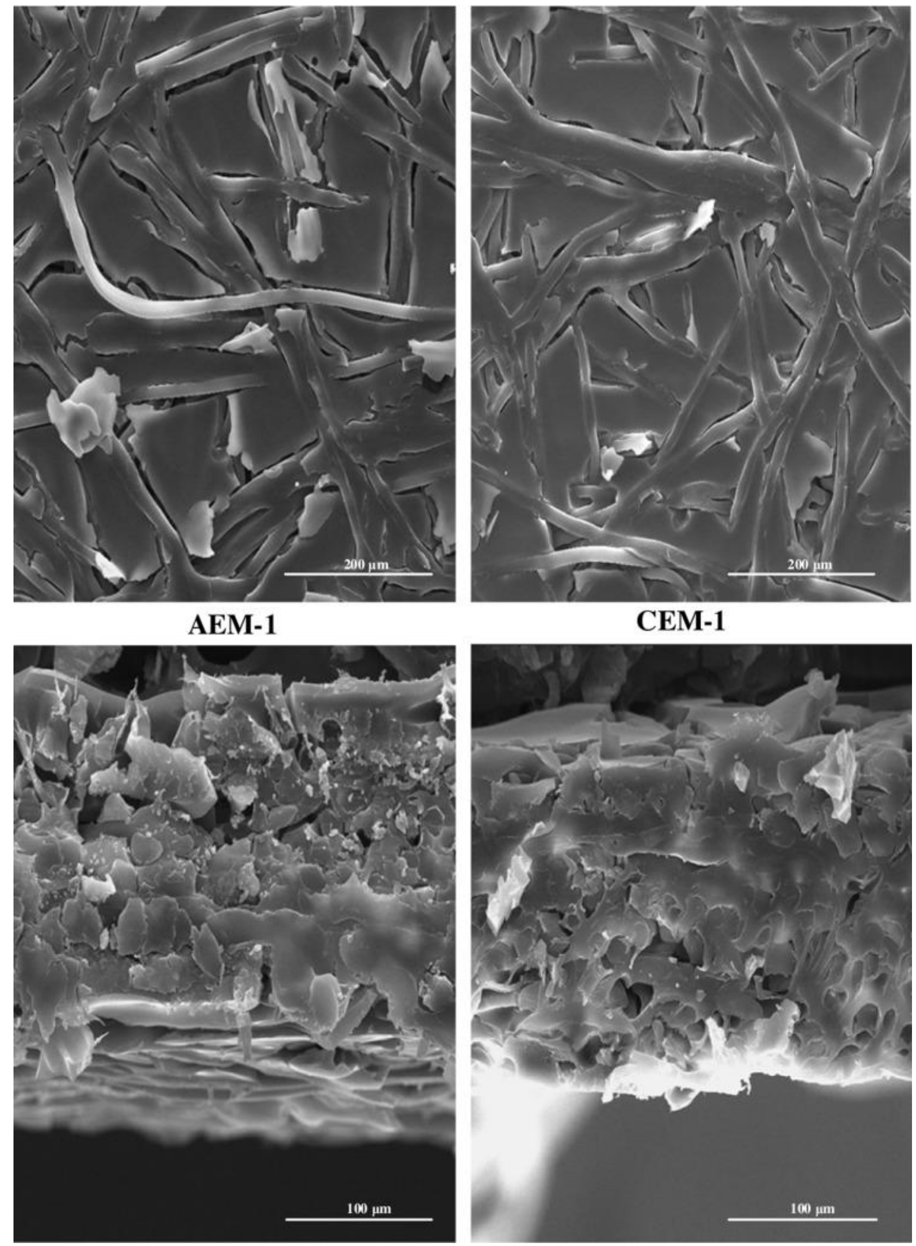


Fig. 1. SEM images of fracture surfaces (a) PMMA/PEO-A and (b) F-MWNTs (6 wt %)/PMMA/PEO-A, (c) PMMA/PEO-B and (d) F-MWNTs (6 wt %)/PMMA/PEO-B composite blends.



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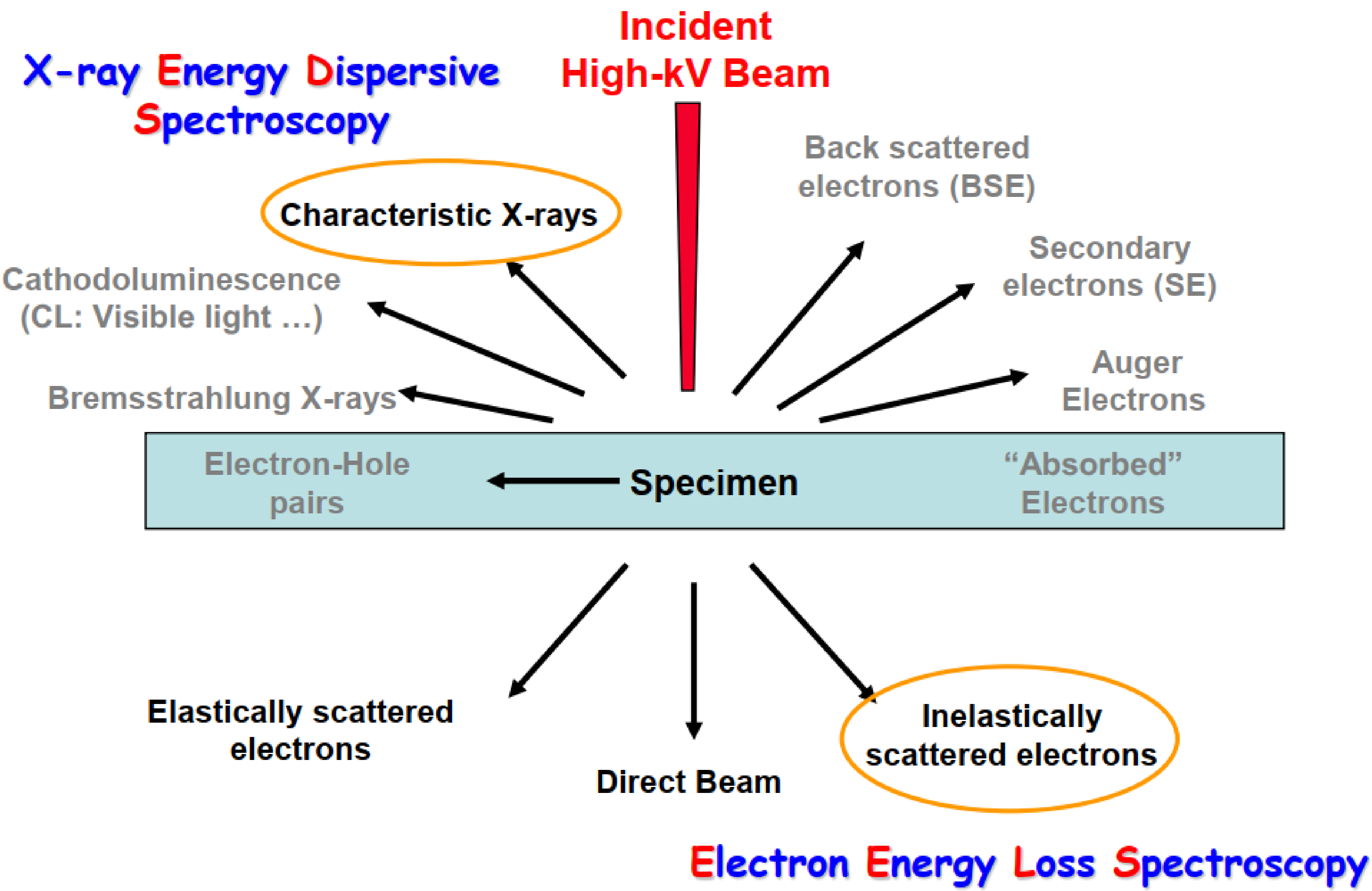
Energy Dispersive Systems (EDX)



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Basics of EDX

a) Generation of X-ray
b) Mechanism of EDX
c) Detection
   Si(Li) Detector, EDS (<-> WDS)
d) Quantification
   EDX in SEM, Interaction volume
   Monte-Carlo-Simulations
   EDX in TEM
e) Examples

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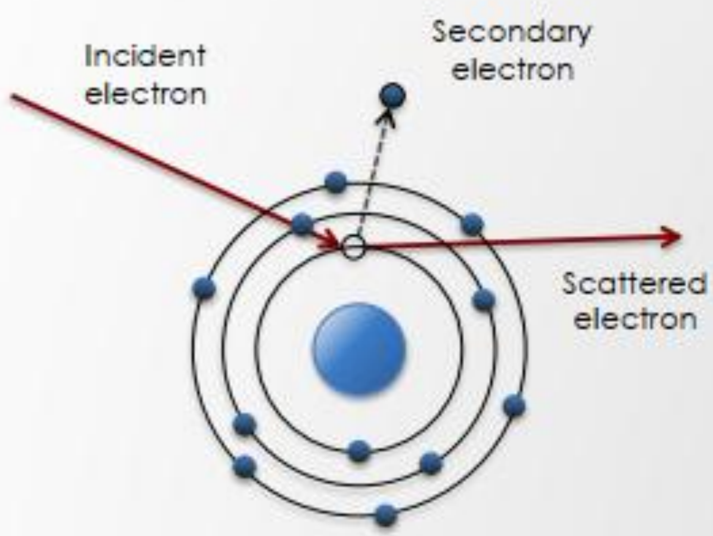
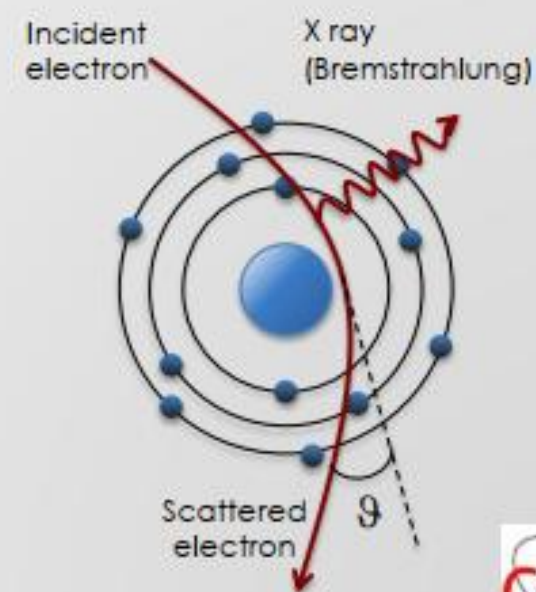
Effect of Inelastic Scattering

- An incident electron ejects a bound electron and scatters with an energy lowered by the electron bound energy.
- The ejected electrons having low energies (5-50 eV) are called secondary electrons (SE) and carry information about the surface topography
- The incident electron can be scattered by Coulomb interaction with the nucleus
- In the case of inelastic interaction, there is **energy transfer**, and the target atom can be ionized





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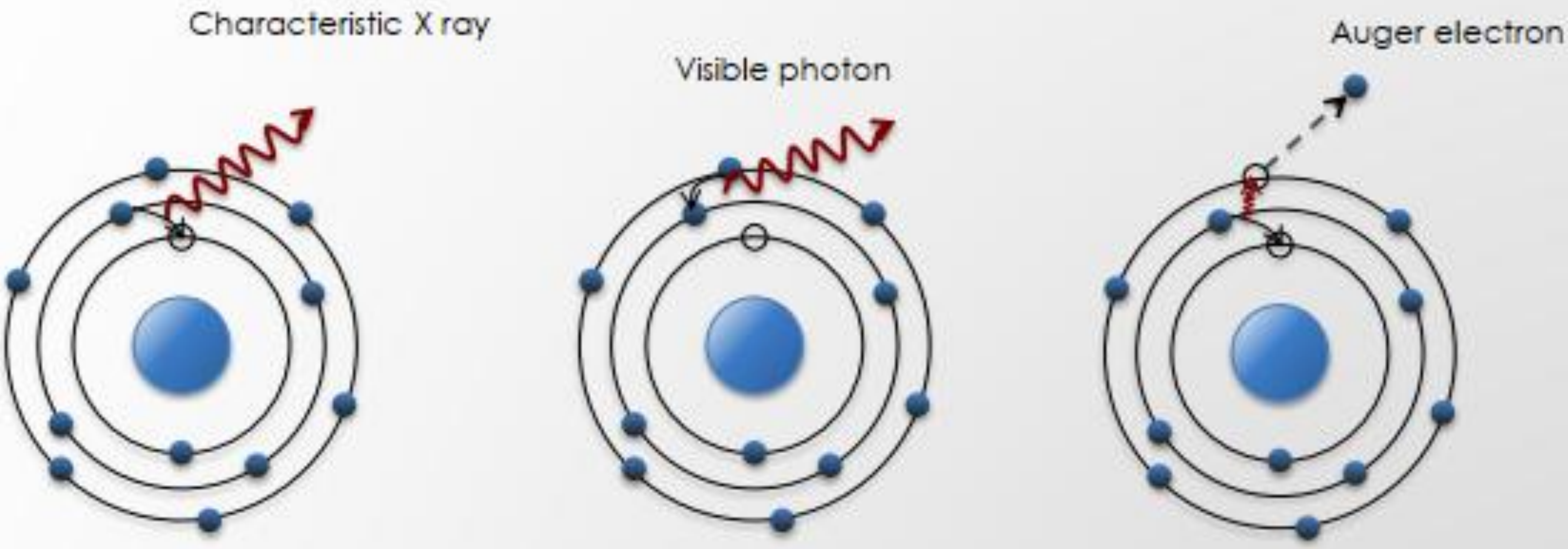
Relaxation processes of the excited state



X-ray generation

X ray energy characteristic interorbital electron transitions and thus of the element

