Nano Sensors

PhD/ MTech/ BTech

Course No.: EEL7450

L-T-P [C]: 3–0–0 [3]

Prof. AJAY AGARWAL

ELECTRICAL ENGINEERING

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Lecture 11 dated 30th January 2025

Nanoscale Characterization

Important characterizations for nanomaterials and nanostructures are:

1. Structural Characterization
    1. X-ray diffraction (XRD),
    2. Various electron microscopy (EM) including
        i. scanning electron microscopy (SEM)
        ii. transmission microscopy (TEM), and
        iii. scanning probe microscopy (SPM)
            i. scanning tunneling microscopy (STM) and
            ii. atomic force microscopy (AFM)
    3. Gas adsorption
2. Chemical Characterization
    1. Optical spectroscopy
    2. Electron spectroscopy
    3. Ionic spectrometry

1. Structural Characterization

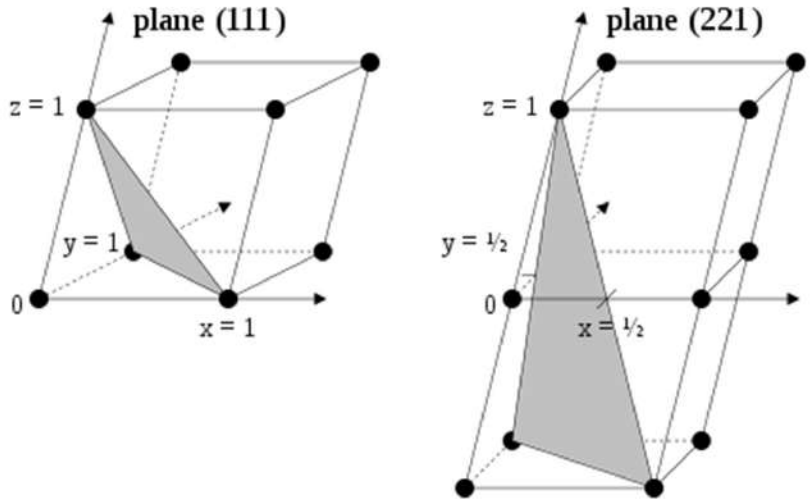
1. X-ray diffraction (XRD)

- **Miller indices** form a notation system in crystallography for lattice planes in crystal (Bravais) lattices.
- There are two equivalent ways to define the Miller indices:
  - via a point in the reciprocal lattice, or
  - as the inverse intercepts along the lattice vectors.
- In either case, one needs to choose the three lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ that define the unit cell.
- Given these, the three primitive **reciprocal** lattice vectors are also determined (denoted $\mathbf{b}_1$, $\mathbf{b}_2$, and $\mathbf{b}_3$).
- Then, given the three Miller indices h, k, ℓ, (hkℓ) denotes planes **orthogonal** to the reciprocal lattice vector:

$$\mathbf{g}_{hk\ell} = h\mathbf{b}_1 + k\mathbf{b}_2 + \ell\mathbf{b}_3 .$$

- (hkℓ) indicates a normal to the planes in the basis of the primitive reciprocal lattice vectors.
- As the coordinates are integers, this normal is always a reciprocal lattice vector
- It is the *shortest* reciprocal lattice vector in the given direction.
- Considering (hkℓ) planes ***intersecting*** one or more lattice points (the *lattice planes*), the perpendicular distance d between adjacent lattice planes is related to the (shortest) reciprocal lattice vector orthogonal to the planes by the formula:

$$d = 2\pi/|\mathbf{g}_{hk\ell}|.$$



Examples of determining indices for a plane using intercepts with axes; left (111), right (221)

- The related notation [hkℓ] denotes the *direction*: $h\mathbf{a}_1 + k\mathbf{a}_2 + \ell\mathbf{a}_3$.

Miller Indices (h k l)

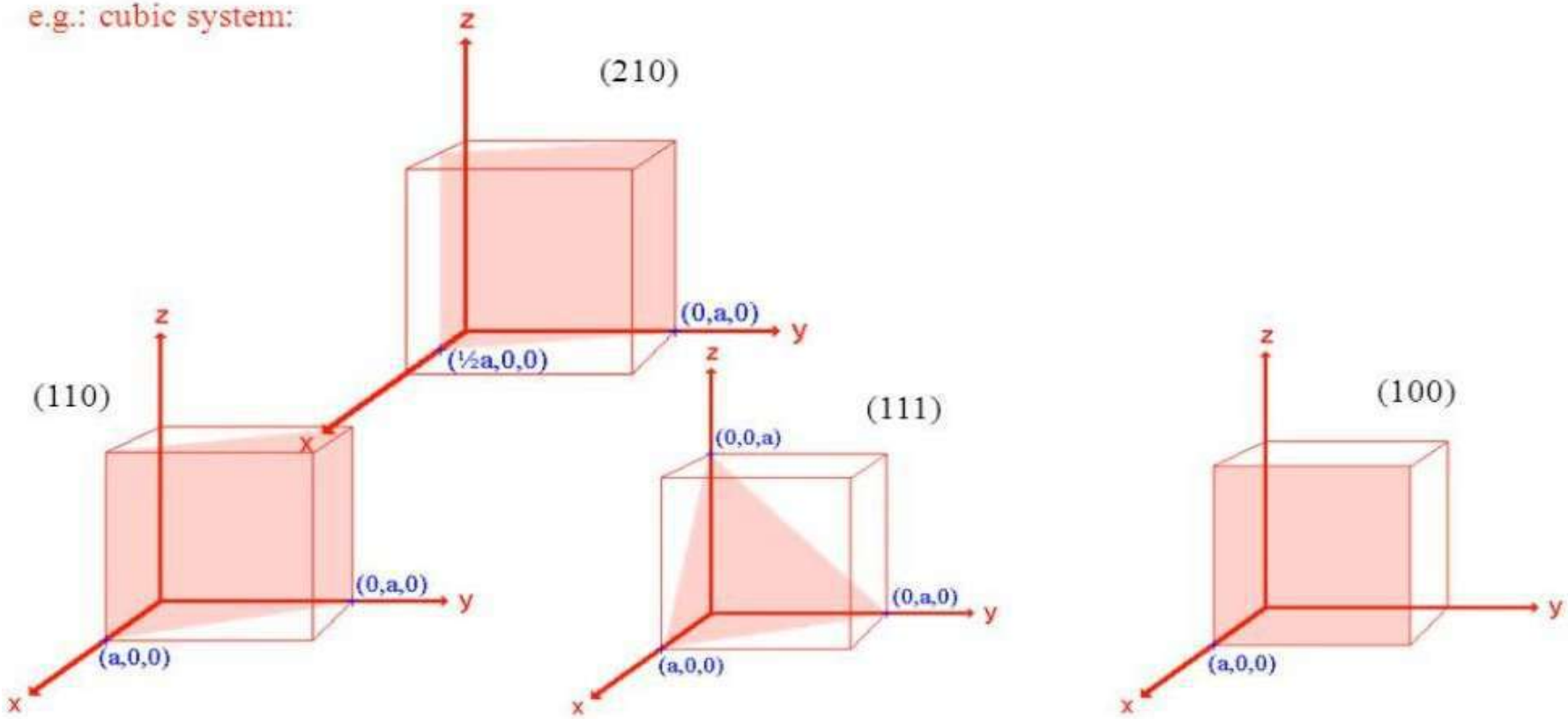
to identify planes:

Step 1 : Identify the intercepts on the x- , y- and z- axes (a/2, ∞, ∞)

