

Scanning Electron Microscopy & Energy Dispersive X-Ray Spectroscopy

Chem 502 Adv. Anal. Chem



The most versatile instrument for a materials scientist?

- *What can we study in a SEM?*

- Topography; the surface features of an object or how it looks, its texture.
- Morphology: the shape and size of the particles making up the object.
- Chemistry: The elements and compounds that the object is composed of and the relative amount of them.
- Crystallography: How the atoms are arranged in the object.

Topography and morphology

- High depth of focus

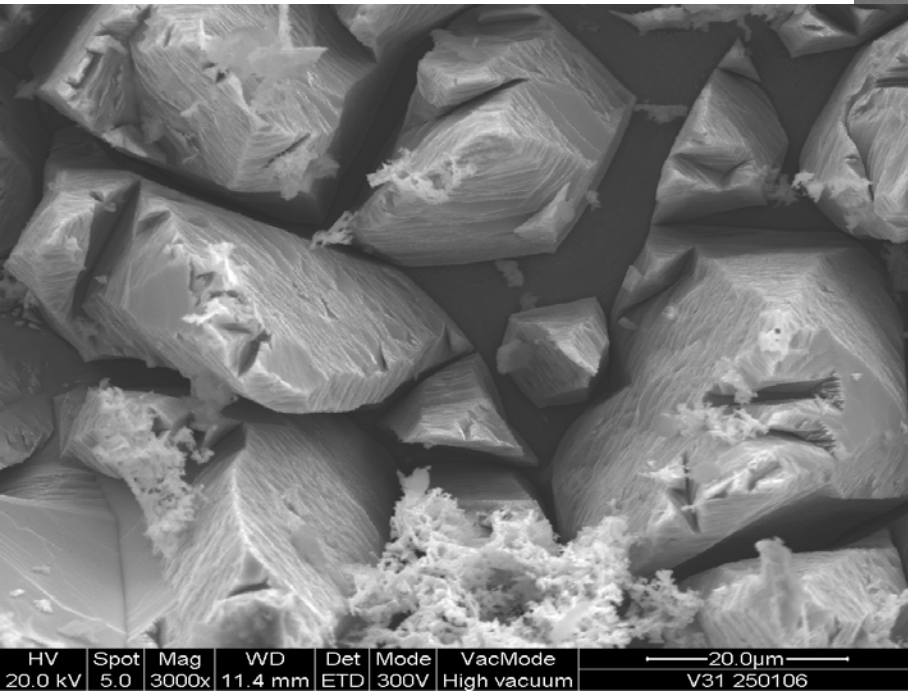


Image: Christian Kjølseth, UiO

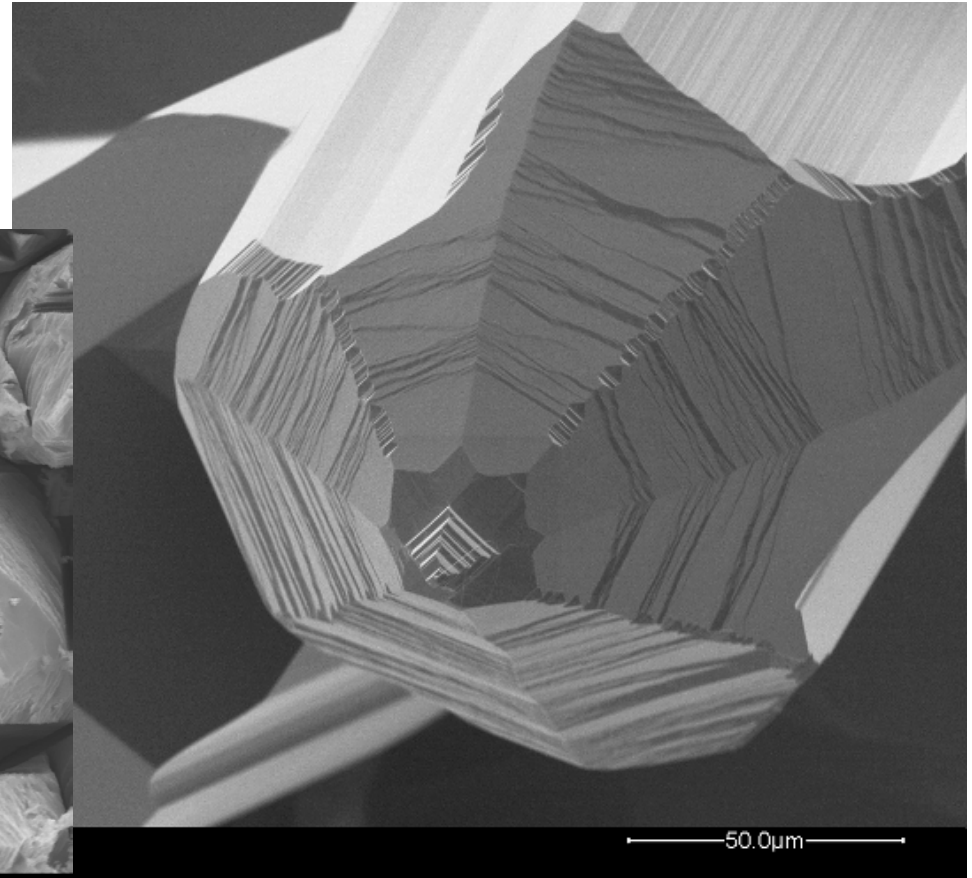
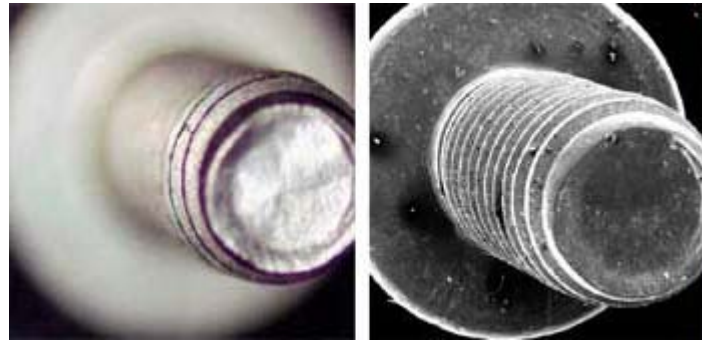