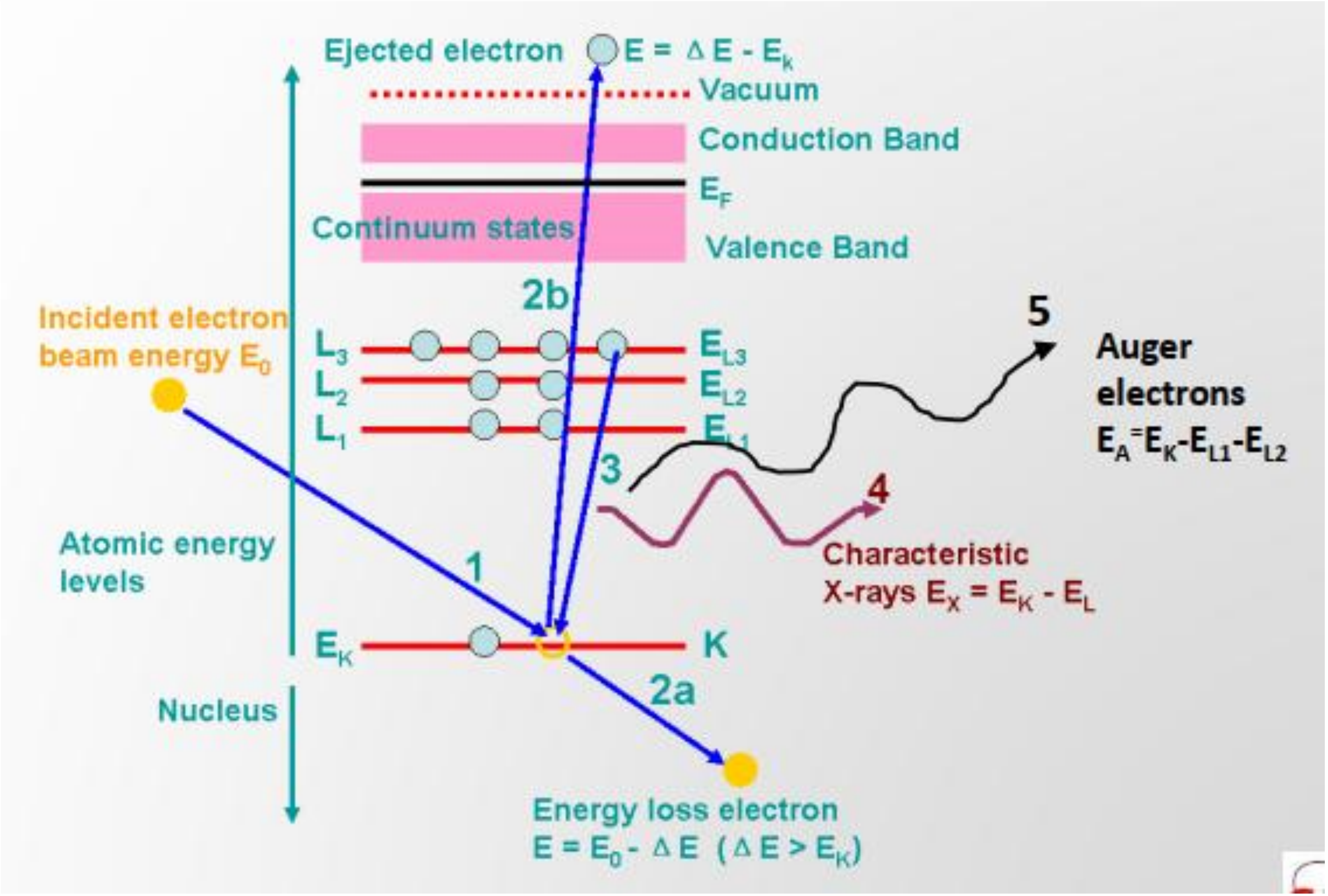
Fluorescence

Low transition energy, visible or UV photon is emitted

Emission Auger

The relaxing process interacts with an electron with a characteristic energy

Generation of X-rays



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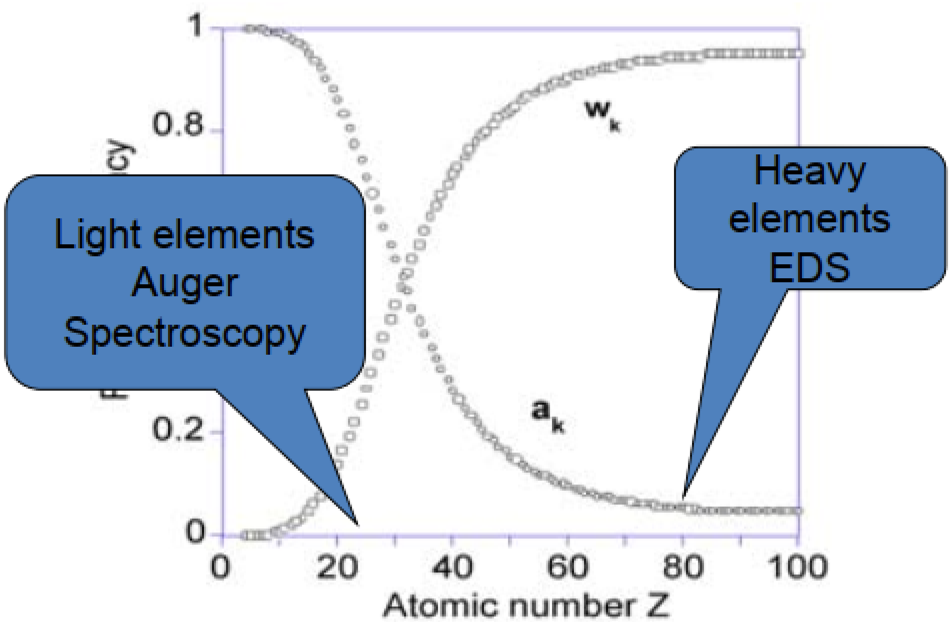
Efficiency of X-ray generation

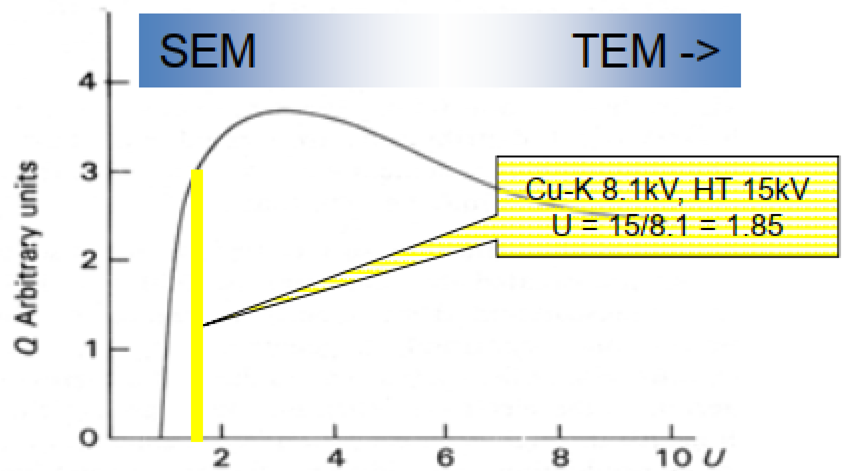
Relative efficiency of X-ray and Auger emission vs. atomic number for K lines



Light element atoms return to fundamental state mainly by Auger emission. For that reason, their K-lines are weak. In addition their low energy makes them easily absorbed.

Ionization cross-section vs. overvoltage U=Eo/Eedge

(electron in -> X-ray out)



To ionized the incident electron MUST have an energy larger than the core shell level U>1. To be efficient, it should have about twice the edge energy U>2.

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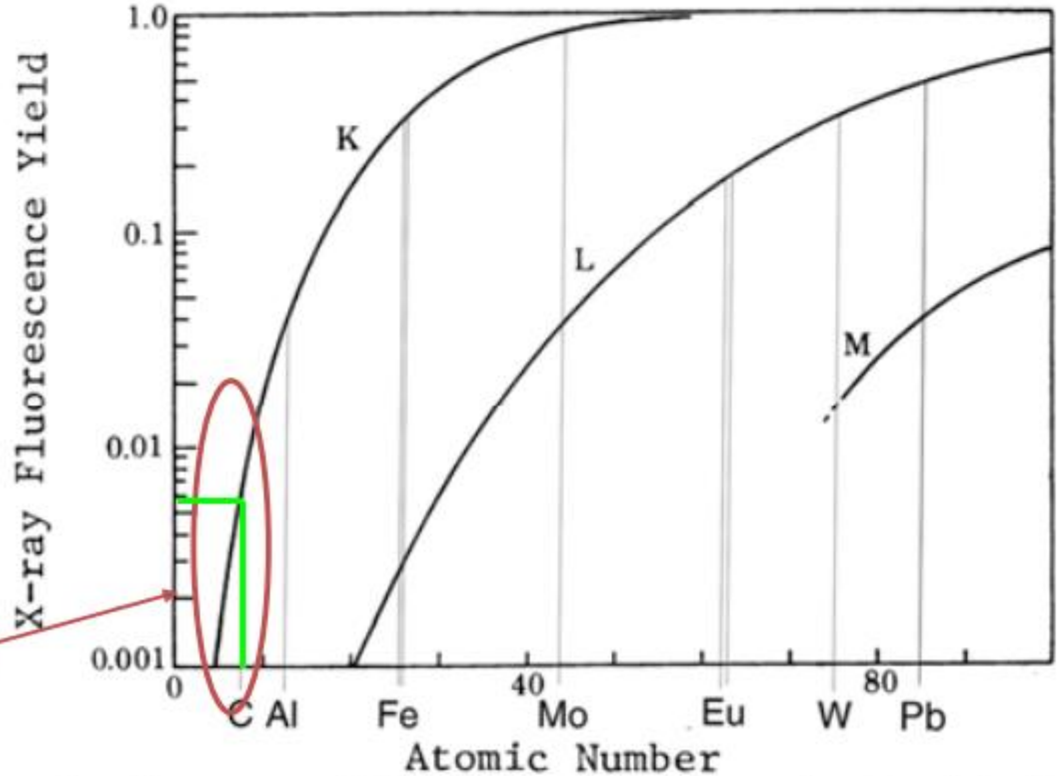
X-ray production vs. atomic number Z

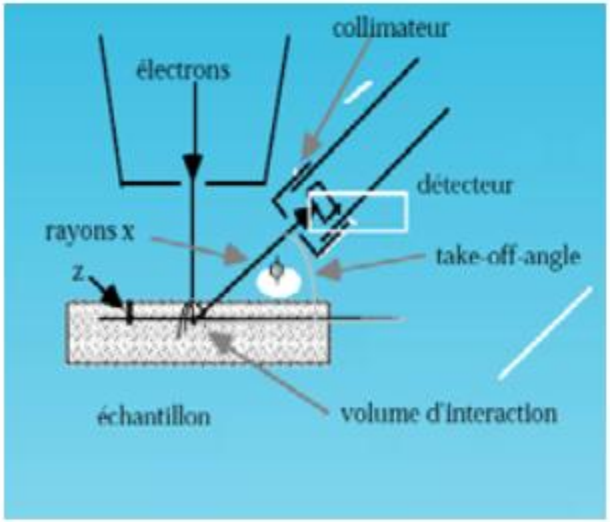
Low efficiency for light elements!



X-ray fluorescence yield for *K*-, *L*-, and *M*-shells, as a function of atomic number.

Obtaining EDX Spectrums

- A high-energy beam of charged particles is focused into the sample
- Ground state (unexcited) electrons in sample are stimulated
- Electrons are excited from lower energy shells to higher energy shell
- The difference in energy between the shells may be released in the form of an X-ray
- The number and energy of the X-rays emitted from a specimen can be measured by an energy dispersive spectrometer



b) Detection of X-rays (EDX)