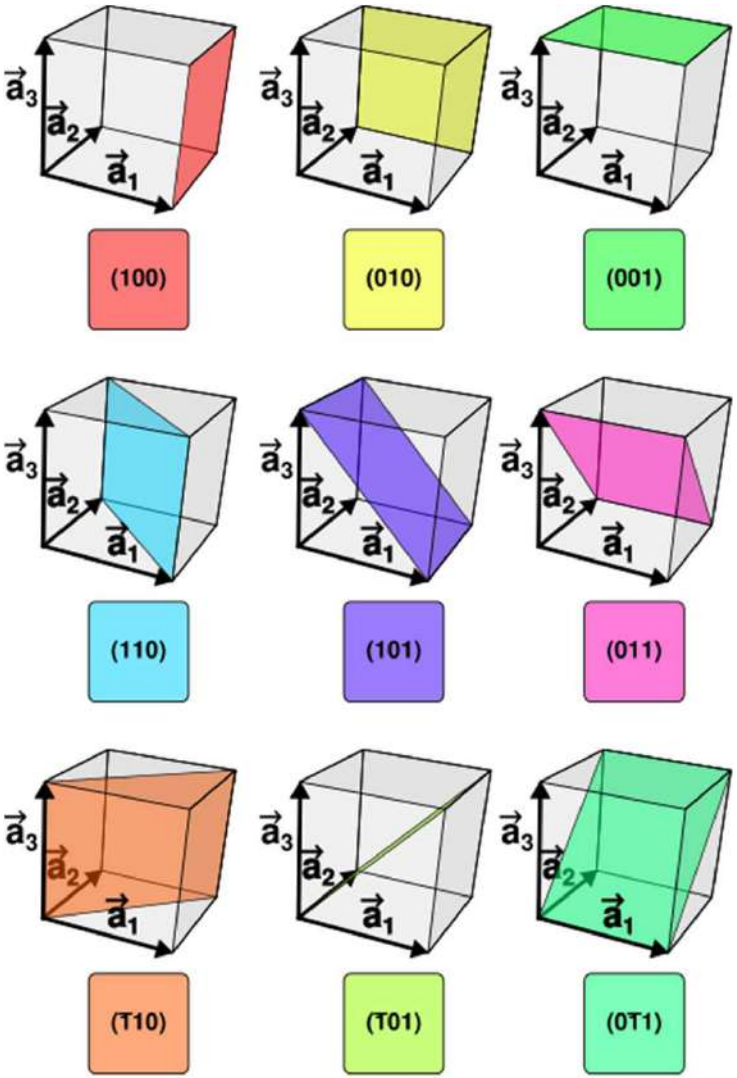
Step 2 : Specify the intercepts in fractional co-ordinates (a/2a, ∞, ∞) = (1/2,0,0)

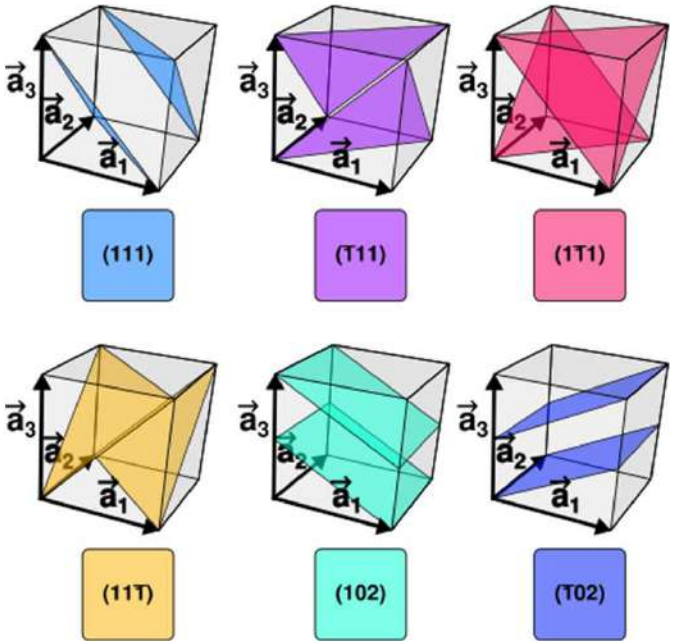
Step 3 : Take the reciprocals of the fractional intercepts (2, 0, 0)

e.g.: cubic system:



- By convention, negative integers are written with a bar, as in 3 for −3.
- The integers are usually written in lowest terms, i.e. their greatest common divisor should be 1.
- the notation {hkℓ} denotes the set of all planes that are equivalent to (hkℓ) by the symmetry of the lattice





Planes with different Miller indices in cubic crystals

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Lecture 12 dated 31st January 2025

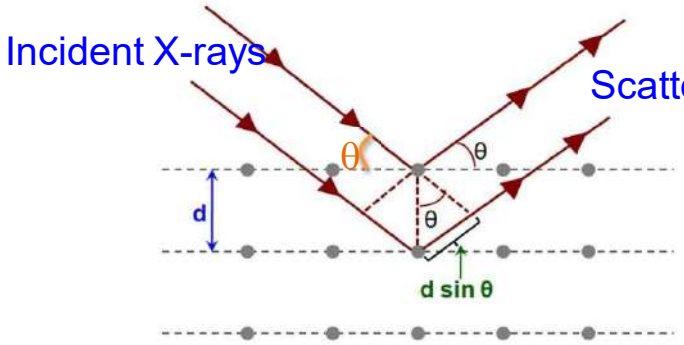
Working Principle of XRD

- X-ray diffraction is based on **scattering of monochromatic x-rays with the crystalline planes of the** sample.
- The scattered X-Rays produces constructive interference when conditions satisfy **Bragg's law:**

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

where **n** is order of reflection, **λ** is the wavelength of the incident X-rays, ***d*** is the interplanar spacing of the crystal and θ is the angle of incidence.

- When X-rays are scattered from a crystal lattice, peaks of scattered intensity are observed owing to maximum intensity.



Atomic planes act as diffraction slits

Lattice Planes

When this constructive interference occurs, a diffracted beam of X-rays will leave the crystal at an angle equal to that of the incident beam.

https://youtu.be/QHMzFUo0NL8

Diffraction direction

- The possible directions, i.e., the possible angles 2θ, in which a given crystal can diffract a beam of monochromatic x-rays needs to be determined
- To predict the diffraction angle for any set of planes, combination of the Bragg law & the plane-spacing equation, applicable to the particular crystal involved

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

$$\frac{1}{d^2} = \frac{(h^2 + k^2 + l^2)}{a^2}.$$

$$\sin^2\theta = \frac{\lambda^2}{4a^2}(h^2 + k^2 + l^2).$$

- This equation predicts, for a particular incident wavelength λ & a particular **cubic crystal** of unit cell size a, all the possible Bragg angles at which diffraction can occur from the planes (hkl).
- For (110) planes:

$$\sin^2\theta_{110} = \frac{\lambda^2}{2a^2}.$$

- For **tetragonal** crystal symmetry:

$$\sin^2\theta = \frac{\lambda^2}{4}\left(\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}\right)$$

Plane Spacing for Seven Crystal System

Cubic:
$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2 + l^2}{a^2}$$

Tetragonal:
$$\frac{1}{d_{hkl}^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

Hexagonal:
$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\left(\frac{h^2 + hk + k^2}{a^2}\right) + \frac{l^2}{c^2}$$

Rhombohedral:
$$\frac{1}{d_{hkl}^2} = \frac{(h^2 + k^2 + l^2)\sin^2\alpha + 2(hk + kl + hl)(\cos^2\alpha - \cos\alpha)}{a^2(1 - 3\cos^2\alpha + 2\cos^3\alpha)}$$

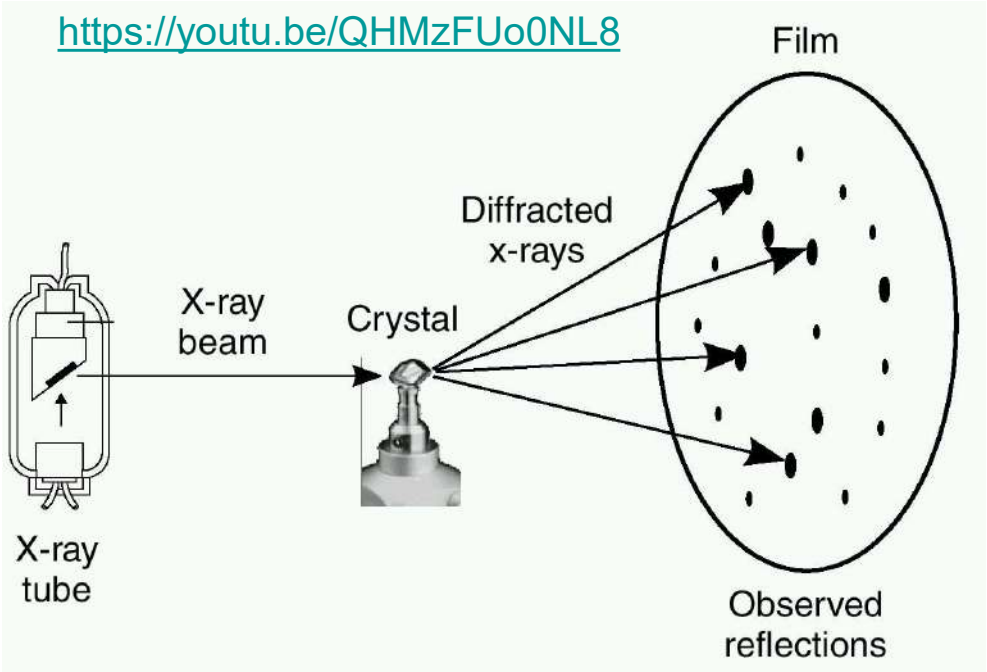
Orthorhombic:
$$\frac{1}{d_{hkl}^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}$$