Image: Camilla Kongshaug, UiO

Depth of focus

Optical microscopy vs SEM



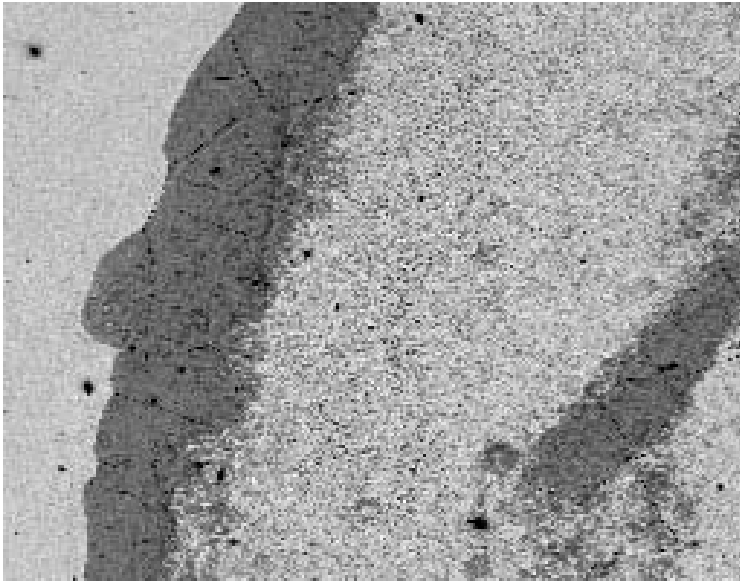
Screw length: ~ 0.6 cm

Images: the A to Z of Materials

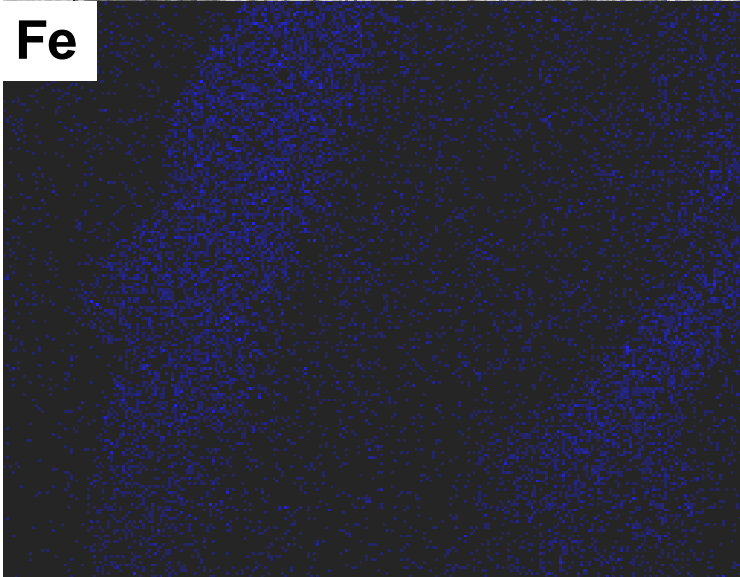
- A SEM typically has orders of magnitude better depth of focus than an optical microscope making SEM suitable for studying rough surfaces
- The higher magnification, the lower depth of focus