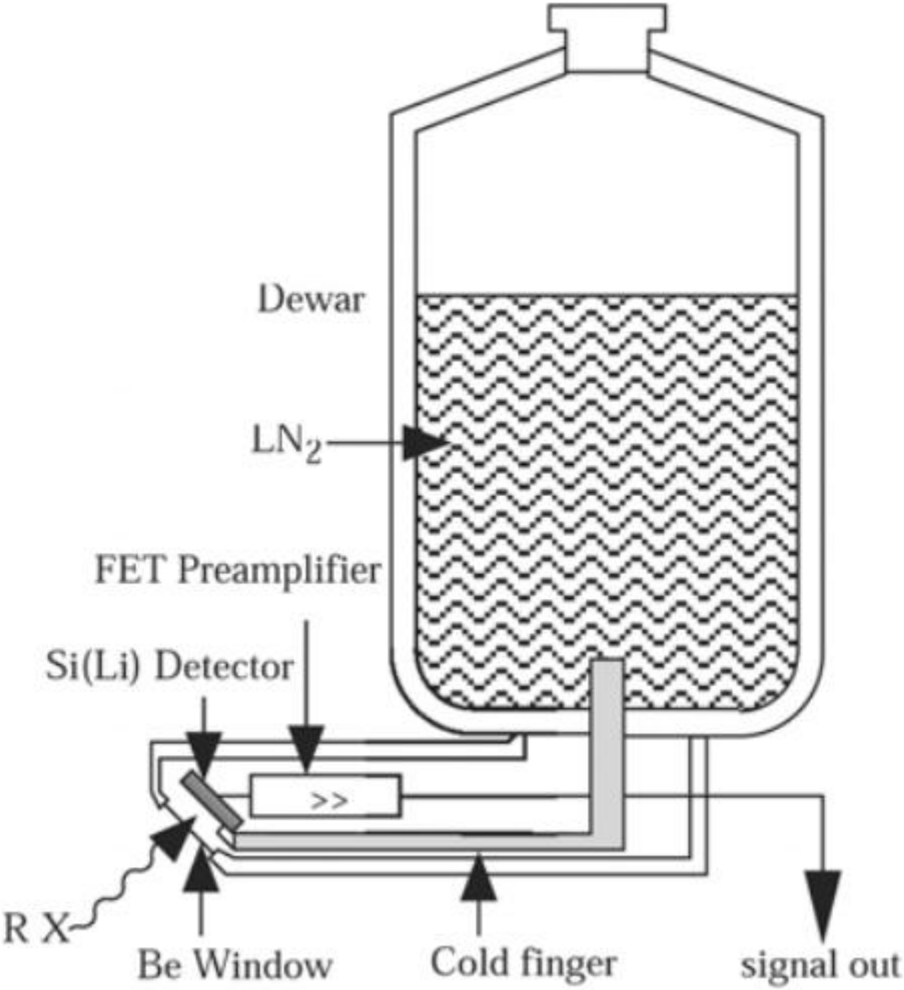


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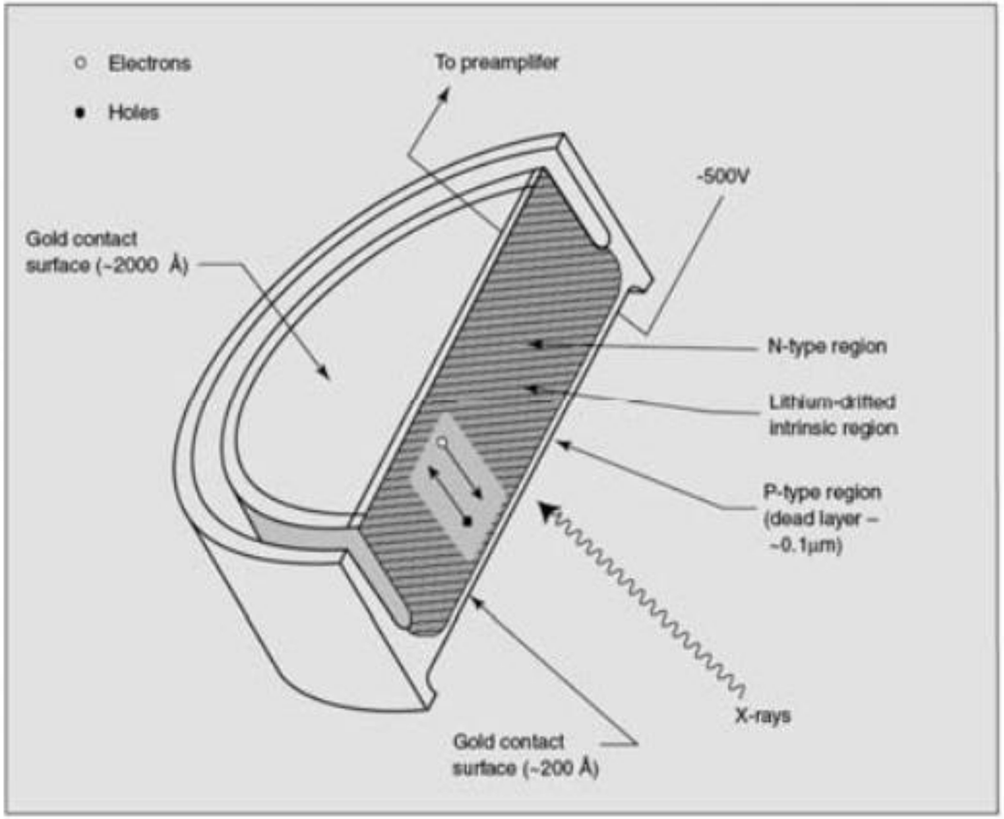
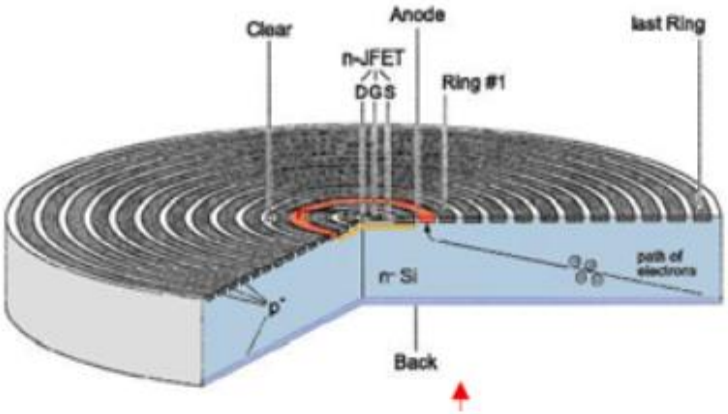
Figure 4-2. Cross section of a typical lithium-drifted silicon detector. X-rays create electron-hole pairs in the intrinsic region of the semiconductor; these charge carriers then migrate to the electrodes under the influence of an applied bias voltage.



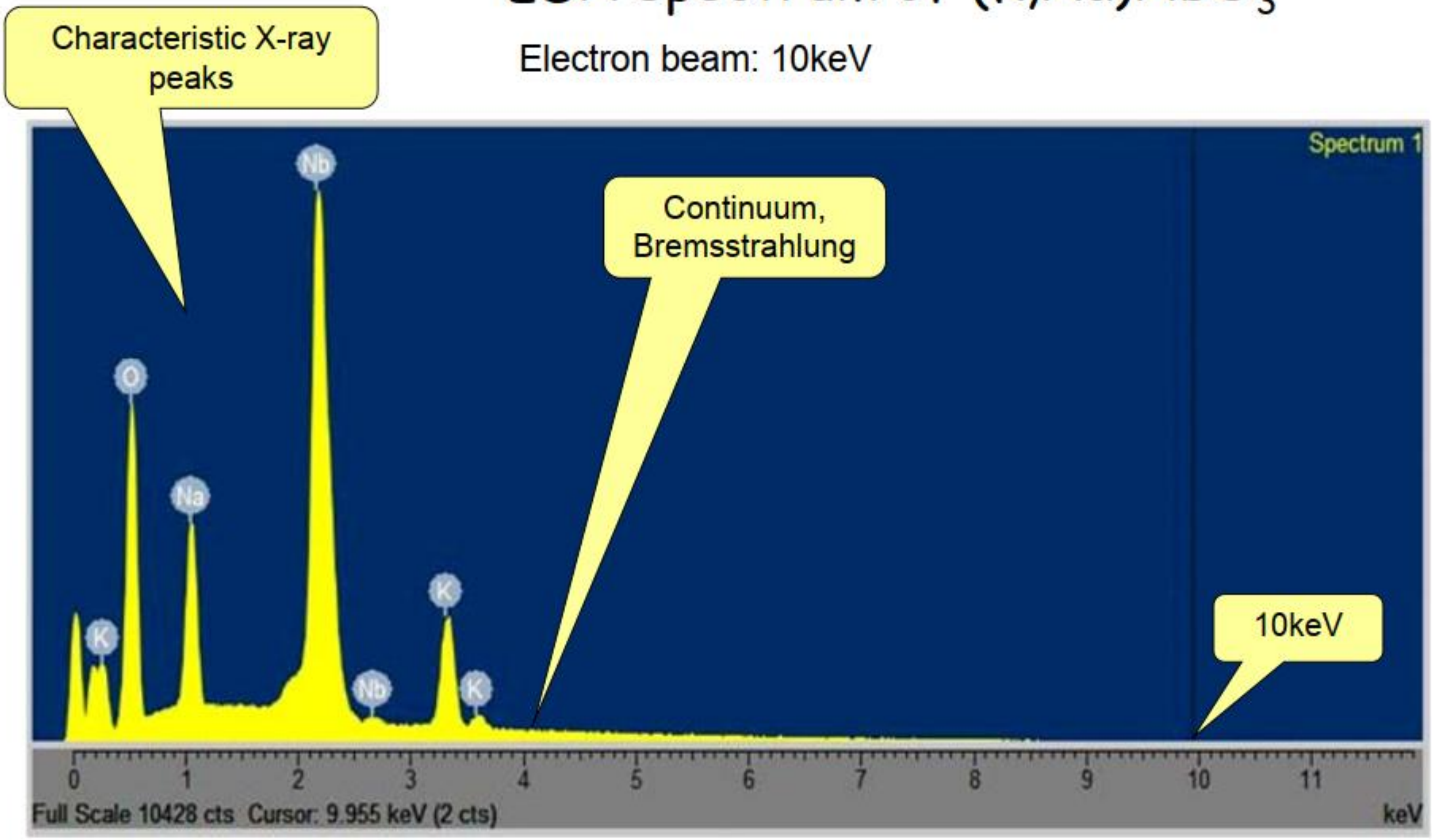
Right: Si(Li) detector
Cooled down to liquid nitrogen temperature



modern silicon drift (SDD) detector:
no LN cooling required

EDX spectrum of (K,Na)NbO_3

Electron beam: 10keV

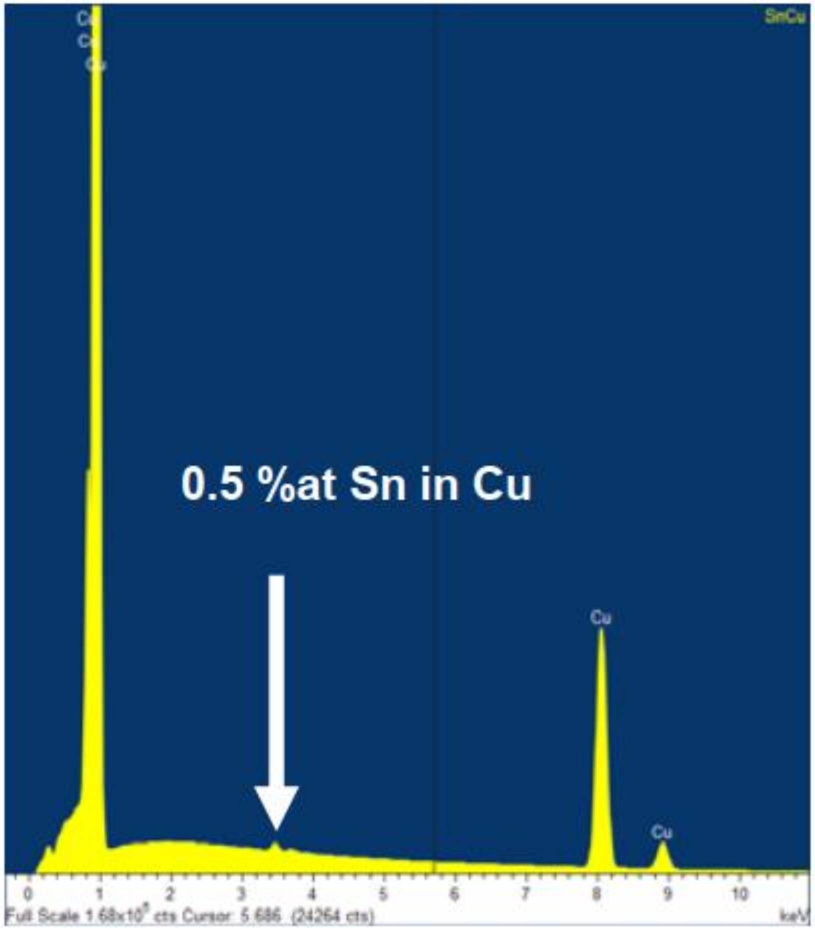


Detection limit EDS in SEM

Acquisition under best conditions

- Flat surface without contamination (no Au coating, use C instead)
- Sample must be homogenous at the place of analysis (interaction volume !!)
- Horizontal orientation of the surface
- High count rate
- Overvoltage U=Eo/Ec >1.5-2

For acquisition times of 100sec. :
detection of ~0.5at% for almost all elements



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c) Quantification

Yes, but.....

First approach:
compare X-ray intensity with a standard (sample with known concentration, same beam current of the electron beam)

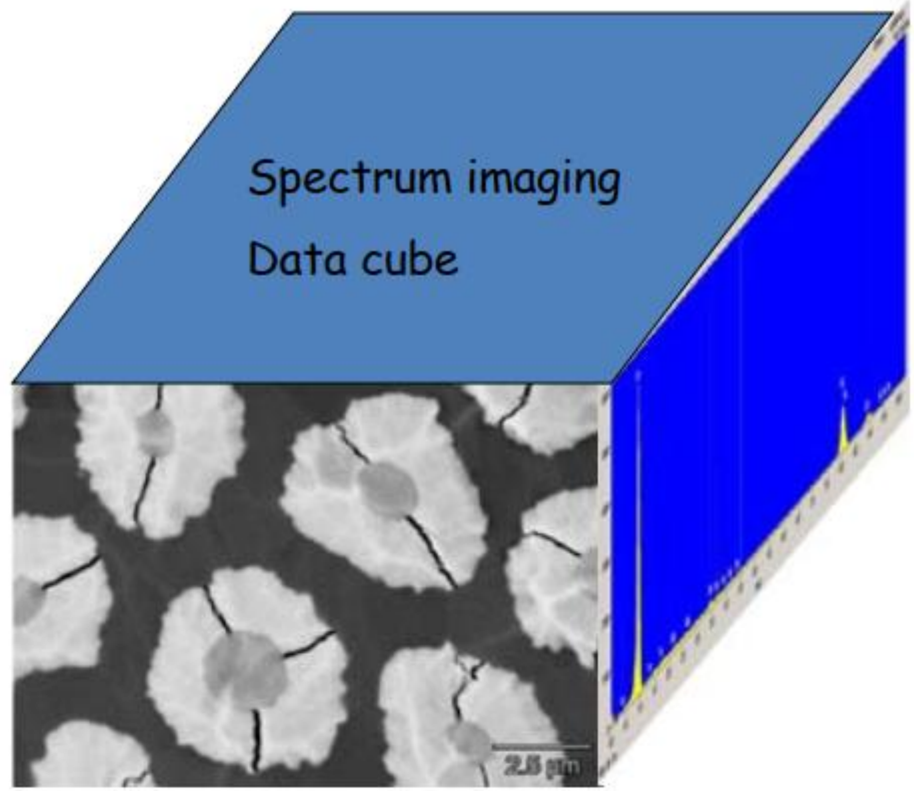
c_i: wt concentration of element i

I_i: X-ray intensity of char. Line

k_i: concentration ratio

$$\frac{c_i}{c_i^{std}} = \frac{I_i}{I_i^{std}} = k_i$$

EDX mapping

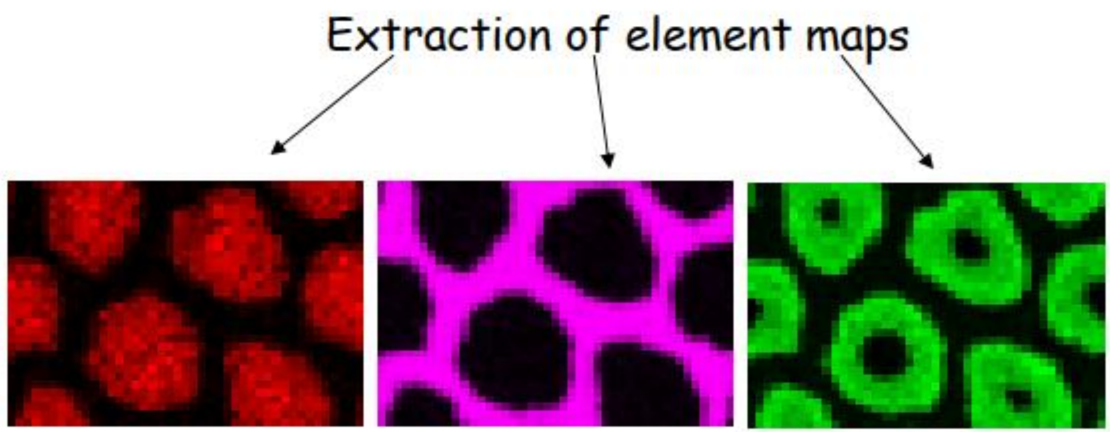


Data cube:

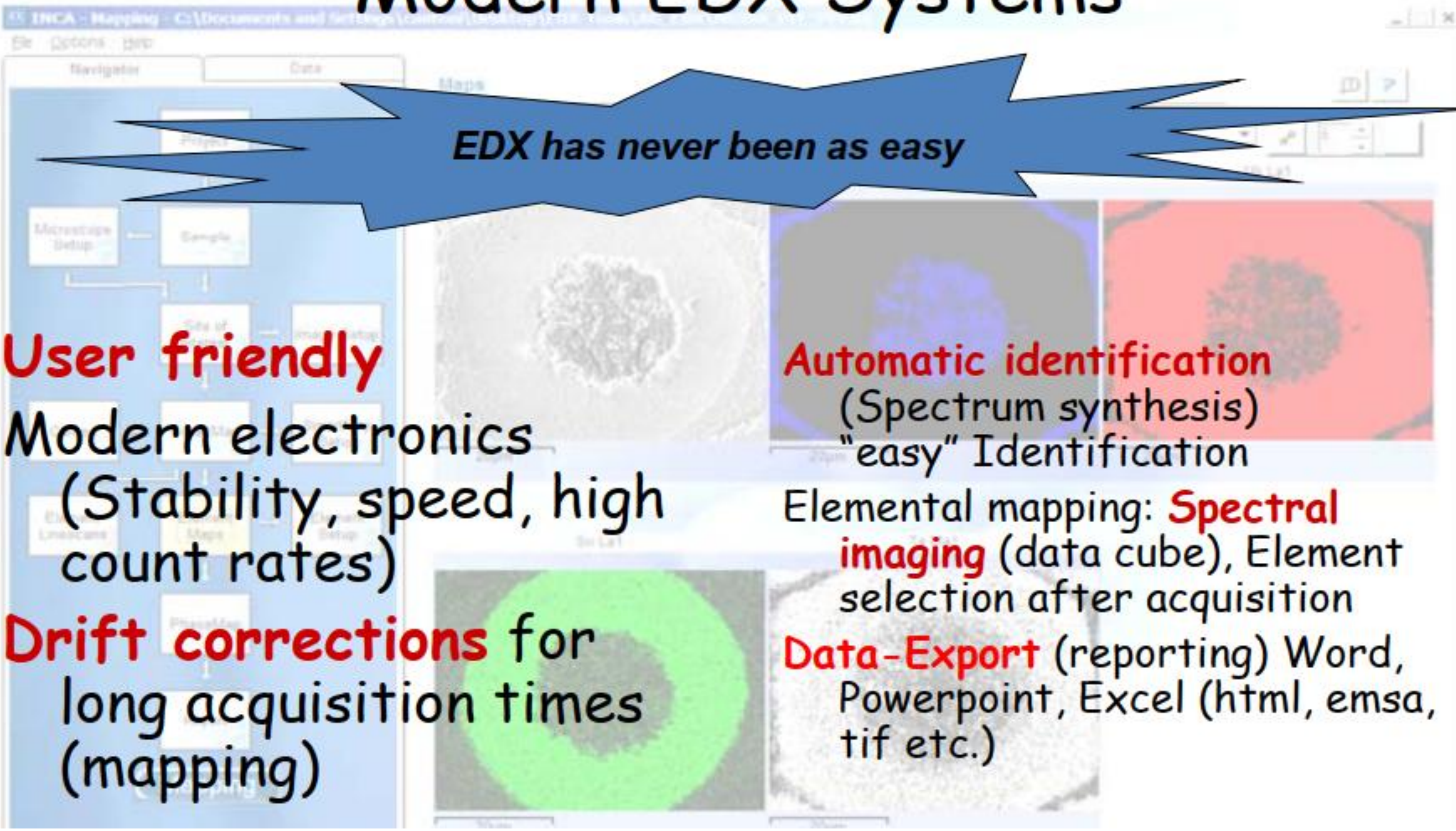
In each pixel a spectrum is recorded and stored

Post-acquisition Analysis:

Each spectrum can be analyzed and quantified off-line



Modern EDX Systems



EDX has never been as easy

User friendly

Modern electronics
(Stability, speed, high count rates)

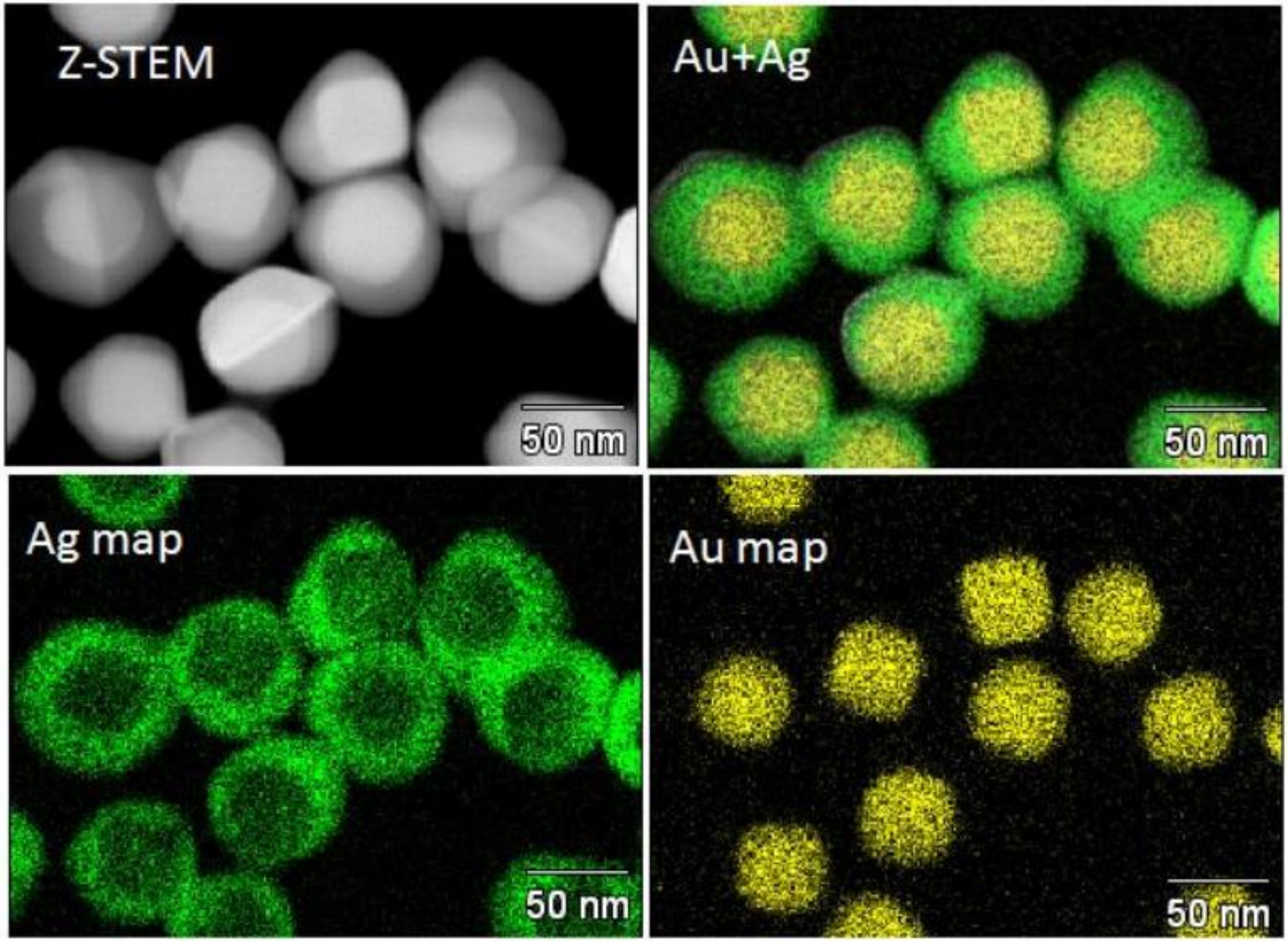
Drift corrections for long acquisition times (mapping)

Automatic identification
(Spectrum synthesis)
"easy" Identification

Elemental mapping: **Spectral imaging** (data cube), Element selection after acquisition

Data-Export (reporting) Word, Powerpoint, Excel (html, emsa, tif etc.)

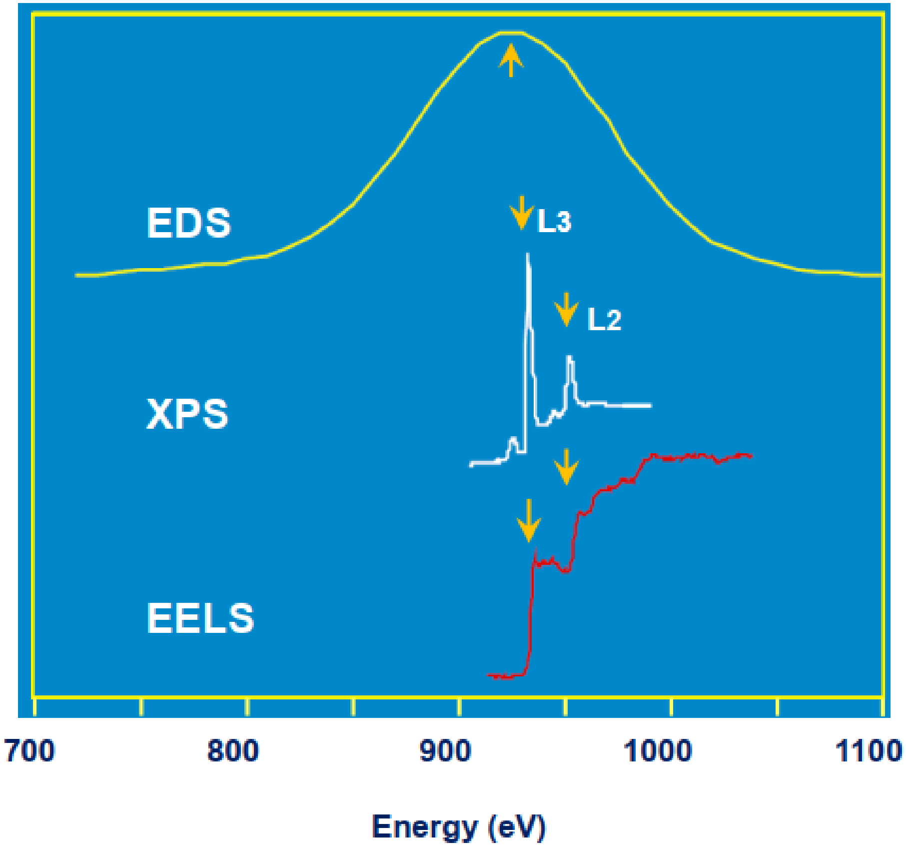
Ag-Au Core-Shell : Elemental (EDS) Mapping



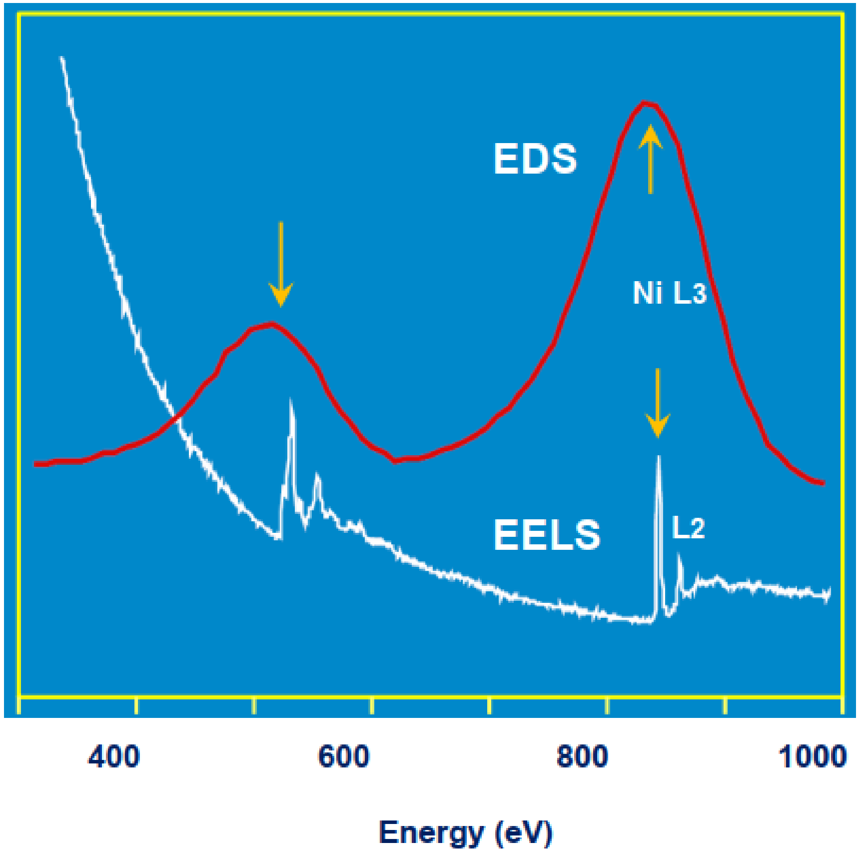
Science 337, 954 (2012)