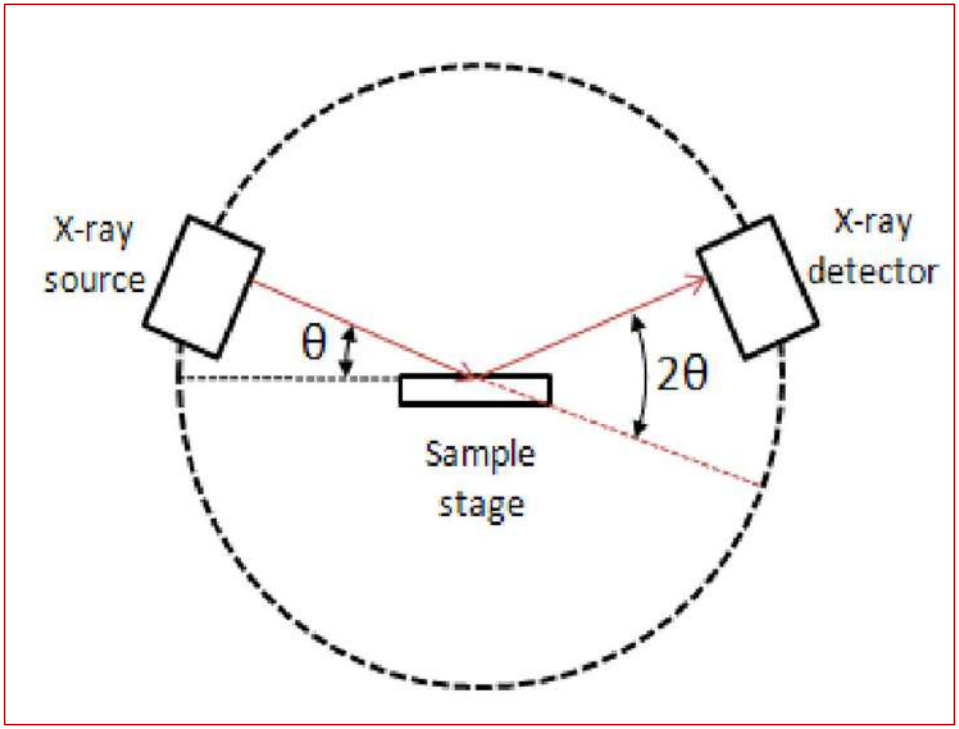
Monoclinic:
$$\frac{1}{d_{hkl}^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right)$$

Triclinic:
$$\frac{1}{d_{hkl}^2} = \frac{1}{V^2}(S_{11}h^2 + S_{22}k^2 + S_{33}l^2 + 2S_{12}hk + 2S_{23}kl + 2S_{13}hl)$$

Instrumentation: X-Ray Diffractometer

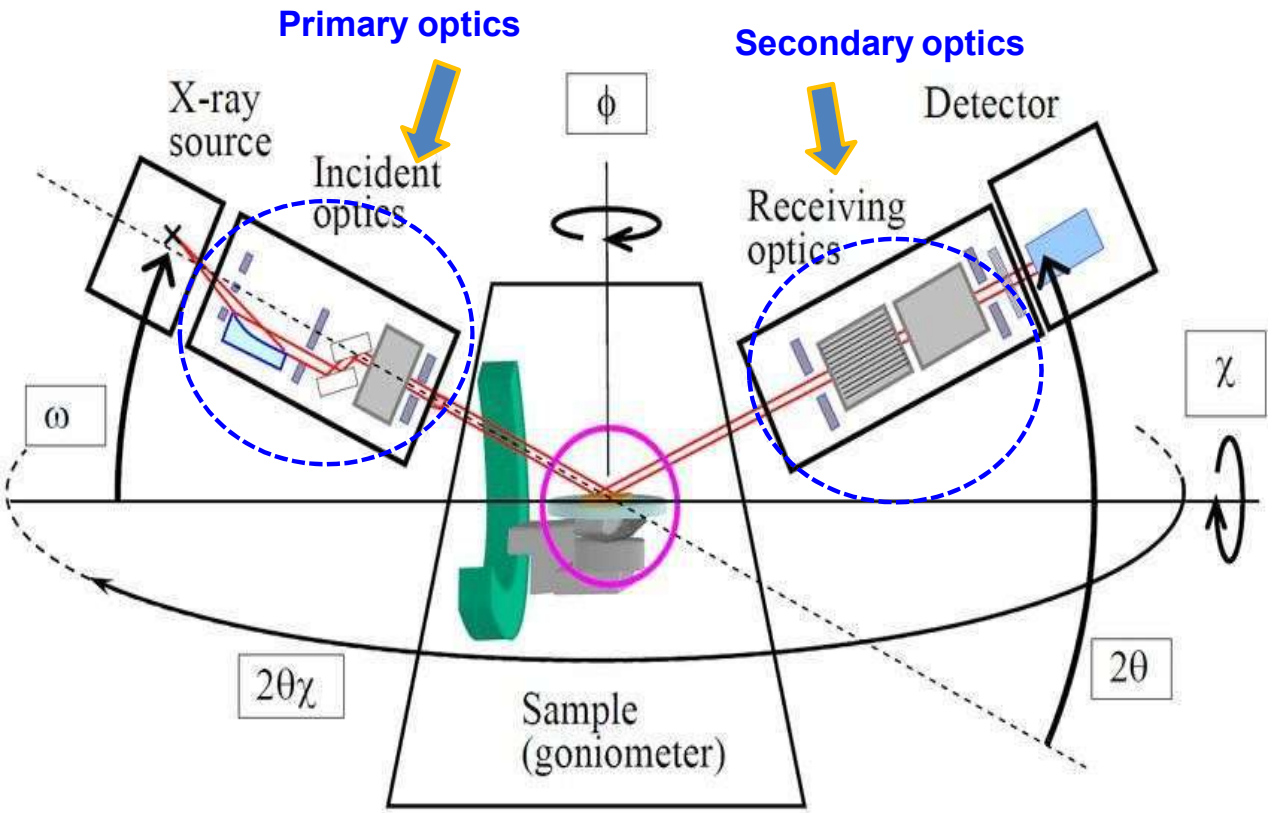
https://youtu.be/QHMzFUo0NL8





The angle between incident and scattered beam is 2θ

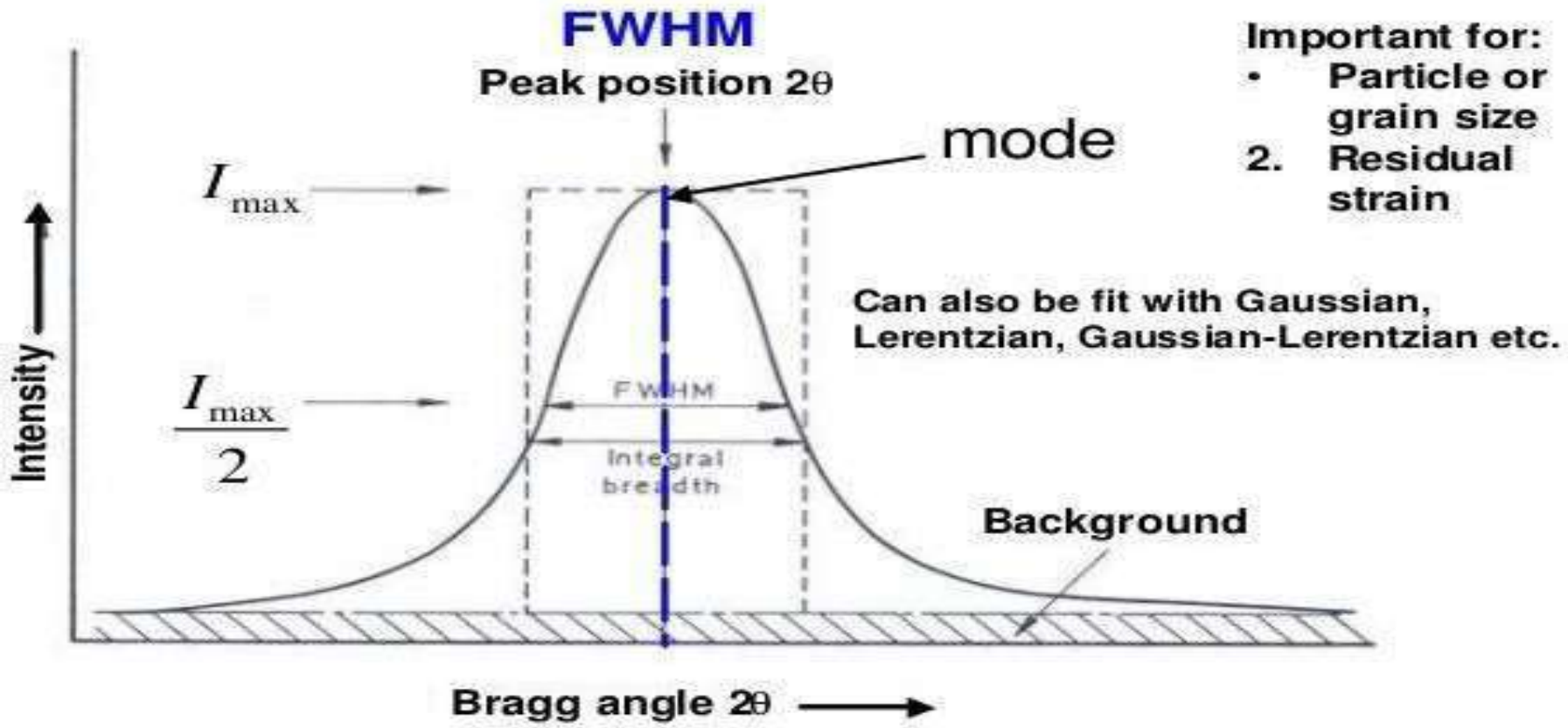
X-Ray Diffractometer



- Production of X-rays
- Collimator
- Monochromator
  - Filter
  - Crystal monochromator
- Detectors
  - Photographic methods
  - Counter methods

https://youtu.be/07iZ7-IEyYE

Peak Width-Full Width at Half Maximum



Particle size calculation:

Scherrer equation:

$$t = \frac{C\lambda}{B\cos\theta}$$

where λ is wavelength (Å), B is FWHM (radians) corrected for instrument broadening, θ is Bragg angle, C is a crystal shape factor from 0.9~1.

For Gaussian profiles,

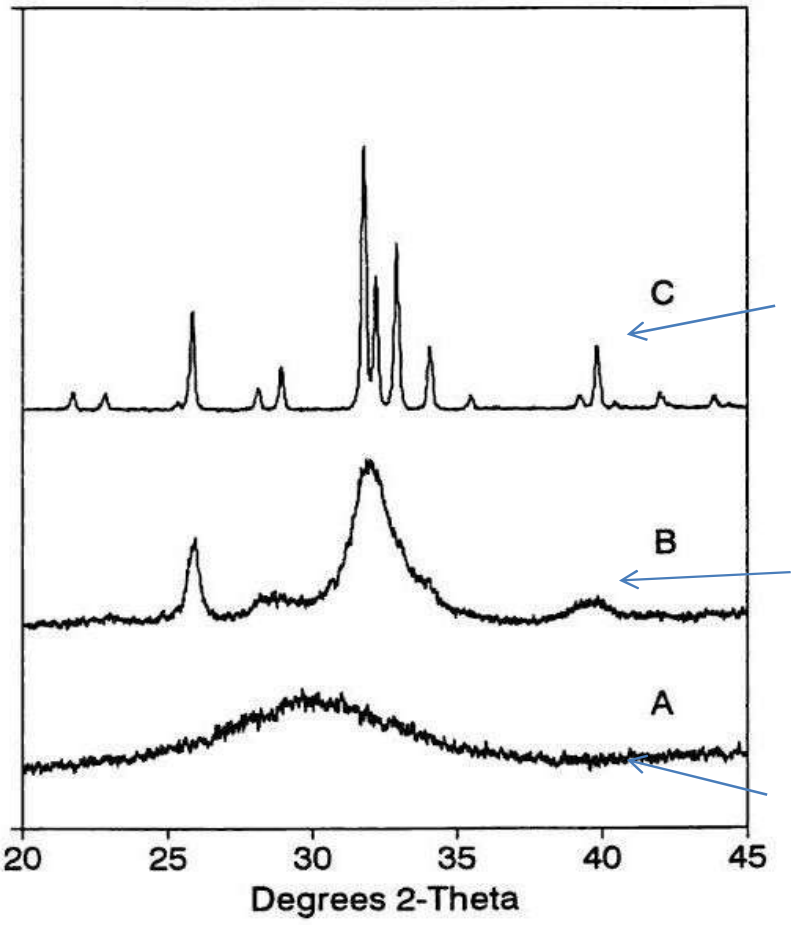
$$B^2 = U^2 - S^2$$

while for Cauchy profiles,

$$B = U - S$$

where ***B*** is the corrected FWHM for crystallite size calculation by Scherrer equation, and ***U*** and S are the FWHM's of the unknown and standard peaks, respectively.

Broad peak in nanomaterials (High FWHM)



Bulk materials(crystalline)

Nano materials(crystalline)

Nano materials(amorphous)

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

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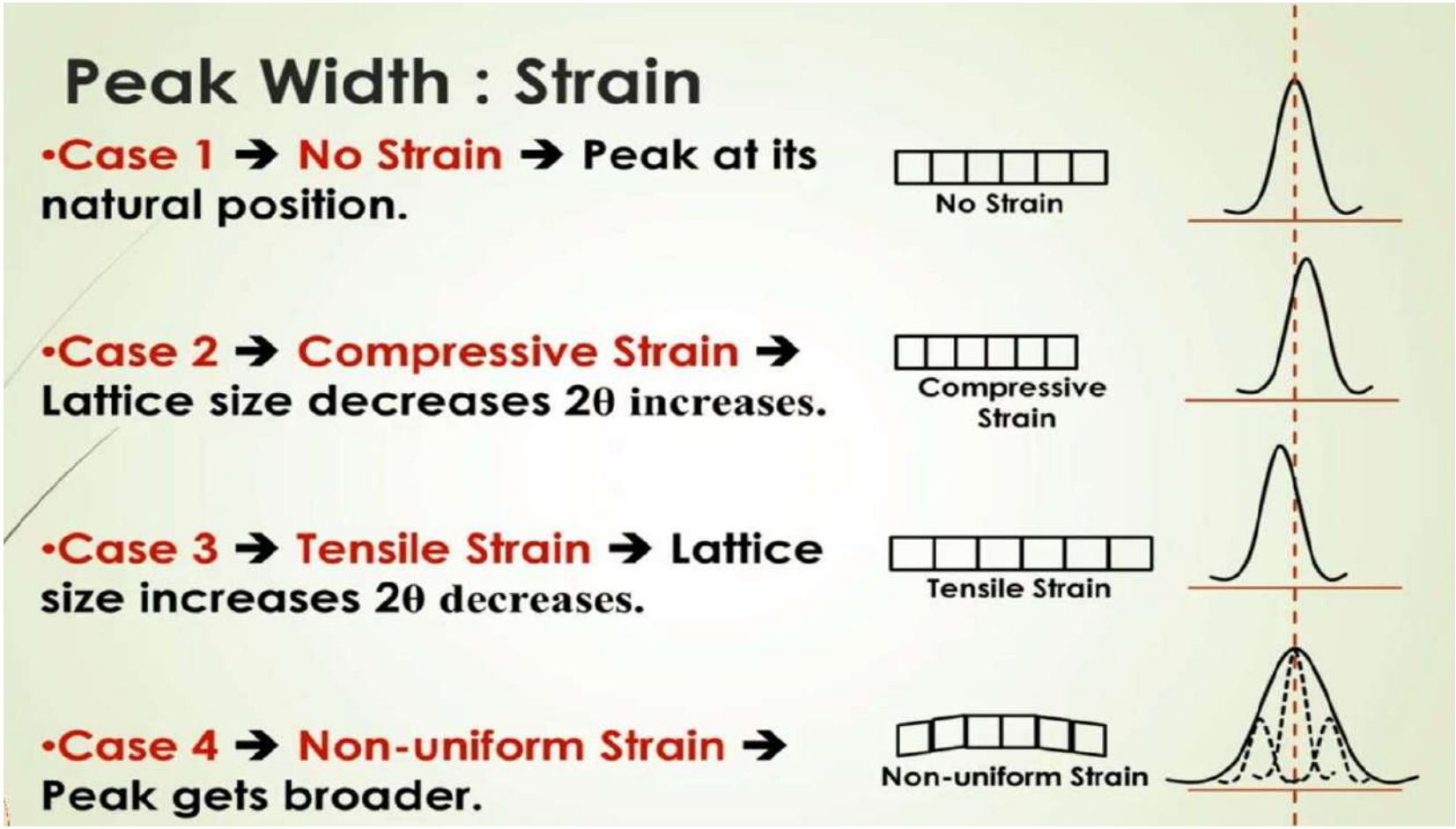
Lecture 13 dated 04th Feb. 2025

Effect of Lattice Strain on Diffraction peak position & width



Advantages of XRD

- X-ray is the cheapest, the most convenient and widely used method.
- X-rays are not absorbed very much by air, so the specimen need not be in an evacuated chamber.

XRD is a nondestructive technique

- To identify crystalline phases
- To determine structural properties:
  Lattice parameters (10^{-4}Å), strain, grain size, expitaxy, phase composition, preferred orientation
  order-disorder transformation, thermal expansion
- To measure thickness of thin films and multilayers
- To determine atomic arrangement
- To image and characterize defects

Limitations of XRD

- They do not interact very strongly with lighter elements.