Chemistry

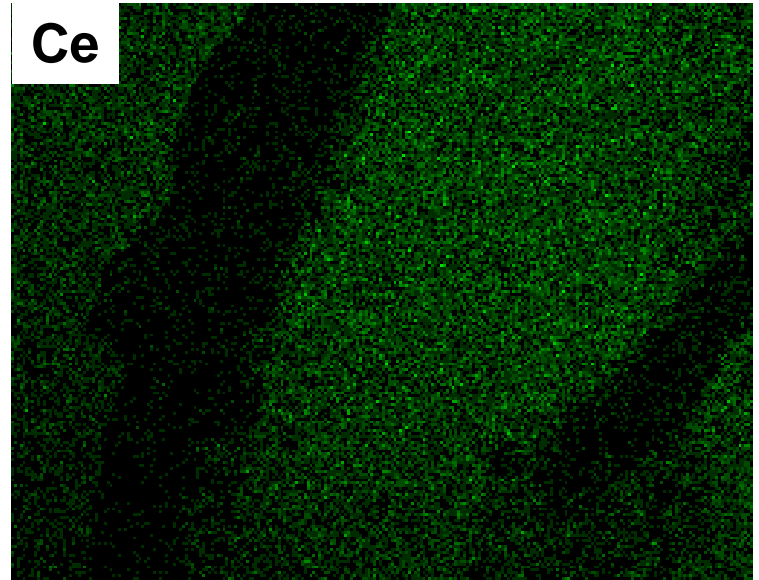
Images: Harald Fjeld, UiO



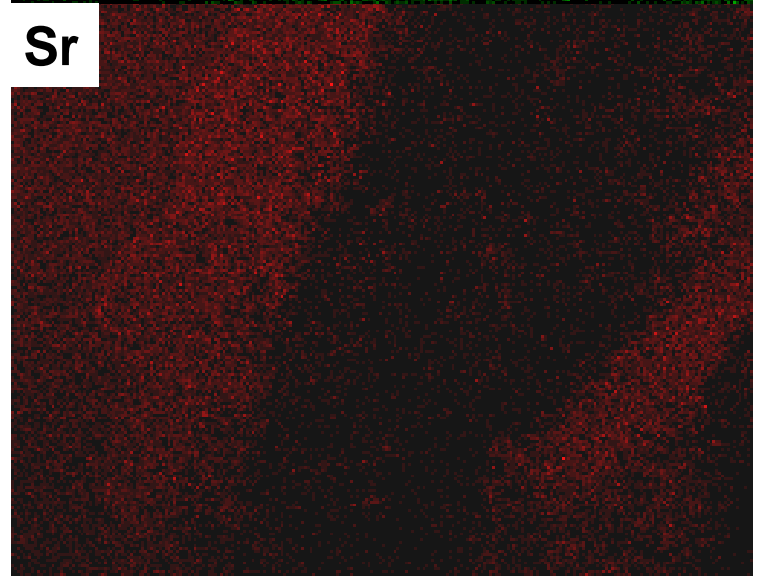
Fe



Ce

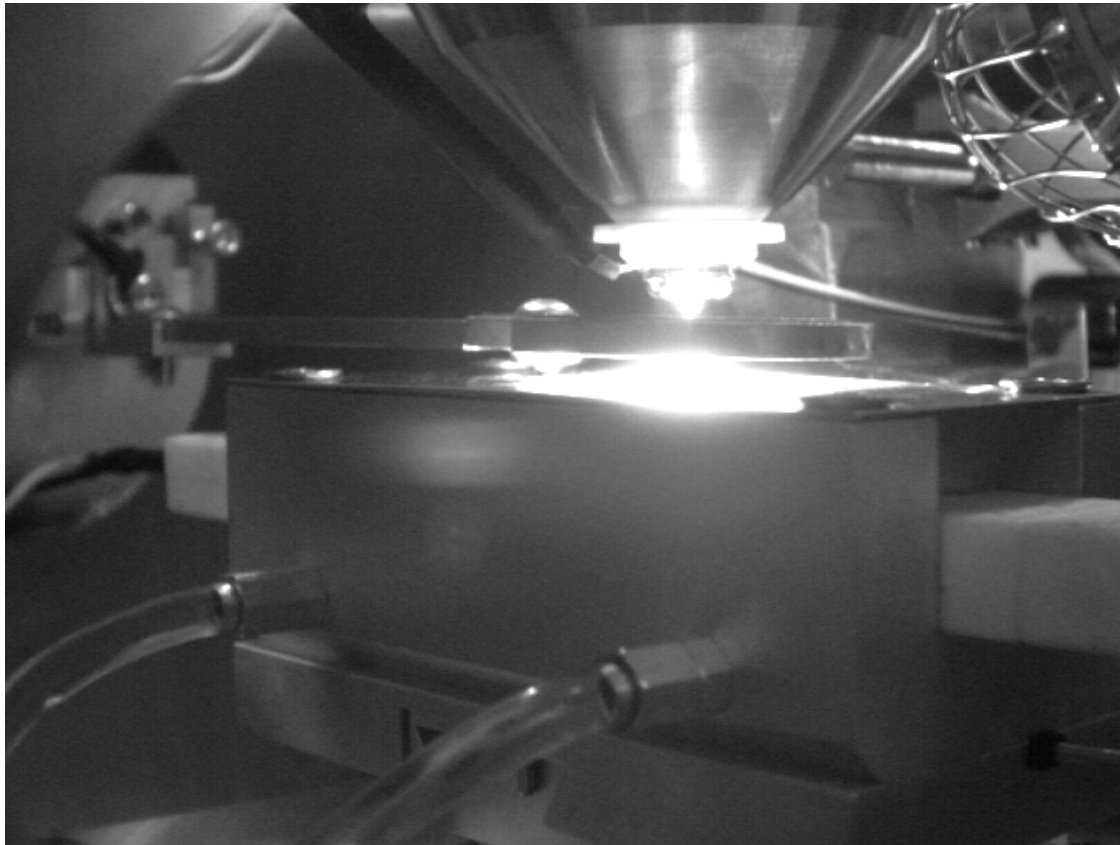


Sr



In-situ imaging

- A modern SEM can be equipped with various accessories, e.g. a hot stage



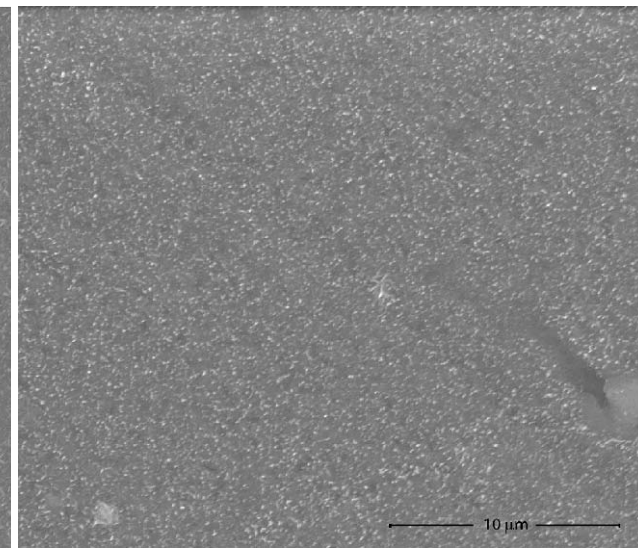
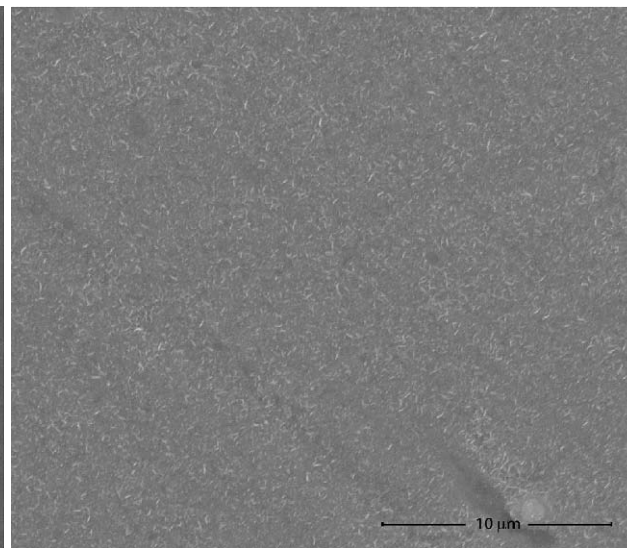
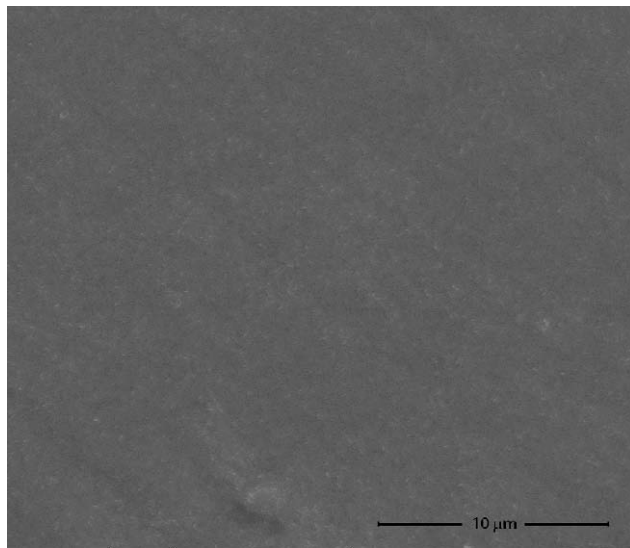
In-situ imaging: oxidation of steel at high temperatures