Experimental XEDS, XPS, & EELS

Copper L shell



NiO: O K-shell and Ni L shell



Energy resolution, Spatial resolution, Elements resolving

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Comparing SEM and TEM

	TEM	SEM
Electron Beam	Broad, static beams	Beam focused to fine point; sample is scanned line by line
Voltages Needed	TEM voltage ranges from 60-300,000 volts	Accelerating voltage much lower; not necessary to penetrate the specimen
Interaction of the beam electrons	Specimen must be very thin	Wide range of specimens allowed; simplifies sample preparation
Imaging	Electrons must pass through and be transmitted by the specimen	Information needed is collected near the surface of the specimen
Image Rendering	Transmitted electrons are collectively focused by the objective lens and magnified to create a real image	Beam is scanned along the surface of the sample to build up the image

Outline

- Motivation
- History of AFM
- Working Principle of AFM
- Instrumental different parts & their functions
- Modes of operation of AFM
- Forces & Force Distance curve
- Applications of AFM in Polymers

Motivation

Digitally image of a topographical surface
Determine the roughness of a surface sample or to measure the thickness of a crystal growth layer
Image of a non-conducting surfaces such as proteins and DNA
Study the dynamic behavior of living and fixed cells

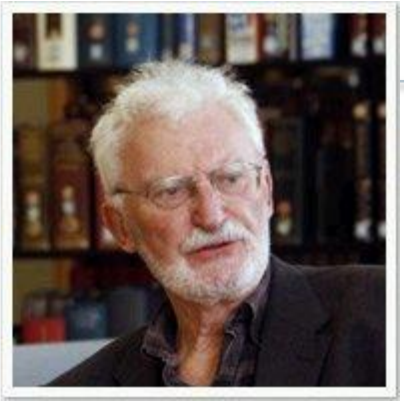
AFM

- *no requirements*
- *atomic resolution possible but hard to get*
- *local electrical information independent of topography*
- *Contact not well defined*
- *Also mechanical information*

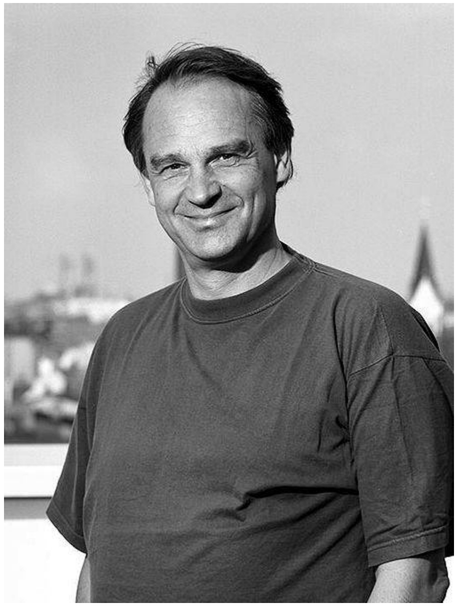
STM

- *sufficiently conductive sample*
- *atomic resolution standard*
- *local electrical information and topography not separable*
- *defined tunneling via single atom*
- *xxx*

History of AFM

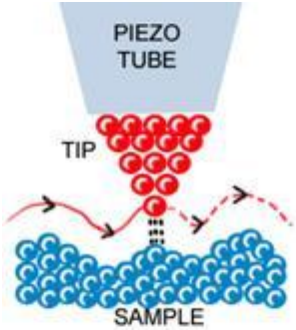


Heinrich Rohrer



Gerd Binnig

- Development of Scanning tunneling microscopy (STM) in 1981 earned its inventors, Gerd Binng and Heinrich Rohrer (at IBM Zürich), the Nobel Prize in Physics in 1986
- Based on the above work Binnig, Quate and Gerber invented the first AFM in 1986



https://www.azonano.com/article.aspx?ArticleID=1725

Working Principle of AFM

- The physical parameter probed is a force resulting from different interactions.
- The origin of these interactions can be ionic repulsion, van der Waals, capillary, electrostatic and magnetic forces, or elastic and plastic deformations.
- Thus, an AFM image is generated by recording the force changes as the probe (or sample) is scanned in the *x* and *y* directions.
- The sample is mounted on a piezoelectric scanner, which ensures three-dimensional positioning with high resolution.
- The force is monitored by attaching the probe to a pliable cantilever, which acts as a spring, and measuring the bending or "deflection" of the cantilever.
- The larger the cantilever deflection, the higher the force that will be experienced by the probe.
- Most instruments today use an optical method to measure the cantilever deflection with high resolution; a laser beam is focused on the free end of the cantilever, and the position of the reflected beam is detected by a position-sensitive detector (photodiode).
- AFM cantilevers and probes are typically made of silicon or silicon nitride by micro fabrication techniques.

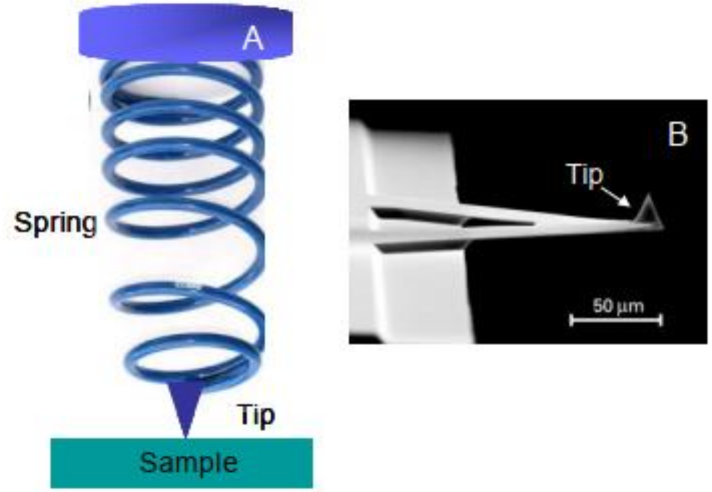


Figure 1. a) Spring depiction of cantilever b) SEM image of triangular SPM cantilever with probe (tip). (Image from MikroMasch)[1]

The probe is placed on the end of a cantilever (which one can think of as a spring). The amount of force between the probe and sample is dependant on the *spring constant* (stiffness) of the cantilever and the distance between the probe and the sample surface. This force can be described using Hooke's Law:

$$F=-k \cdot x$$

F = Force
k = spring constant
x = cantilever deflection

Atomic Force Microscopy (AFM) :
General Components and Their Functions

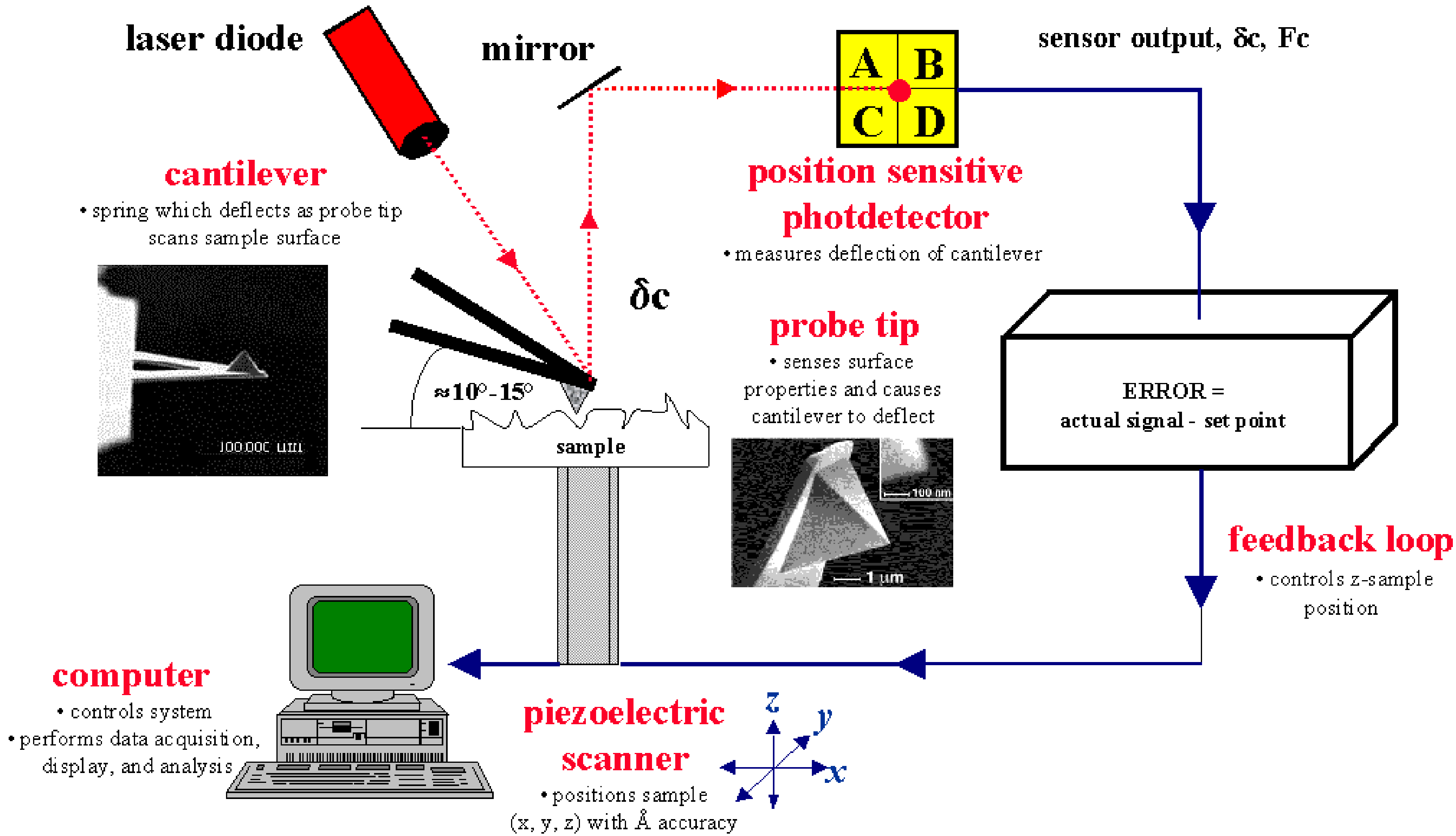


Image from http://web.mit.edu/cortiz/www/afm.gif

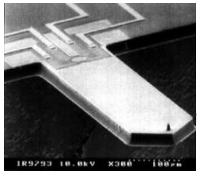
Basic set-up of an AFM

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:
(1) a cantilever with a sharp tip,
(2) a scanner that controls the *x-y-z* position, and
(3) the feedback control and loop.

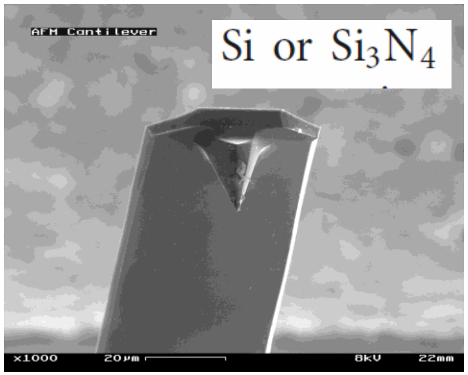
1. *Cantilever with a sharp tip*. The stiffness of the cantilever needs to be less the effective spring constant holding atoms together, which is on the order of 1 - 10 nN/nm. The tip should have a radius of curvature less than 20-50 nm (smaller is better) a cone angle between 10-20 degrees.

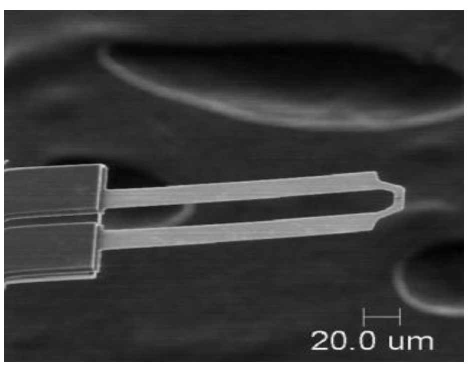
2. *Scanner*. The movement of the tip or sample in the *x*, *y*, and *z*-directions is controlled by a piezo-electric tube scanner, similar to those used in STM. For typical AFM scanners, the maximum ranges for are 80 mm x 80 mm in the *x-y* plane and 5 mm for the *z*-direction.

3. *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 difference signal in the photodiode quadrants, the amount of deflection can be correlated with a height . Because the cantilever obeys Hooke's Law for small displacements, the interaction force between the tip and the sample can be determined.



Micro Cantilever of AFM

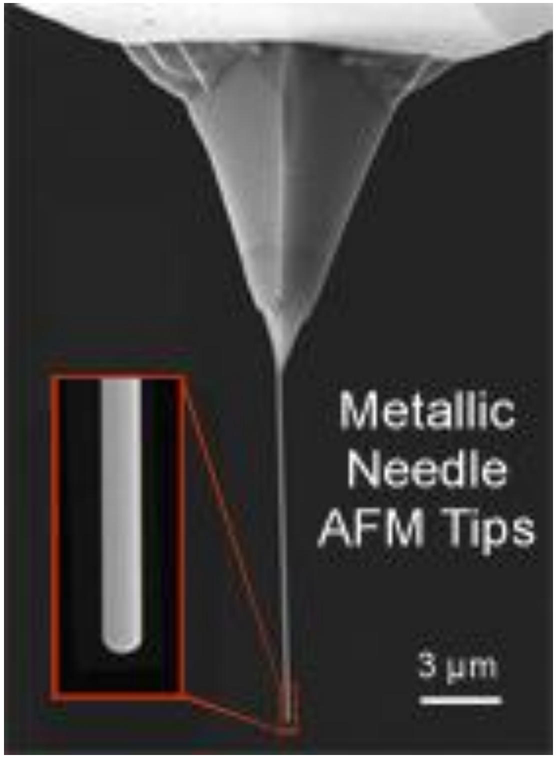




- Tip is made up of Silicon Nitride or Silicon
- Tip radius ranges from 10nm to 2 00nm,Normal radius is 50 nm
- Spring constant is 0.1 to 100 N/m
- Nowadays CNT tips were used for special applications. In this case radius will be 15nm to 10 nm