- Homogenous and single phase materials is best for identification of an unknown
- For mixed materials, detection limit is ~2% of sample
- Must have access to a standard reference file of inorganic compound
- Requires tenths of gram materials
- Peak overlay may occur and worsens for high angle reflections

Questions / Discussions

Nanoscale Characterization

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2. Chemical Characterization
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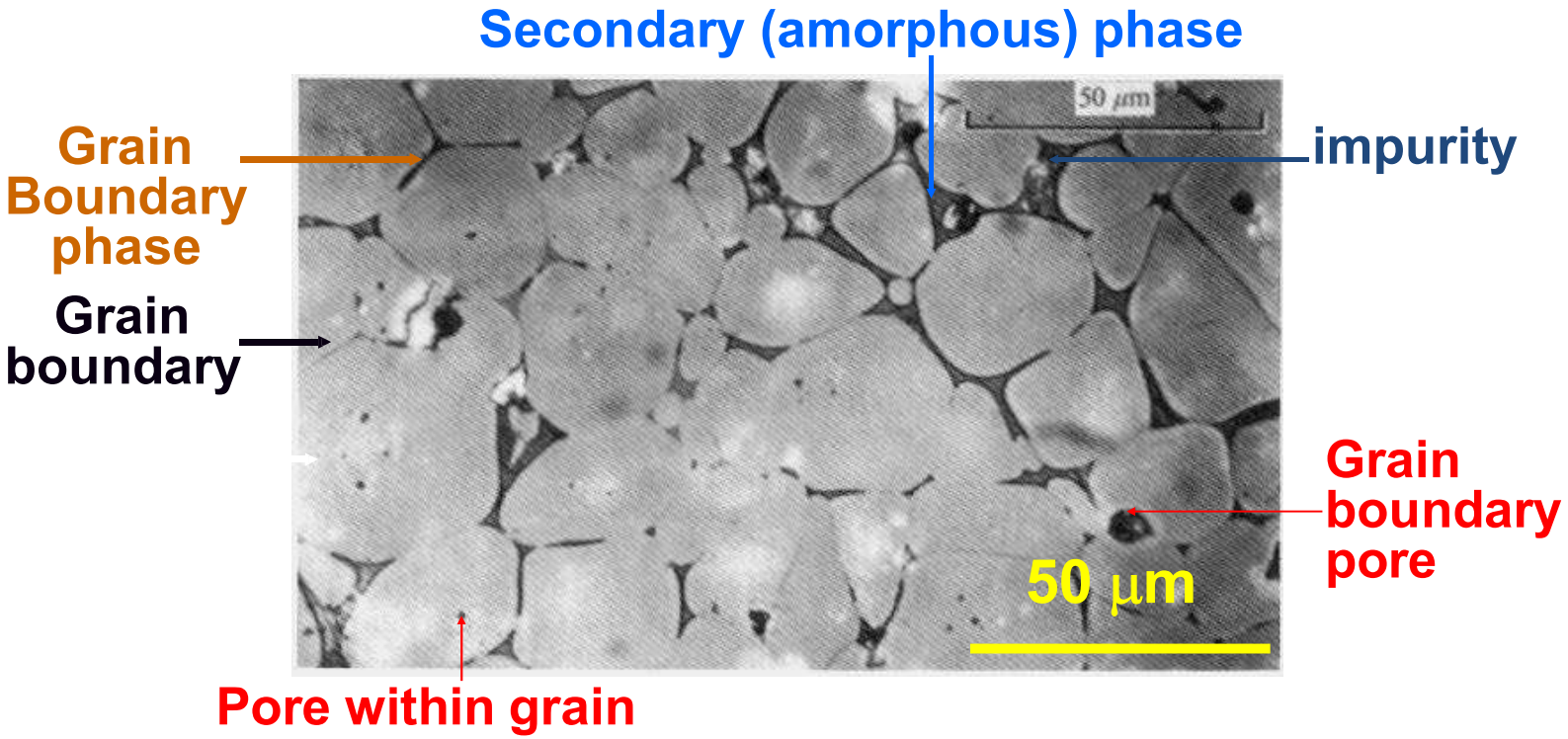
Microstructure

Nature, **quantity** and **distribution** of **phases** in the material: crystals, glass, porosity, grain boundary and impurity (secondary) phase.



Phase - **A homogeneous portion of a system that has uniform physical and chemical characteristics.**

Optical Microscope

The **optical microscope**, often referred to as the "**light microscope**", is a type of **microscope** which uses visible **light** and a system of lenses to magnify images of small samples. **Optical microscopes** are the oldest design of **microscope.**

Resolution of light microscope is limited:

$$\sin\Theta = 1.22 \cdot \frac{\lambda}{D}$$

- wavelenght of visible light
- less diffraction for smaller wavelenghts

D = diameter of the lens' aperture

➢ possible magnification: ~ 2 000

Electron Microscope

1. Motivation

Different approach: use electrons instead of light

- Access to much smaller wavelengths
  $\lambda = \frac{h}{p}$ (3.7 pm for 100 keV)
  h is plank's constant, momentum (p) of a photon and wavelength (λ)
- electrostatic/electromagnetic lenses instead of glass lenses

➢ possible magnification: ~ 2 000 00

- *Light microscopes are typically capable of providing a resolution of up to 200 nm*
- *In the case of electron microscopes, the resolution is about 0.1 nm.*
- **This means that electron microscopes are capable of providing as much as 2000 times more detail than a light microscope**
- **A light microscope provides a magnification of up to 1000 x.**
- **Electron microscope's ability to achieve a magnification of up to 250,000x.**

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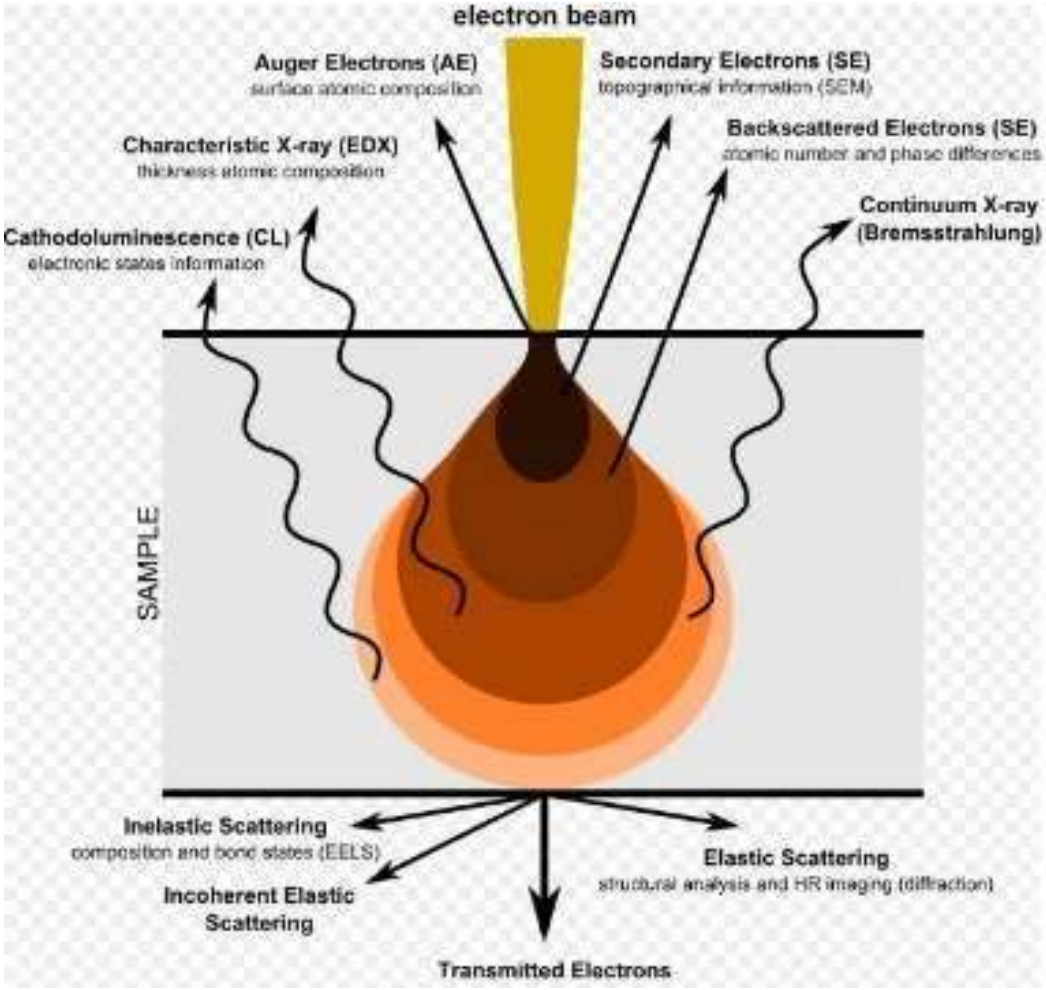
Lecture 14 dated 06th Feb. 2025

2. Interaction with matter



Electron–matter interactions and the different types of signals that are generated.