- 800 °C, $p_{\text{H}_2\text{O}} = 667 \text{ Pa}$
- Formation of Cr_2O_3

2 min

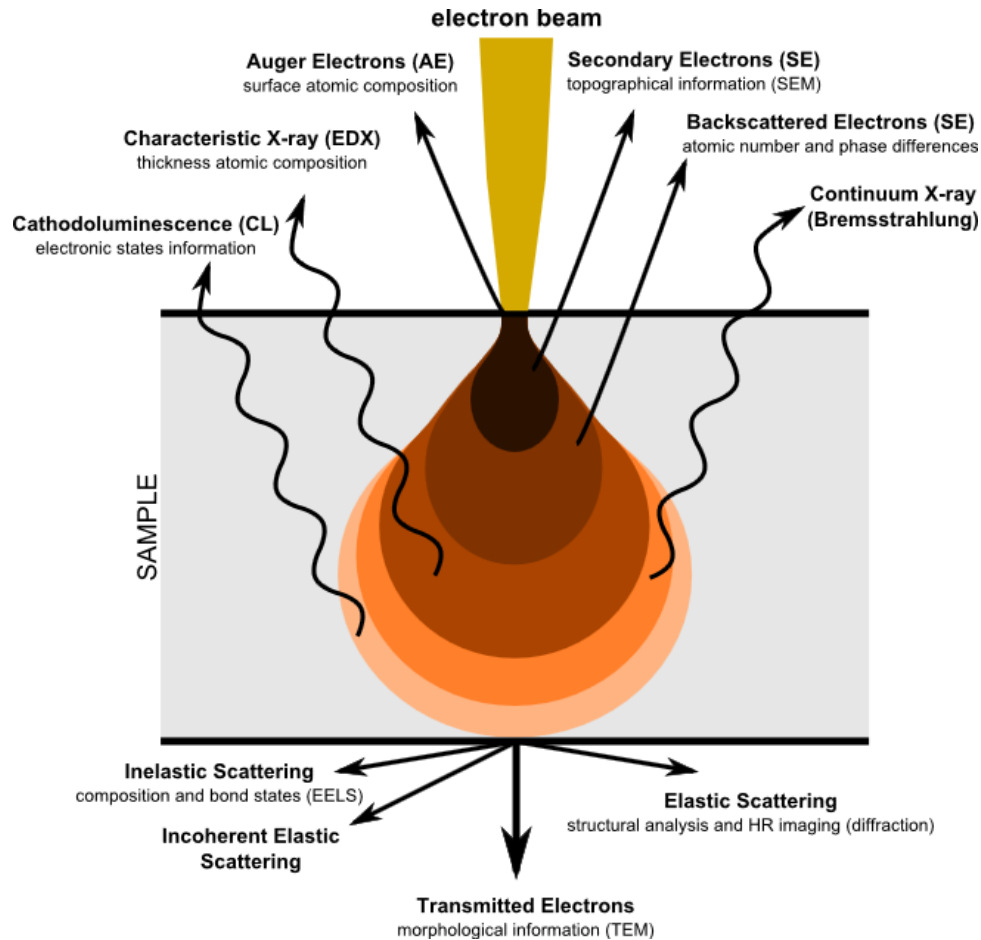
10 min

90 min



Images: Anders W. B. Skilbred, UiO

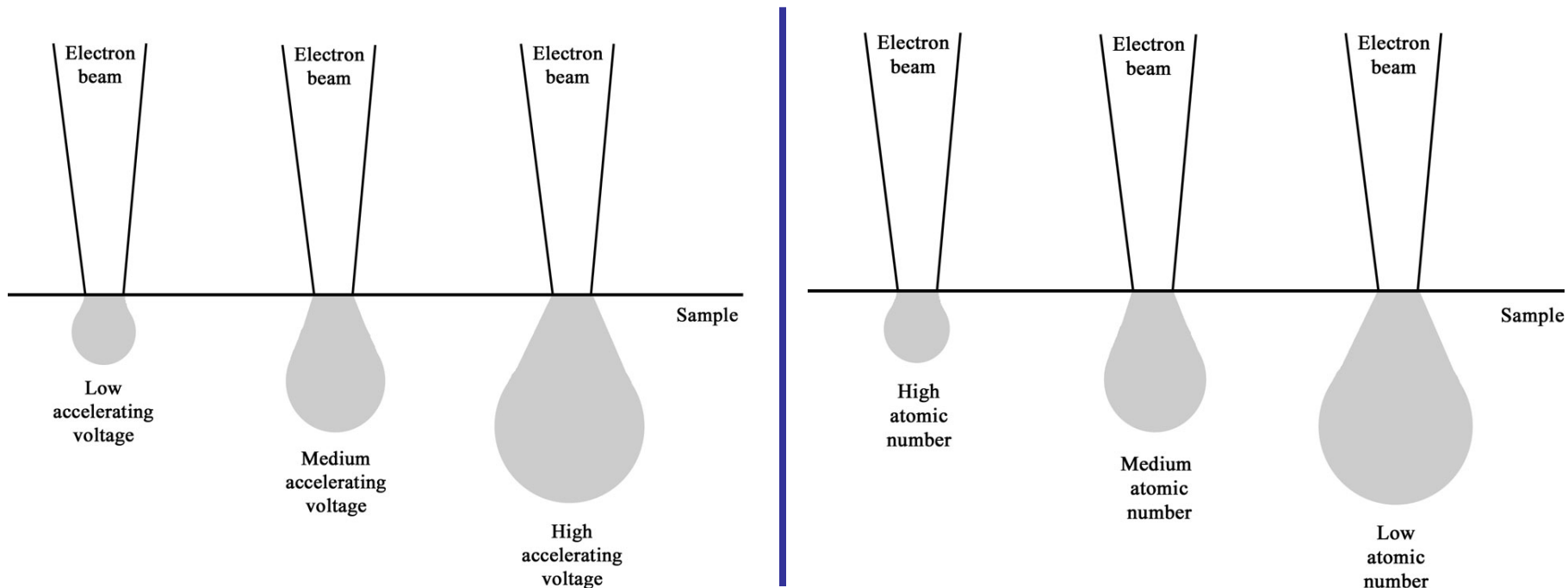
ELECTRON BEAM – SAMPLE INTERACTIONS



- In the scanning electron microscope a stream of primary electrons is focused onto the sample surface resulting in a number of different particles or waves being emitted (secondary electrons, back-scattered electrons, X-rays, photons, Auger electrons...).
- The secondary and backscattered electrons are used for imaging while the X-rays give characteristic chemical information of the emitting atoms.
- The probed depth in EDX analysis is around 1-3 μm

Parameters on Electron beam-sample interactions