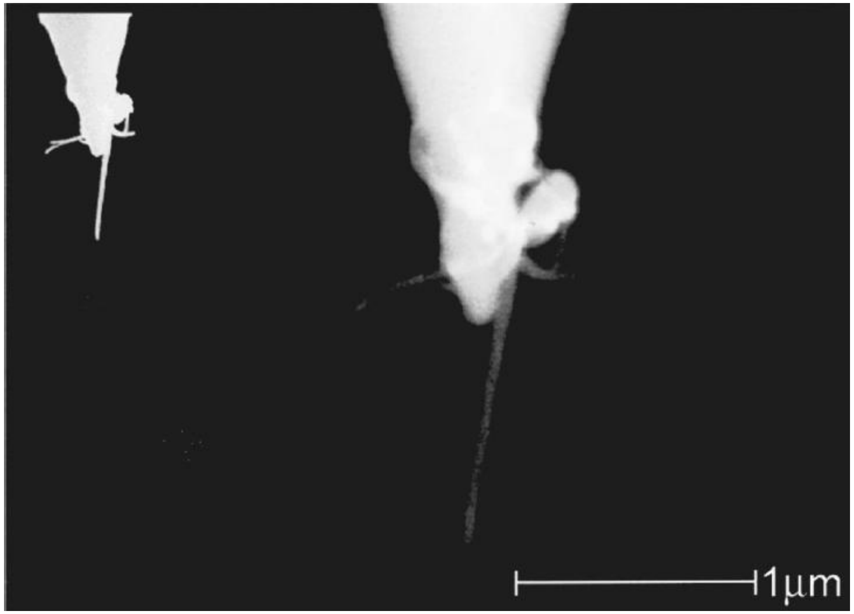
Needle AFM Tip

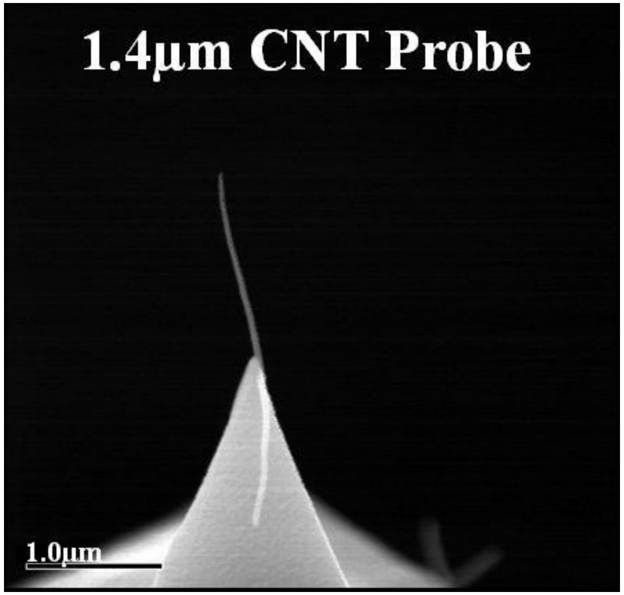
- Needle is fabricated with Ag_2Ga material
- It is manufactured by Nano science Instruments
- It is available in varying lengths, diameters, and attachment angles
- Needle AFM tips are available in standard lengths of 1, 5, or 10 μm with a diameter of 50 nm.
- The simple geometry and high conductivity of the Needle probes provides a wide range of enhanced sensing and manipulation capabilities

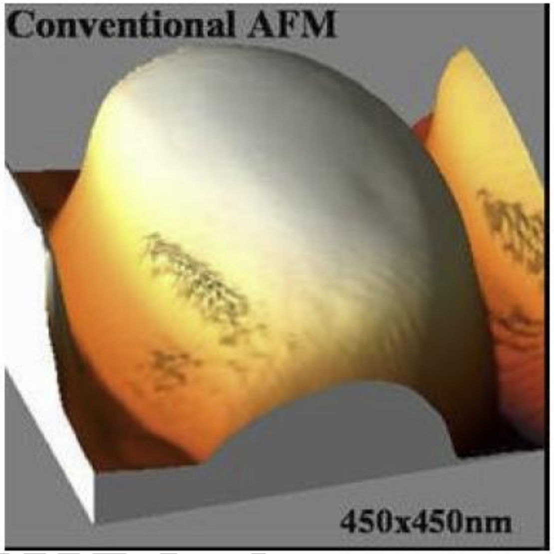


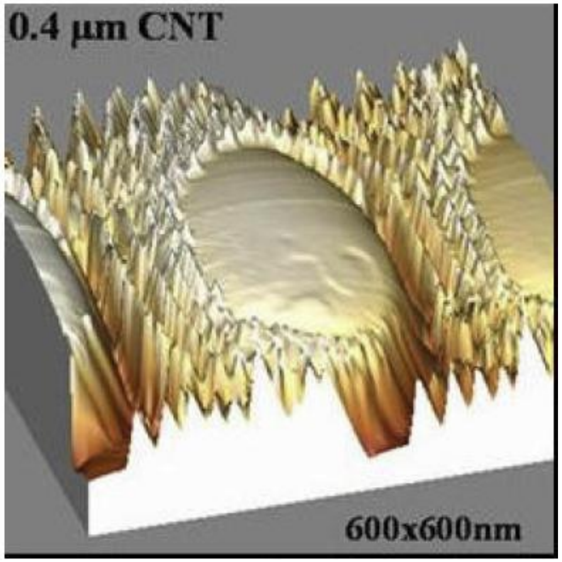
http://www.nanoscience.com/news/2009-Mar24.html

MWCNT AFM Tip:





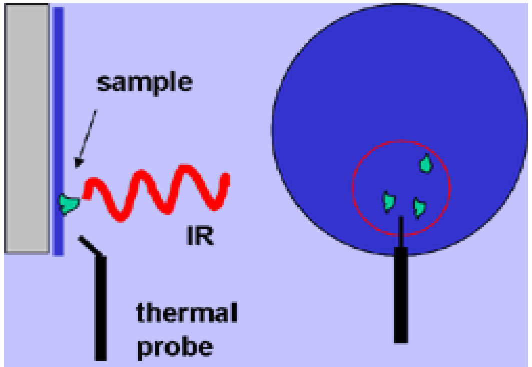


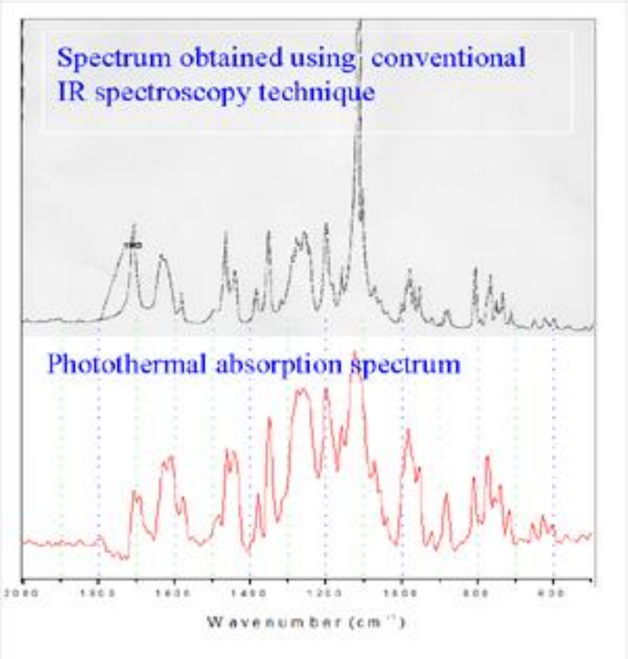


CNT V/S Conventional Image:

Ref: Appl. Phys. Lett., Vol. 82, No. 23, 9 June 2003

Thermocouple Tip:





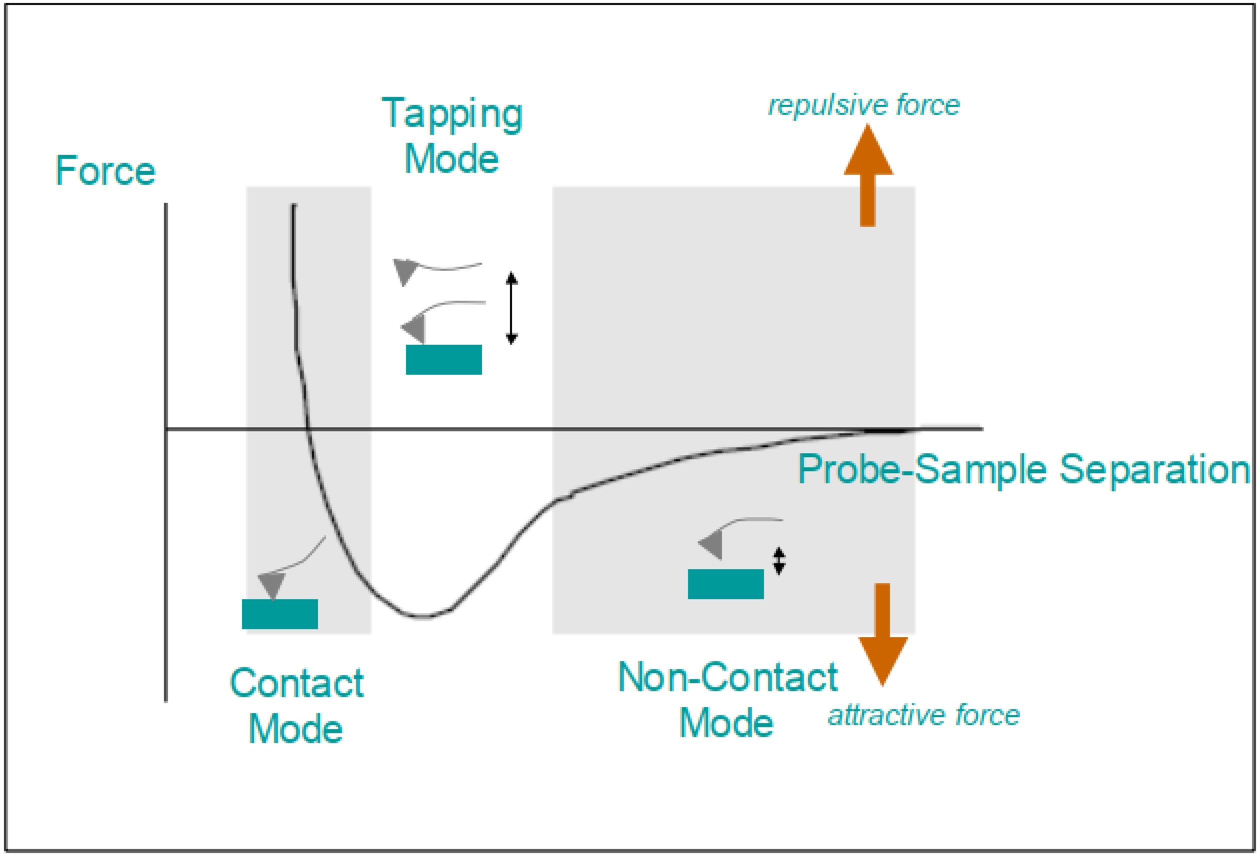
- Here thermocouple probes were used for scanning the surface.
- It maps the local temperature and thermal conductivity of an interface.
- It can be used to detect phase changes in polymer blends
- Measuring material variations in Conducting Polymers.
- Hot-spots in integrated circuits

http://en.wikipedia.org/wiki/Scanning_thermal_microscopy

Modes of operation:

AFM Can be operated in 3 modes

- •Contact Mode AFM
- •Non-Contact Mode AFM
- •Taping Mode AFM



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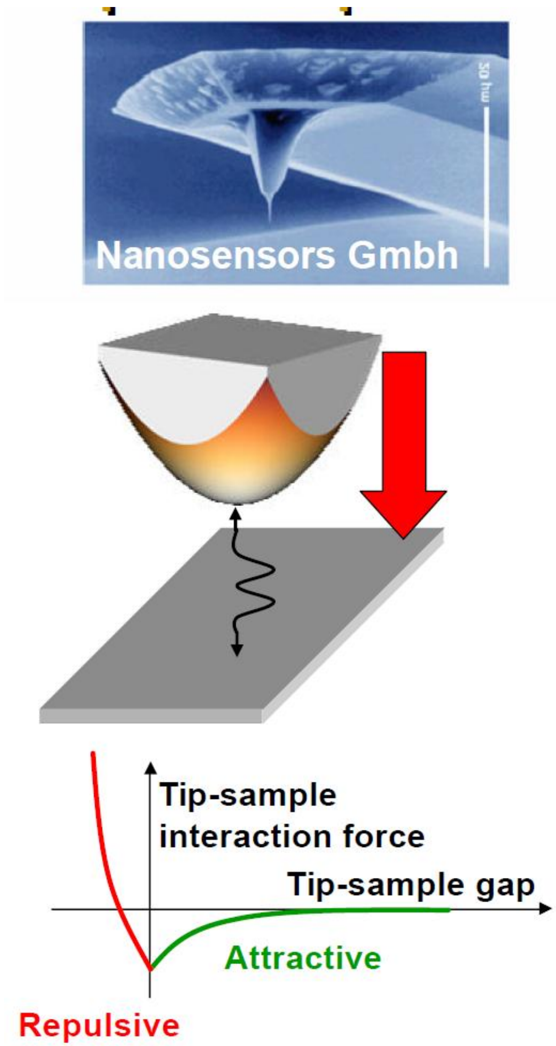
	Contact Mode	**Taping Mode**	**Non Contact Mode**
Force on Tip	Constant Force	Applied force are lower, Oscillation amplitude 20 nm to 200 nm	Oscillating frequency about 100 KHz, tip sample separation and amplitude are 1-10 nm
Rate of Scan	High	Less	Very Less
Usage	Limited	Wide Usage	Limited
Advantages & Disadvantages	Probability of contamination on the surface, combination of normal force with lateral force will damage the surface of soft materials	It is good for soft materials	It is good in hydrophobic surfac es & lateral resolution is lower

Types of Forces:



- Long-range electrostatic and magnetic forces (up to 100 nm)
- Capillary forces (few nm)
- Vander Waals forces (few nm) that are fundamentally quantum mechanical (electrodynamic) in nature
- Casimir forces
- Short-range chemical forces (fraction of nm)
- Contact forces
- Electrostatic double-layer forces
- Salvation forces
- Neoconservative forces

https://nanohub.org/resources/522/download/2005.11.28-raman.pdf

Applications

✓The AFM is useful for obtaining three-dimensional topographic information of insulating and conducting structures with lateral resolution down to 1.5 nm and vertical resolution down to 0.05 nm.

✓These samples include clusters of atoms and molecules, individual macromolecules, and biologic al species (cells, DNA, proteins).