Topography and composition ← Backscattered electrons

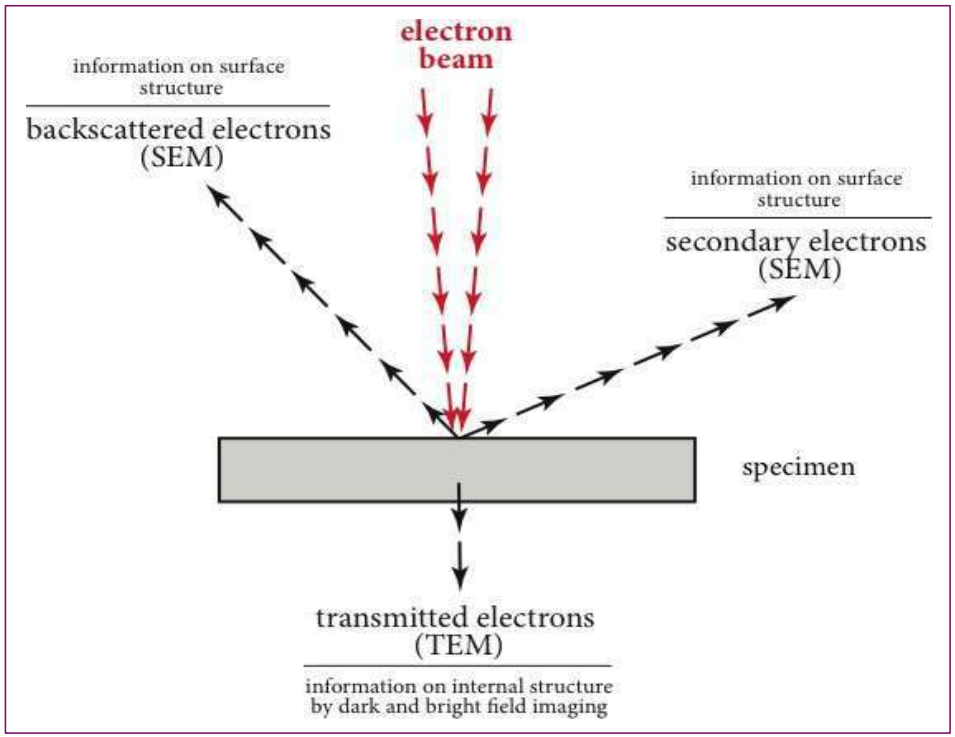
Topography ← Secondary electrons

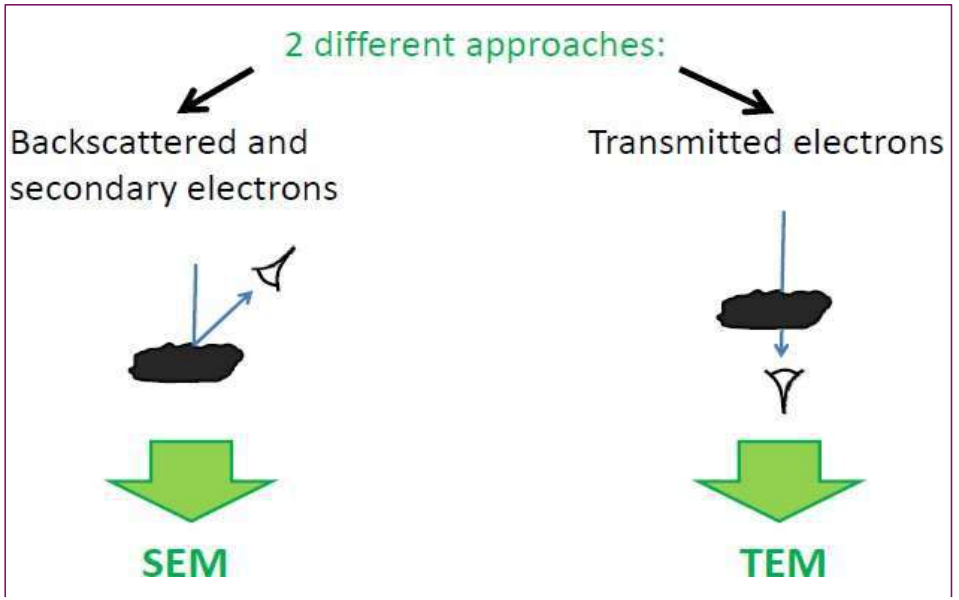
Auger electrons

Structure and composition ← Transmitted electrons

Composition ← X-Rays

phonons

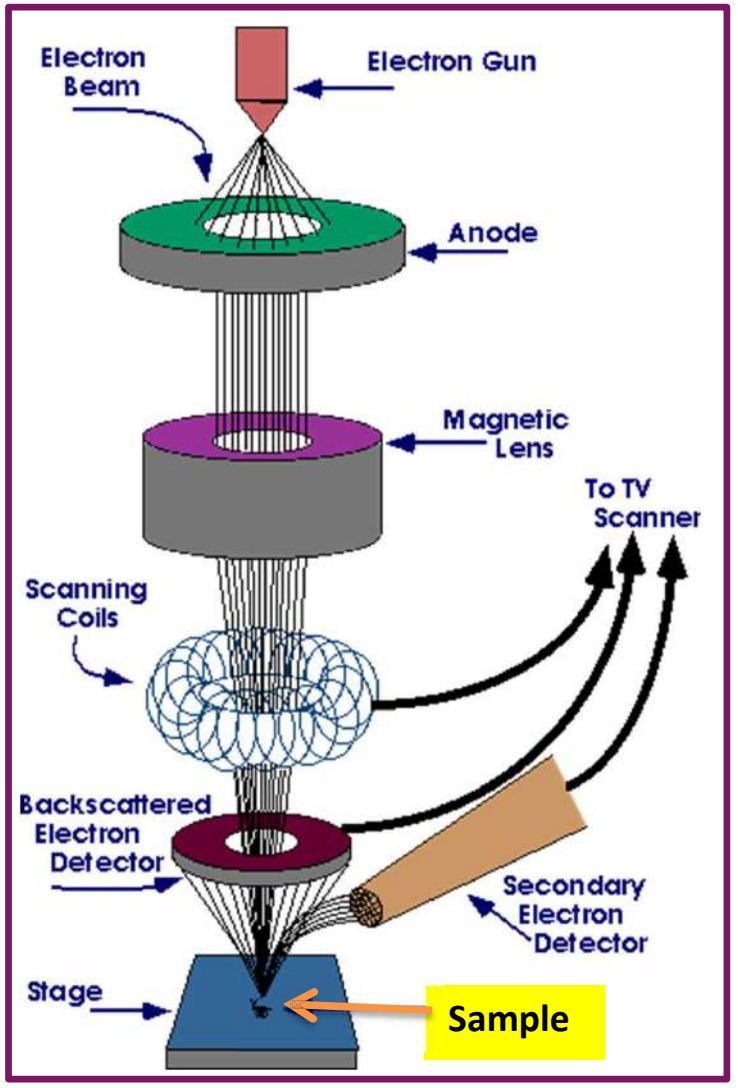




- **SE** are **specimen electrons** ejected by interactions with the beam electrons. They are used for imaging because of their high spatial resolution and topographical sensitivity. They carry very little information about elemental composition. They typically have energies less than 50eV.
- **BSE's** are **beam electrons** that interact with the nucleus of a sample atom & are **elastically** scattered with little loss of energy. BSE's come from greater depths within the specimen so they have lower spatial resolution. They **provide elemental** information.

How does a SEM work?