- The incident electron beam is **scattered** in the sample, both elastically and inelastically
- This gives rise to various signals that we can detect
- Interaction volume increases with increasing acceleration voltage and decreases with increasing atomic number

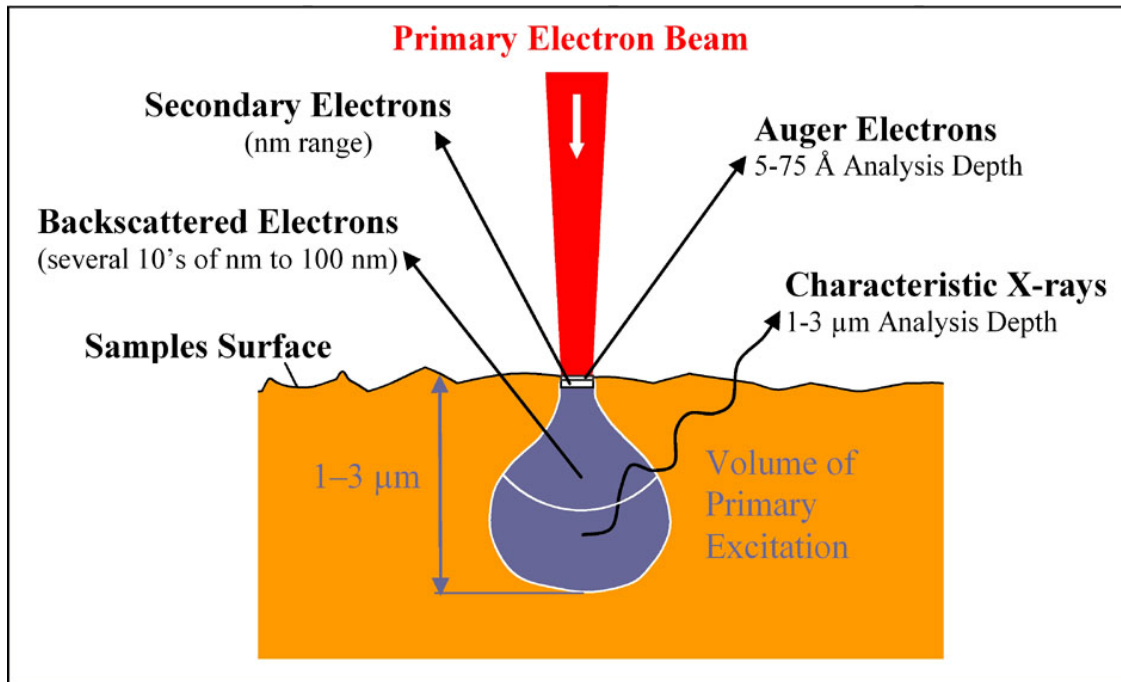


acceleration voltage

atomic number

Where does the signals come from?

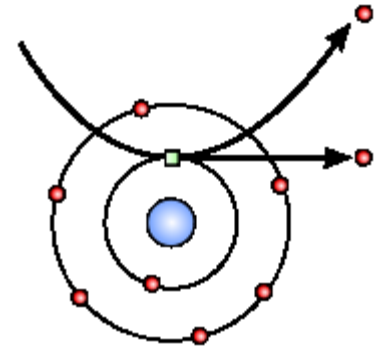
- The electron beam follows a vertical path through the column of the microscope.
- Once it hits the sample, other electrons are ejected from the sample.
- Detectors collect the **secondary or backscattered electrons**, and convert them to a signal that is sent to a viewing screen similar to the one in an ordinary television, producing an image.