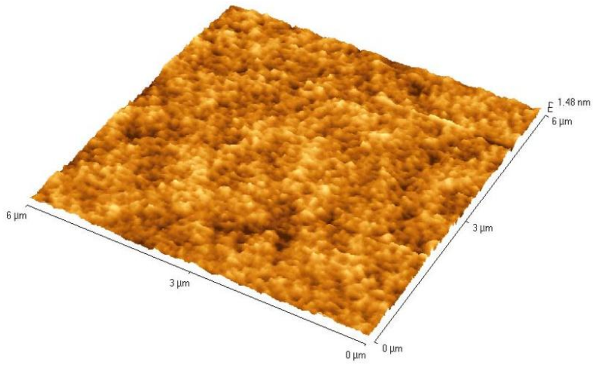
✓Unlike the preparation of samples for STM imaging, there is minimal sample preparation involved for AFM imaging.

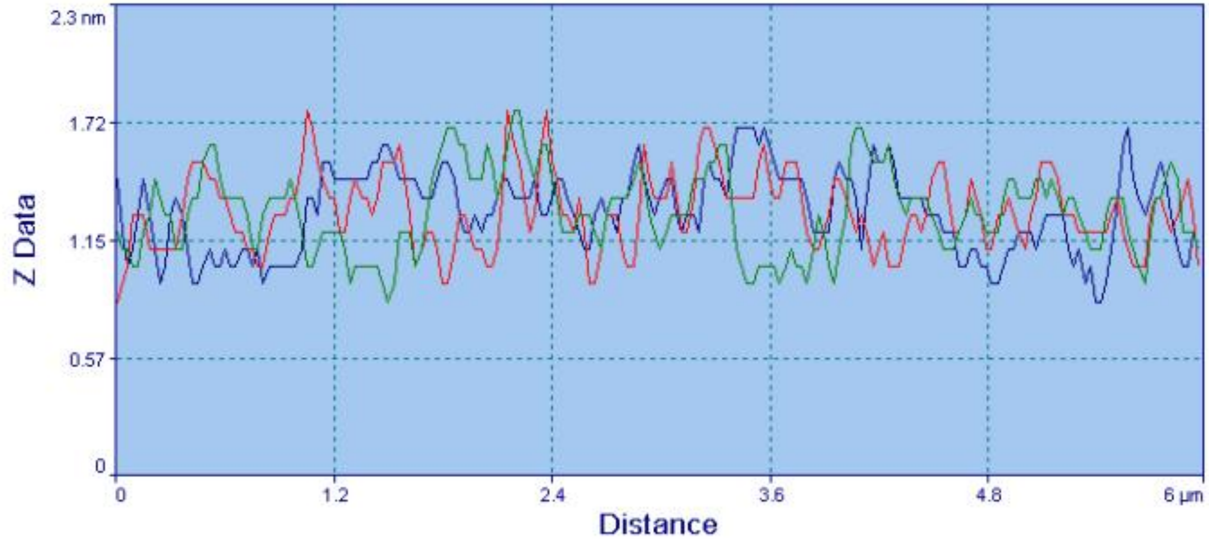
✓Similar to STM operation, the AFM can operate in gas, ambient, and fluid environments and can measure physical properties including elasticity, adhesion, hardness, friction and chemical functionality.

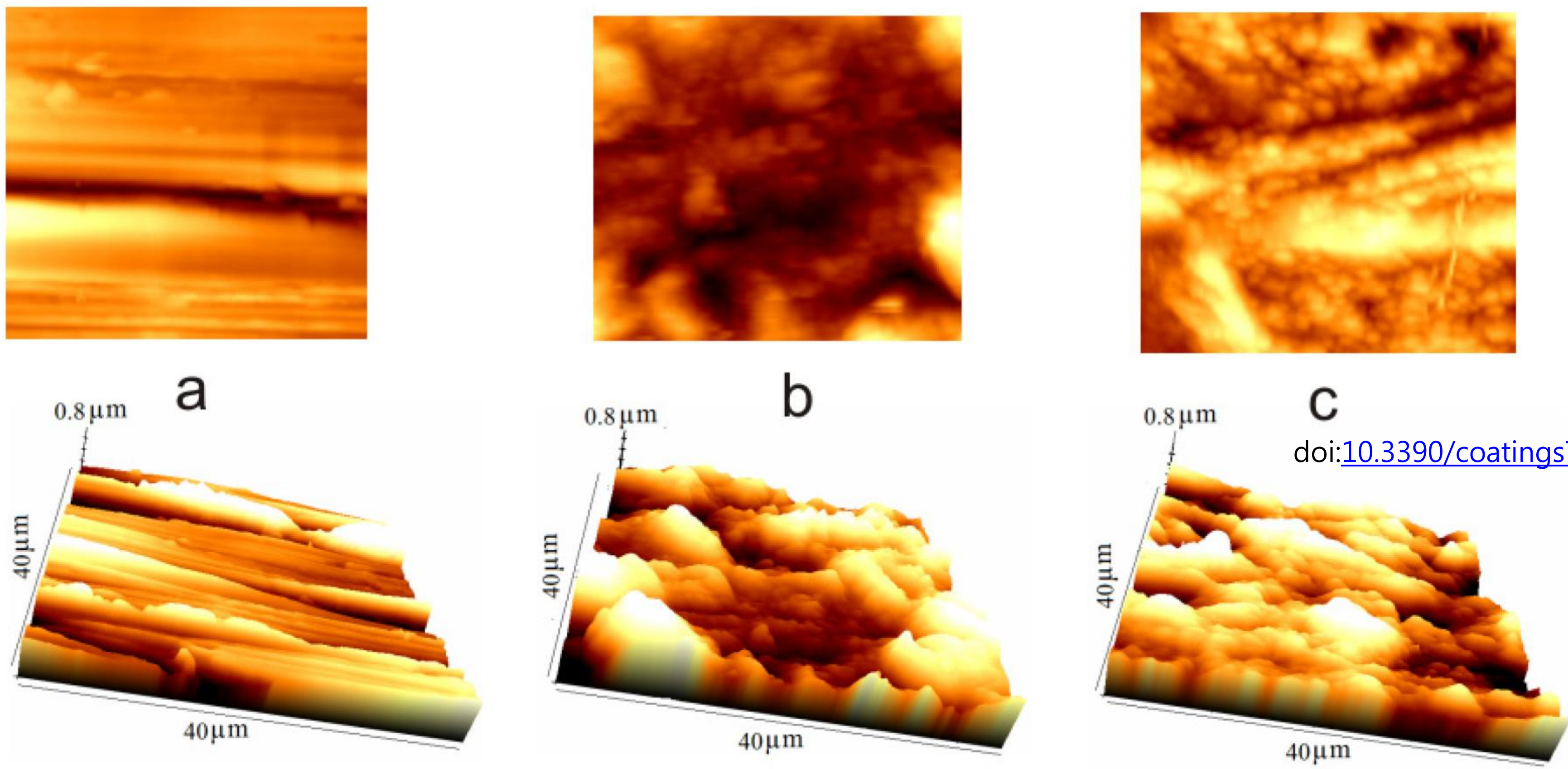
✓A concise applications listing is given below.

I. Metals: tooling studies, roughness measurements, corrosion studies…
II. Solid powder catalysts: aggregate structural determination,
III. Polymers: determination of morphology and surface properties, kinetic studies, aging phenomena, surface treatment modifications, adhesion force measurement and indentation,
IV. Biological samples, biomaterials: macromolecules association and conformation studies, adsorption kinetic of molecules on polymer surfaces,
V. Nano- and microparticle structures, Langmuir-Blodgett. Film studies…

Clean glass surface: roughness ~ 0.8 nm







doi:10.3390/coatings7110181

AFM for Membranes

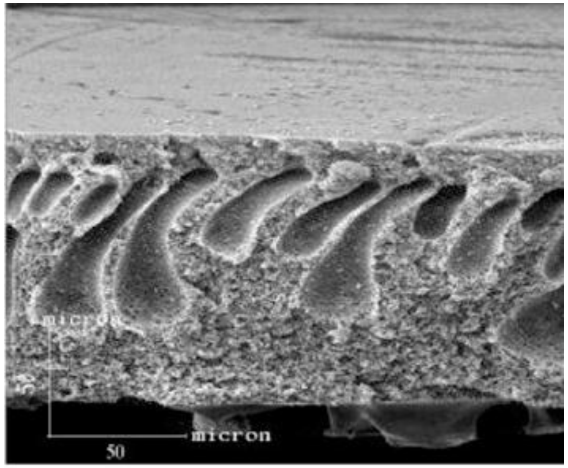
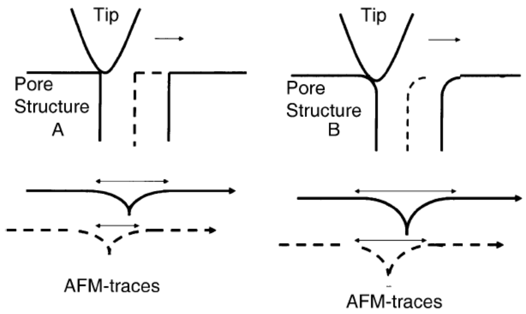


Figure 1. Scanning electron micrograph of cross-section of the asymmetric PSf membrane.



- Pore size by TEM, SEM are very small when compared to AFM
- By Using AFM we can find the Pore Size, Density, Size Distribution, Pore Connectivity, Surface Roughness can be calculated.
- From above data we can calculate the Mean pore size ,Median pore size…etc
- The above date is very impotent when we want to design a good filtration equipment.
- AFM is a good Quality Control tool for the membrane process engineers

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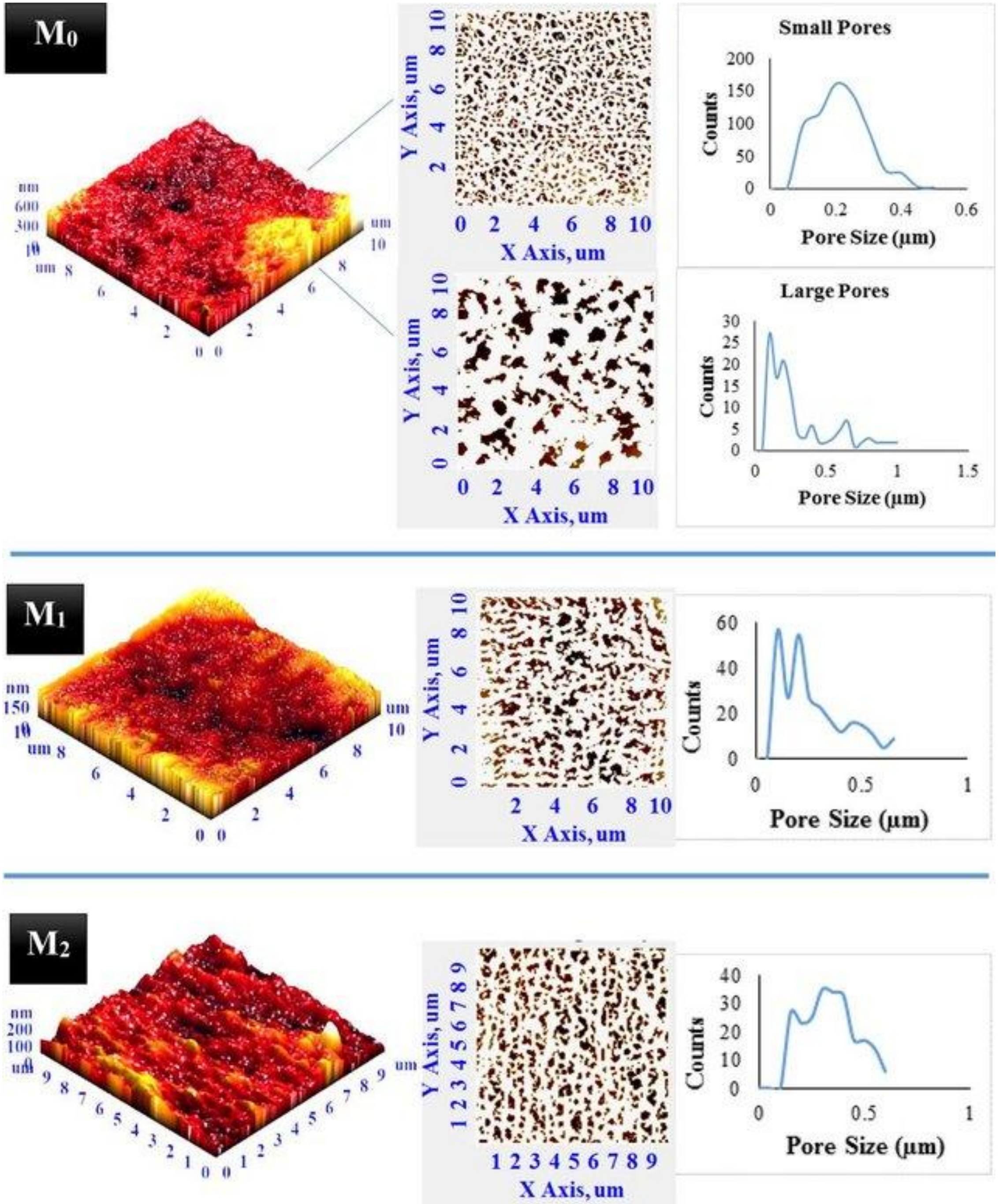

M0
Small Pores
Counts
Pore Size (µm)
Large Pores
Counts
Pore Size (µm)
X Axis, um
Y Axis, um
M1
Counts
Pore Size (µm)
X Axis, um
Y Axis, um
M2
Counts
Pore Size (µm)
X Axis, um
Y Axis, um