- *The SEM is an instrument that produces a magnified image by using electrons instead of light to form an image.*
- *A beam of electrons is produced at the top of the microscope by an electron gun, accelerate to energies up to few eV to 50 KeV, is focused at the surface of the specimen in the microscope & scanned across it in a 'raster' or pattern of parallel lines.*
- *Once the beam hits the sample, electrons and X-rays are ejected from the sample.*
- *Detectors collect these backscattered electrons, & secondary electrons and convert them into a signal that is sent to a screen similar to a television screen. This produces the final image.*



Working of SEM

- A number of phenomena occur at the surface under electron impact:
  - most important for scanning microscopy are the emission of secondary electrons with energies of a few tens eV and
  - re-emission or reflection of the **high-energy** backscattered electrons from the primary beam.
- The intensity of emission of both secondary and backscattered electrons is very sensitive to the a**ngle at which the electron beam strikes** the surface, i.e. to topographical features on the specimen.
- The emitted electron current is collected and amplified; **variations** in the resulting signal strength as electron probe is scanned across the specimen are used to vary the brightness of the trace of a cathode ray tube being scanned in synchronism with the probe. There is thus a **direct positional correspondence between the electron beam scanning across the specimen** & the **fluorescent image** on the cathode ray tube.
- The **magnification** produced by scanning microscope is the ratio between the dimensions of the final image display and the field scanned on the specimen. Usually magnification range of SEM is between **10 to 300 000 X** and the resolution (resolving power) is between **4 to 10 nm** (40 - 100 Angstroms) .

https://youtu.be/VWxYsZPtTsI

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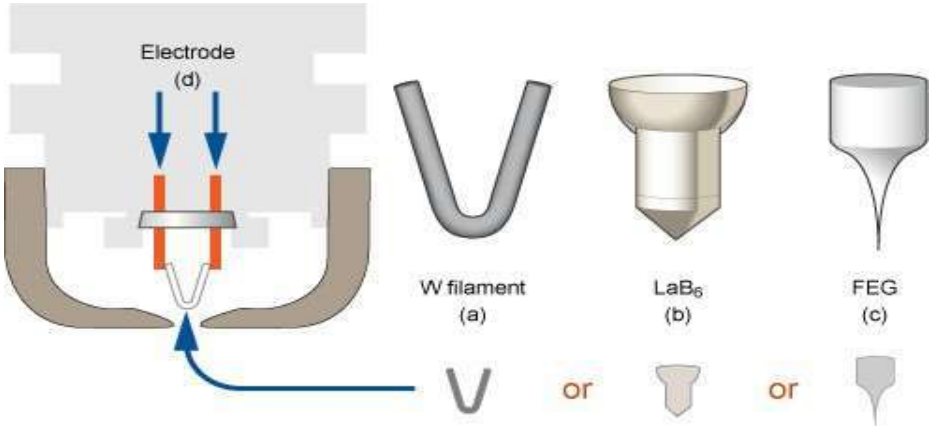
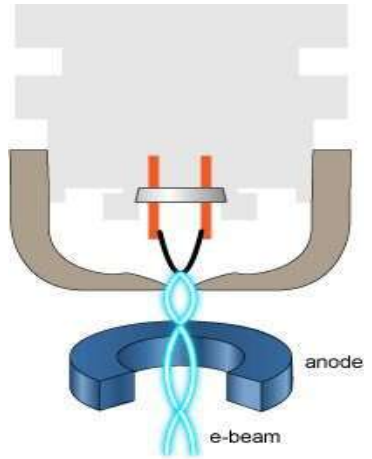
Electron gun



- The electron gun produces a source of electrons in an energy range typically 1-40kV.
- The conventional electron gun (triode) has three components, a **hot wire** (called the filament or cathode [- ve] or electron emitter), a Wehnelt (grid) **cap** [-ve], and an **anode** [+ ve]
- Lanthanum hexaboride (LaB6) filaments have advantage in this area, offering an electron source size of about 5 µm compared to tungsten's larger 50 µm. The **smaller source size** allows **LaB6** to focus the electron beam more sharply, resulting in **higher resolution** & **better image clarity**.
- The **hole** in the **anode** allows a fraction of the electrons to continue down the column through the lenses to produce a smaller, more cohesive beam
- Two important parameters for any electron gun are the **amount** of current produced & the current **stability**. At the **saturation point** the beam is **most stable**

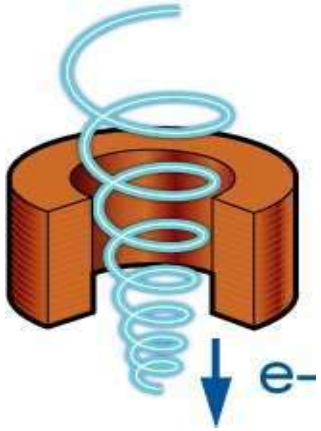


Condenser and objective lens

- The purpose of a lens is to change the path of the rays in a desired direction
- Since electrons are charged particles and they can be bent in a magnetic field
- These produce a focal length which can be changed by varying the current through the coil. They are called electromagnetic lenses
- Under the influence of a magnetic field, electrons assume a helical path, spiraling down the column

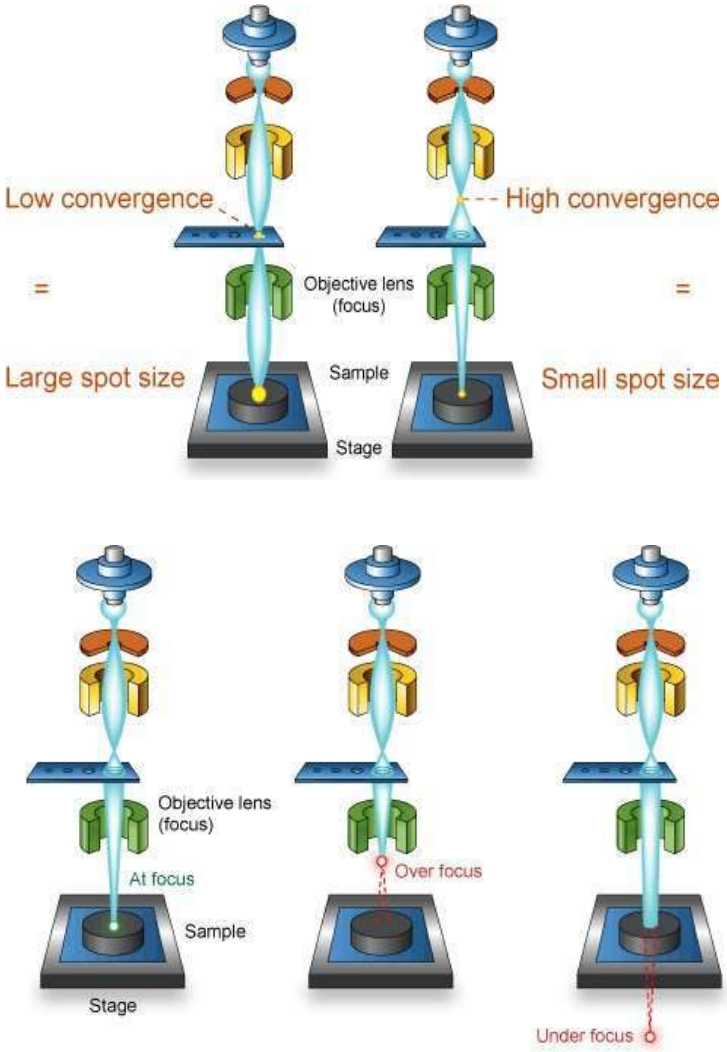
There are two lens, condenser lens and objective lens:

- **Condenser** lens: The condenser lens converges the cone of the electron beam to a spot below it
- **Objective** lens: converged back again by the objective lens and down onto the sample

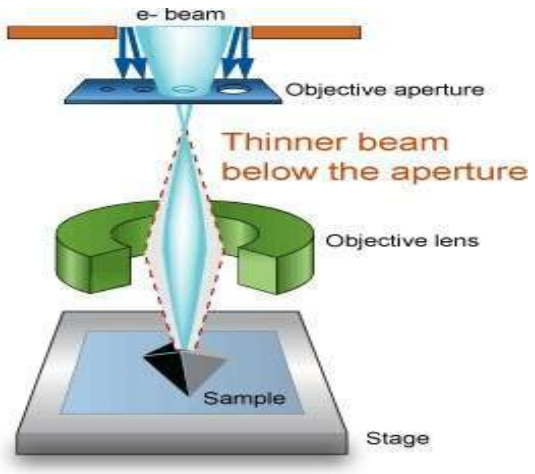


Condenser and objective lens

- This initial convergence can be at different heights, that is, close to the lens, or further away
- The closer it is to the lens, the **smaller** the **spot diameter** at the point of convergence. The further away, the larger the diameter of this point
- So, the **condenser** lens current controls this **initial spot size** and is referred to as the spot size control
- The **objective lens also** has **some** influence over the **diameter of the spot size** of the electron beam on the specimen surface. But its **main role** is in **focusing** the **beam onto the sample**
- A **focused beam** produces a **smaller spot** on the **surface** than an under or over- **focused** beam