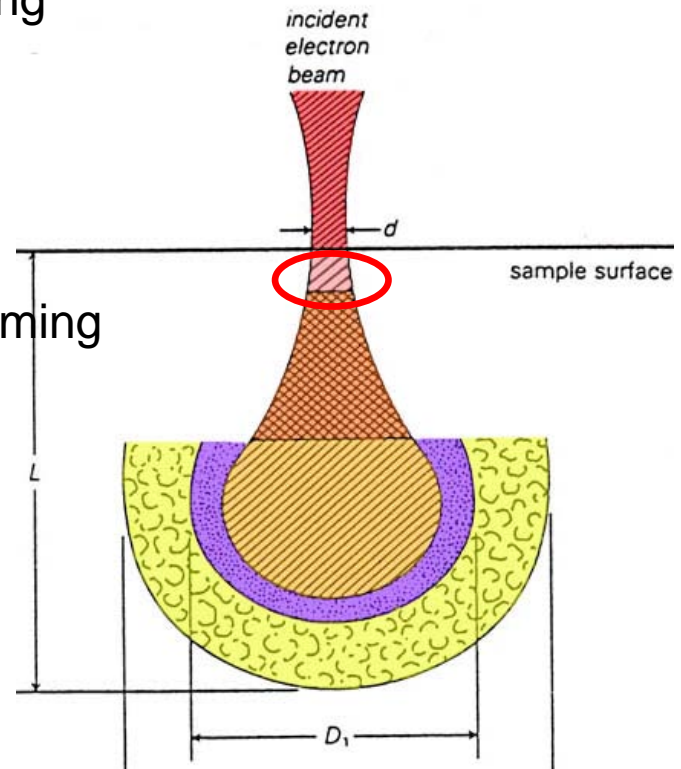
- Diameter of the interaction volume is larger than the electron spot → resolution is poorer than the size of the electron spot

Secondary electrons (SE):

- The most common imaging mode collects low energy $<50\text{eV}$ Secondary electrons that are ejected from the k-shell of the specimen atoms by inelastic scattering interactions with beam electrons. Due to their low energy, these electrons originate within a few nanometers from the sample surface.

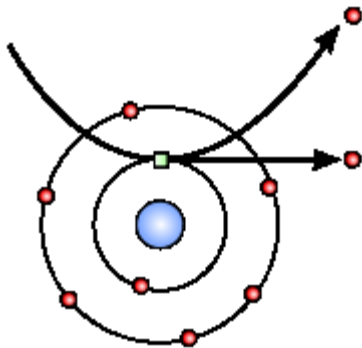


- Generated from the collision between the incoming electrons and the loosely bonded outer electrons
- Low energy electrons ($\sim 10\text{-}50\text{ eV}$)
- Only SE generated close to surface escape (topographic information is obtained)
- Number of SE is greater than the number of incoming electrons
- We differentiate between SE1 and SE2



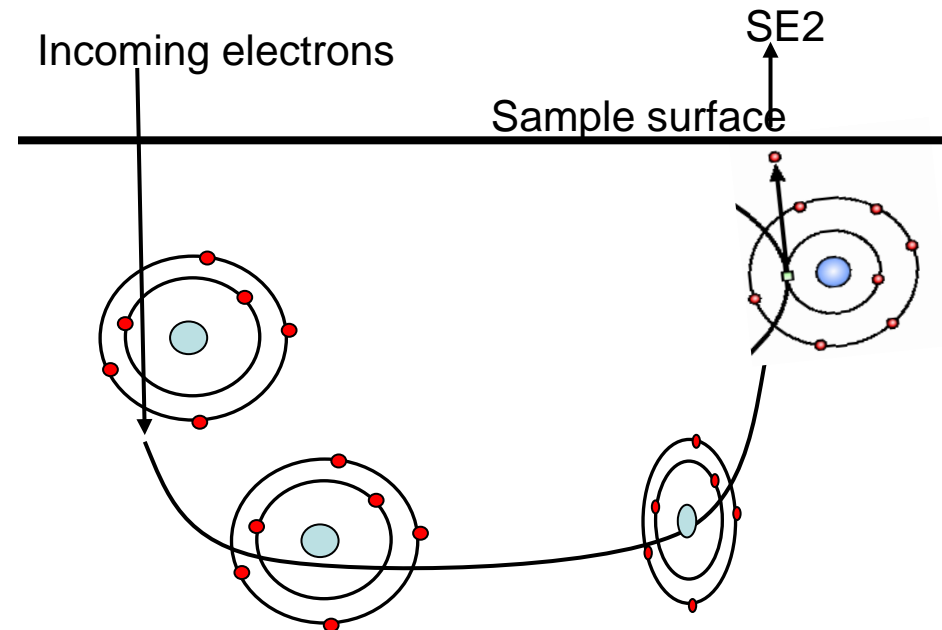
SE1

- The secondary electrons that are generated by the incoming electron beam as they enter the surface
- High resolution signal with a resolution which is only limited by the electron beam diameter