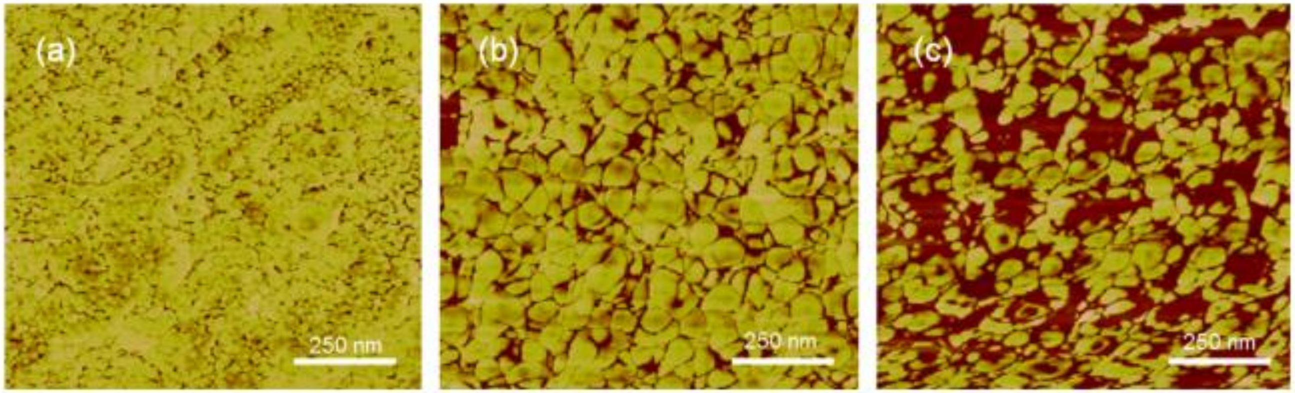
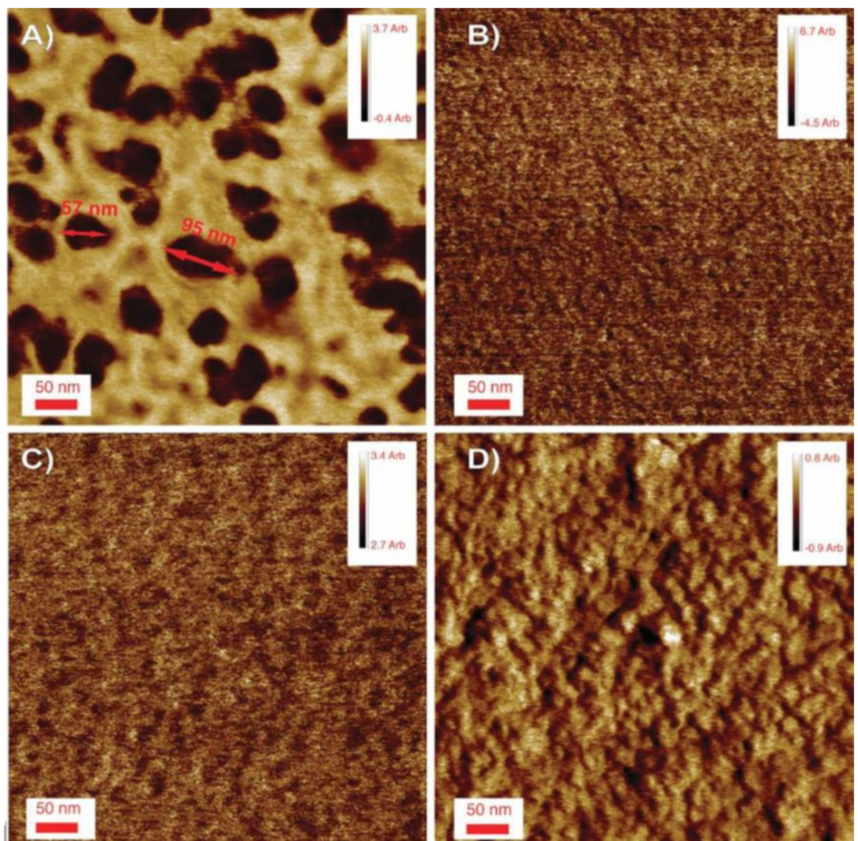


Figure 7. AFM images of PMP-based polyolefin membranes: (a) PMP-TMA-4, (b) PMP-TMA-20, and (c) PMP-TMA-41.



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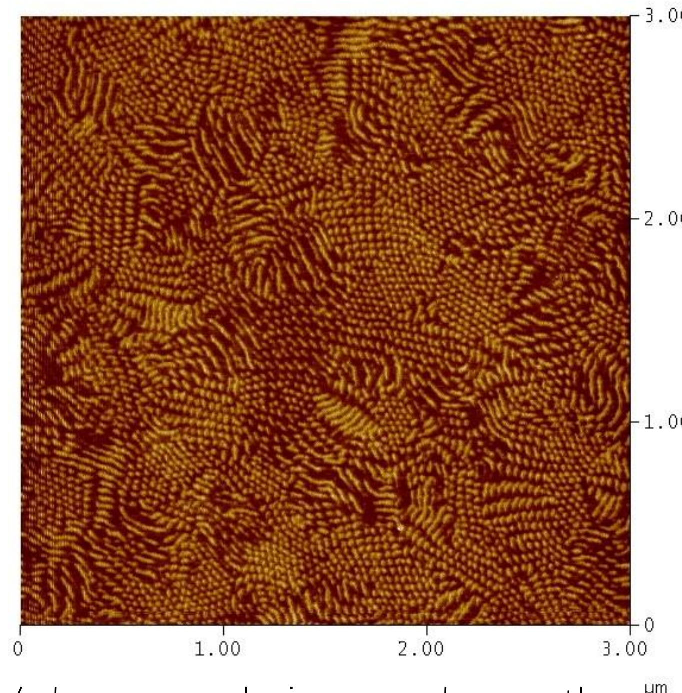
Zhongyang Wang et al. J. Electrochem. Soc. 2017;164:F1216-F1225



The tapping/phase mode image shows the bulk-morphology of a poly(styrene-b-ethylene/butylene/styrene-b-styrene) tri-block-copolymer.

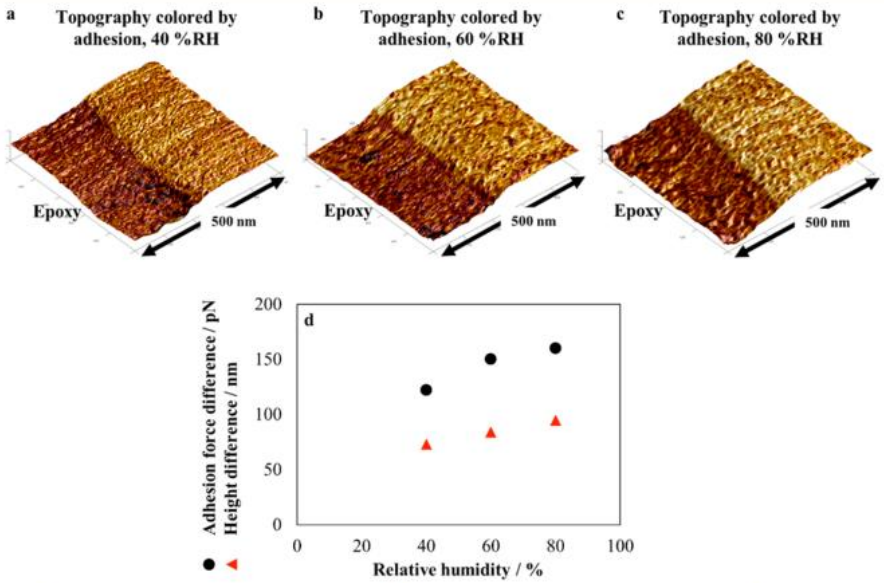


Figure 7. AFM adhesion mappings overlaid on 3D topography of the cross-sectioned interface of HMT-PMBI at (a) 40% RH, (b) 60% RH, and 80% RH. (d) Dependence of adhesion force and height of membrane above embedding material on RH.

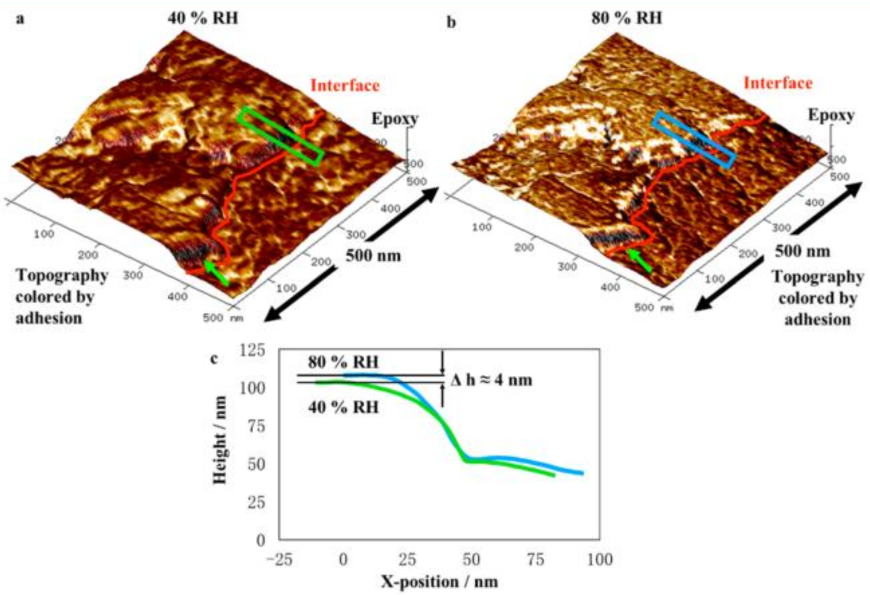


Figure 8. AFM adhesion mappings overlaid on topography of the cross-sectioned interface of PPO-TMA at (a) 40% RH and (b) 80% RH. (c) Line profiles of height at different RH at the same spot marked by the green and blue box in (a) and (b), respectively.

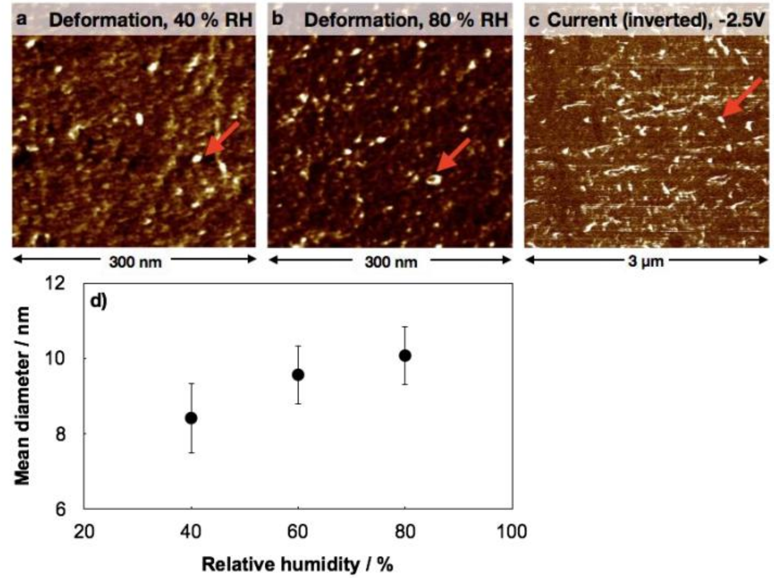


Figure S2. AFM deformation image of cross-sectioned HMT-PMBI membrane at (a)

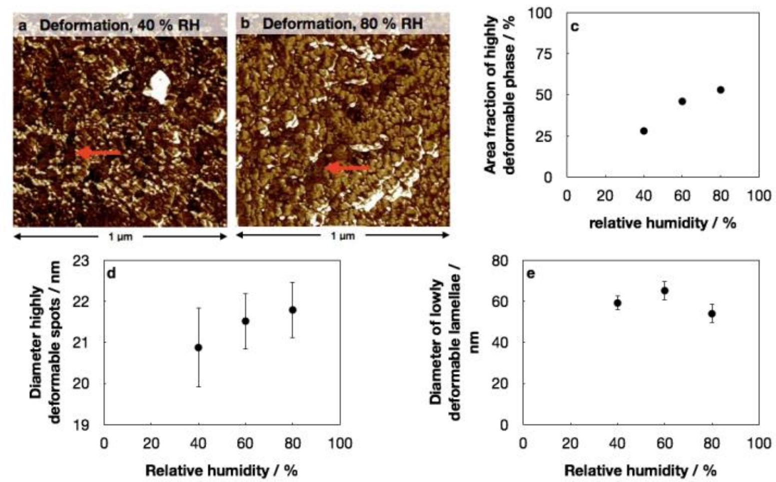


Figure S3. AFM deformation images of PPO-AGO cross-section at (a) 40 % RH, and (b) 80 % RH. (c) Fraction of highly deformable area, (d) dependence of diameter of the highly deformable phase on relative humidity. (e) Diameter of lowly adhesive phase over relative humidity level.

Advantages

✓The AFM has several advantages over the scanning electron microscope (SEM).
✓Unlike the electron microscope AFM provides **a true three-dimensional surface profile**.
✓Samples viewed by AFM **do not require any special treatments (such as metal/carbon coatings)** that would irreversibly change or damage the sample.
✓While an electron microscope **needs an expensive vacuum environment** for proper operation, most **AFM modes can work perfectly well in ambient air or even a liquid**.
✓Possible to **study biological macromolecules and even living organisms.**
✓In principle, **AFM can provide higher resolution than SEM.** It has been shown to give true atomic resolution in ultra-high vacuum (UHV).

Disadvantages

✓A disadvantage of AFM compared with the scanning electron microscope (SEM) is the **image size**.
✓The SEM can image an area on the order of millimeters by millimetres with a depth of field **on the order of millimetres**.
✓The AFM can only image a maximum height on the **order of micrometres** and a maximum scanning area of around 150 by 150 micrometres.
✓Another inconvenience is that at high resolution, the quality of an image is limited by the radius of curvature of the probe tip, and **an incorrect choice of tip for the required resolution can lead to image artifacts.**
✓Traditionally the AFM could not scan images as fast as an SEM, **requiring several minutes for a typical scan,** while an SEM is capable of scanning at near real-time (although at relatively low quality) after the chamber is evacuated.
✓AFM images can be **affected by hysteresis** of the piezoelectric material .

References:

- Polymer Microscopy By Linda C. Sawyer, David T.Grubb
- Synthetic Polymeric Membranes By K.C.Khulbe, C.Y.Feng, T.Matsuura
- Atomic Force Microscopy in Cell Biology By Bhanu P.Jena, J.K.heinrich Horber, American Society for Cell Biology
- Atomic Force Microscopy By Pier Carlo Braga, Davide Ricci
- Ref: Appl. Phys. Lett., Vol. 82, No. 23, 9 June 2003
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