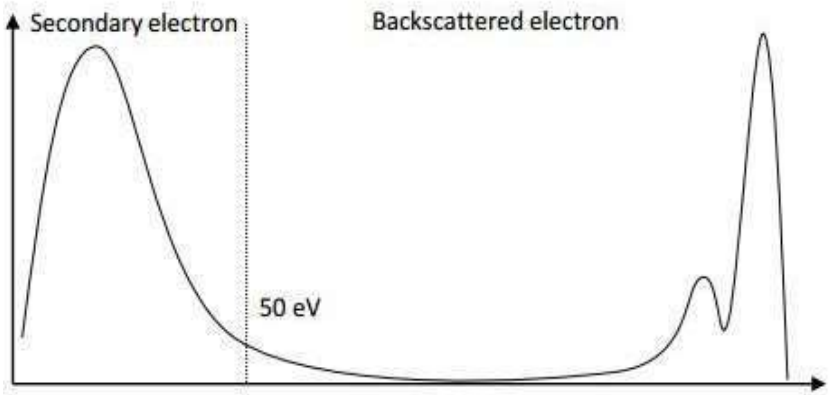
Aperture

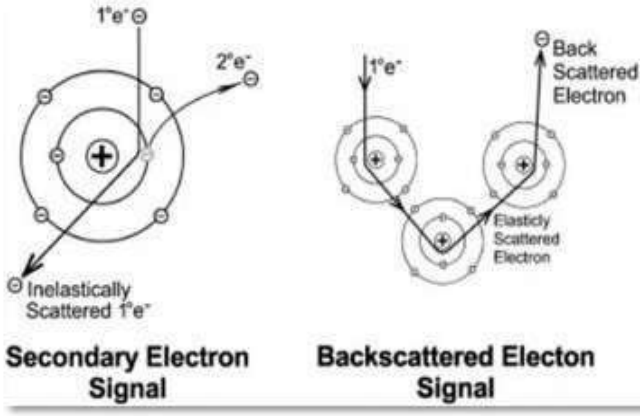


- The objective aperture arm fits above the objective lens in the SEM. It is a metal rod that holds a thin plate of metal containing four holes
- Over this fits a much thinner rectangle of metal with holes of different sizes. By moving the arm in and out different sized holes can be put into the beam path
- The aperture stops electrons that are off-axis or off-energy from progressing down the column. It can also narrow the beam below the aperture, depending on the size of the hole selected
- A large aperture is chosen for low magnification imaging to increase signal and for BSE and microanalysis work

Secondary and back scattered electron imaging

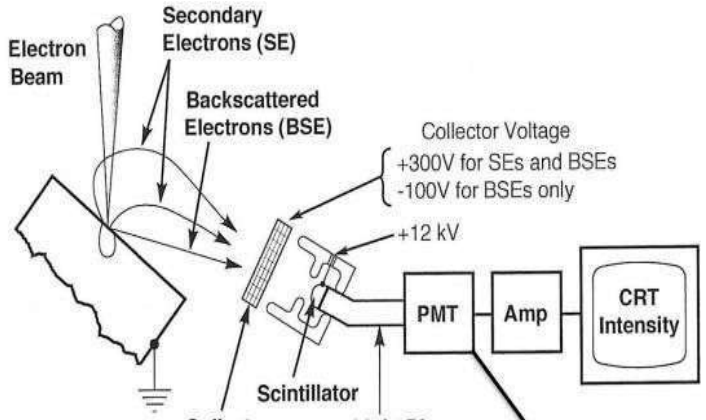
- **Secondary Electrons** produced through inelastic scattering that results in the ejection of loosely bound electrons from the specimen. Secondary electrons have energies from ~2-50 eV
  - The low energy of these electrons allows them to be collected easily. This is achieved by placing a positively biased grill on the front of the SE detector, which is positioned off to one side of the specimen
  - Shallow escape depth (~2nm), information of specimen surface only
- **BSE**
  - Elastically and inelastically scattered primary electrons
  - > 50% primary electron energy

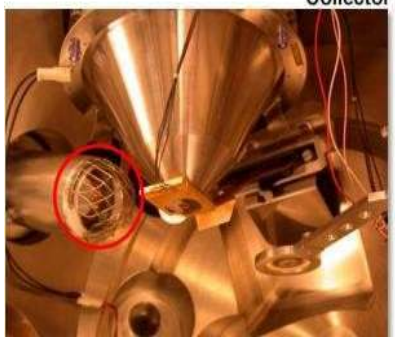


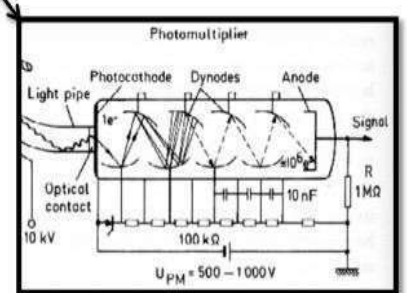


Yield of secondary electron emission

- Average number of secondary electrons produced per incident electron, 0.1-10
- Strongly dependent on
  - material,
  - **surface** structure,
  - **angle** of incidence,
  - **energy** of incident electron
- Large at specimen edge due to edge effect contrast at edge
- Larger for inclined incidence as volume
- SE yield sensitive to surface detail





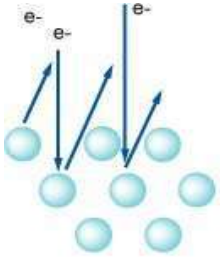


Secondary electron imaging

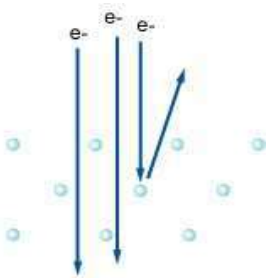
- The major influence on SE signal-generation is the shape (topography) of the specimen surface. Secondary electrons provide particularly good edge detail. **Edges** (and often pointy parts) look **brighter** than the rest of the image because they produce **more electrons**
- To increase the yield of SE emitted from the specimen, heavy metals such as gold or platinum are routinely used to coat specimens with conducting layer
- An extremely thin layer is applied (~10 nm). This coating is applied for two main reasons:
  1. Non-conductive specimens are often coated to reduce surface charging that can block the path of SE and cause distortion of signal level and image form &
  2. Low atomic number (Z) specimens (e.g. biological samples) are coated to provide a surface layer that produces a higher SE yield than the specimen material
- Electrons emitted from a surface that **faces away** from the detector, or which is **blocked** by the topography of the specimen, will appear darker than surfaces that face towards the detector
- Another mechanism to increase SE contrast in an image is to **tilt** the sample so that it is at an angle to the probe (typically 30 to 60°). As a result of tilting, more SE are generated per unit of projected specimen area. and this enhances contrast by making the distribution of light and dark areas more pronounced

Backscattered electron

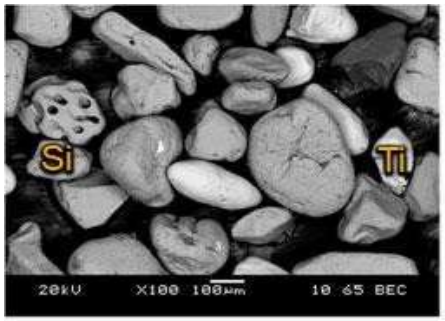
- Backscattered (BS) electrons are **high-energy electrons** (>50 eV) from the primary incident beam that are **ejected back out from the sample**. These BSE are used to produce a different kind of image. Such an image uses contrast to tell us about the **average atomic number** of the sample
- For example, a grain of sand that is made up of a titanium mineral looks whiter than a grain made of a silicon material (Ti versus Si)



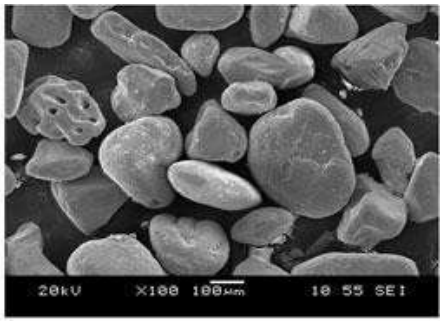
Titanium
atomic number 22



Silicon
atomic number 14



Backscattered electon image (BSE)



Secondary electron image (SE)

- The backscattered electron has an energy up to the incident beam energy & is usually very near that energy. The greater energy of BSE, compared with SE, means that BSE produced from deeper within the interaction volume are able to escape from the sample and be collected by the BSE detector: lower resolution than SE images
- For non-conducting sample carbon can be coated (a low atomic number material) to enhance conductivity without obscuring the compositional detail from below

Advantages of SEM

The scanning electron microscope has many advantages over traditional microscopes:

1. The SEM has a large depth of field, which allows more of a specimen to be in focus at one time.
2. The SEM also has much **higher resolution (few nm),** so closely spaced specimens can be magnified at much higher levels.
3. Because the SEM uses electromagnets rather than lenses, the researcher has much more control in the degree of magnification.
4. **High Magnification** up to (**10-300000x**)

SEM provides the following information:

1. **Topography**- The surface features of the sample.
2. **Morphology**- The shape, size, and arrangements of the particles present in the sample.
3. **Composition**- The elements and the compounds, the sample is composed of.
4. **Crystallographic Information**- The crystal structure and the degree of order present in the sample.

Questions / Discussions