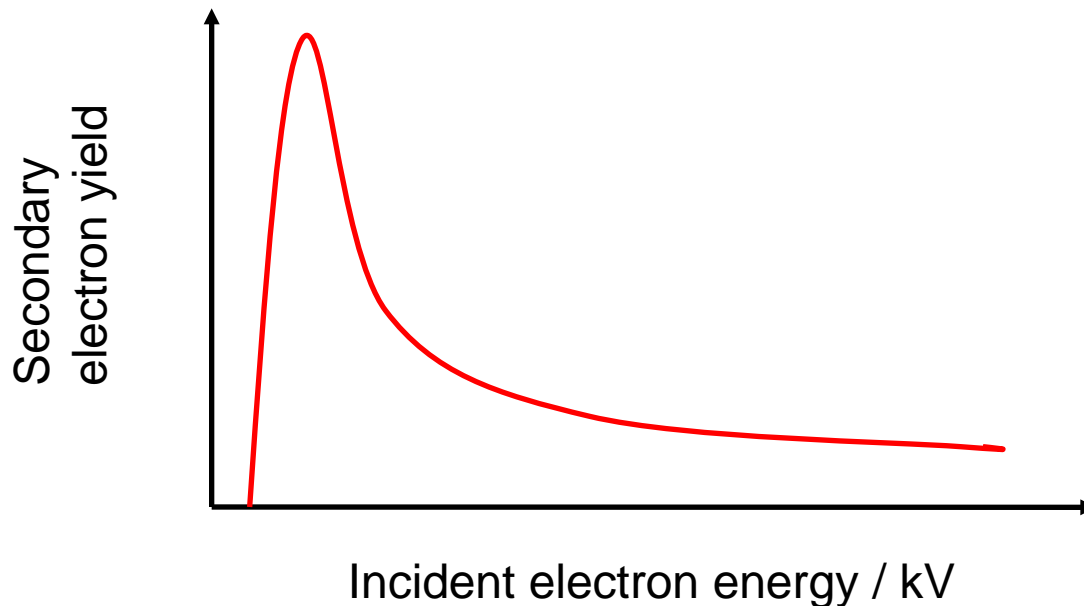
SE 2

- The secondary electrons that are generated by the backscattered electrons that have returned to the surface after several inelastic scattering events
- SE2 come from a surface area that is bigger than the spot from the incoming electrons → resolution is poorer than for SE1 exclusively



Factors that affect SE emission

1. Work function of the surface
 2. Beam energy and beam current
- Electron yield goes through a maximum at low acc. voltage, then decreases with increasing acc. voltage (page 283)

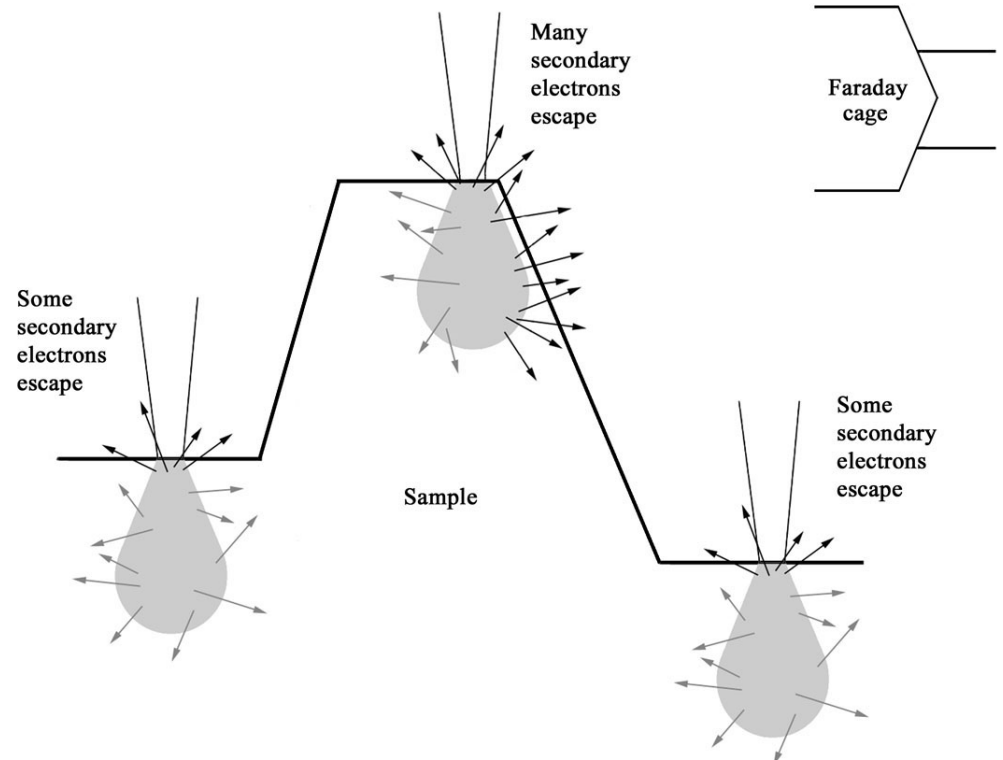


Factors that affect SE emission

3. Atomic number (Z)

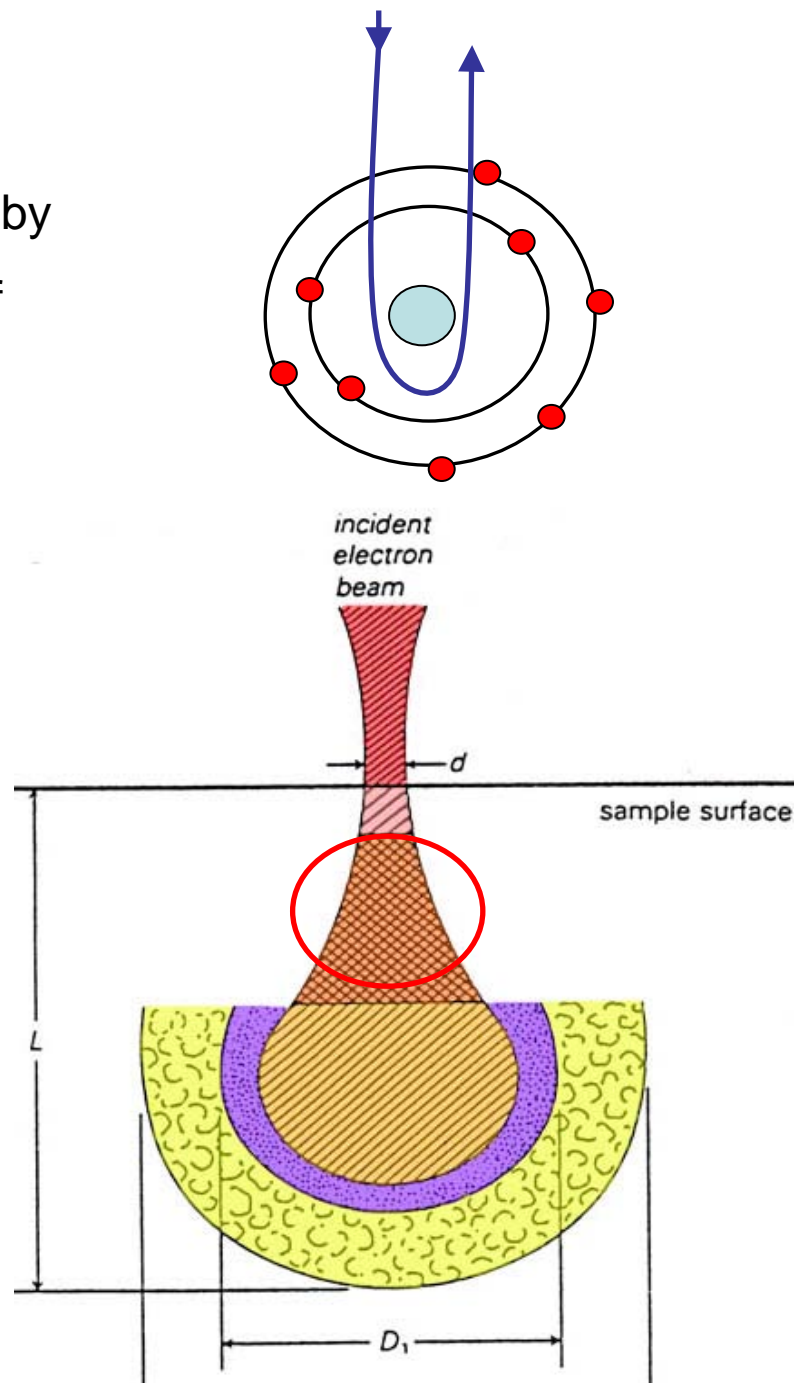
- More SE2 are created with increasing Z
- The Z-dependence is more pronounced at lower beam energies

4. The local curvature of the surface (the most important factor)



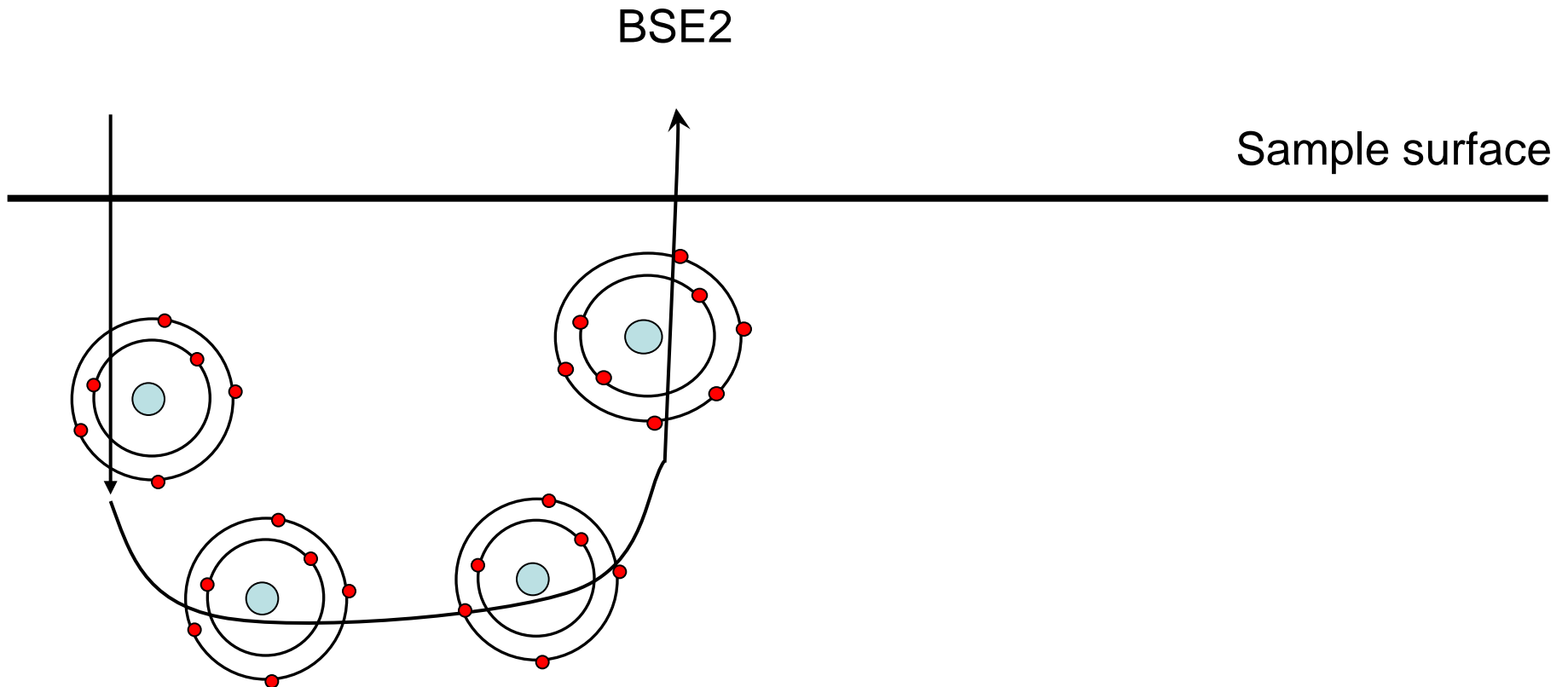
Backscattered electrons (BSE)

- A fraction of the incident electrons is retarded by the electro-magnetic field of the nucleus and if the scattering angle is greater than 180° the electron can escape from the surface
- Back scattered electrons(BSE) consist of high-energy electrons originating in the electron beam, that are reflected or back-scattered out of the specimen interaction volume by elastic scattering interactions with specimen atoms.
- Since heavy elements (high atomic number) backscatter electrons more strongly than light elements (low atomic number), and thus appear brighter in the image.



Backscattered electrons (BSE)

- High energy electrons (elastic scattering)
- Fewer BSE than SE



BSE as a function of atomic number

- For phases containing more than one element, it is the average atomic number that determines the backscatter coefficient η

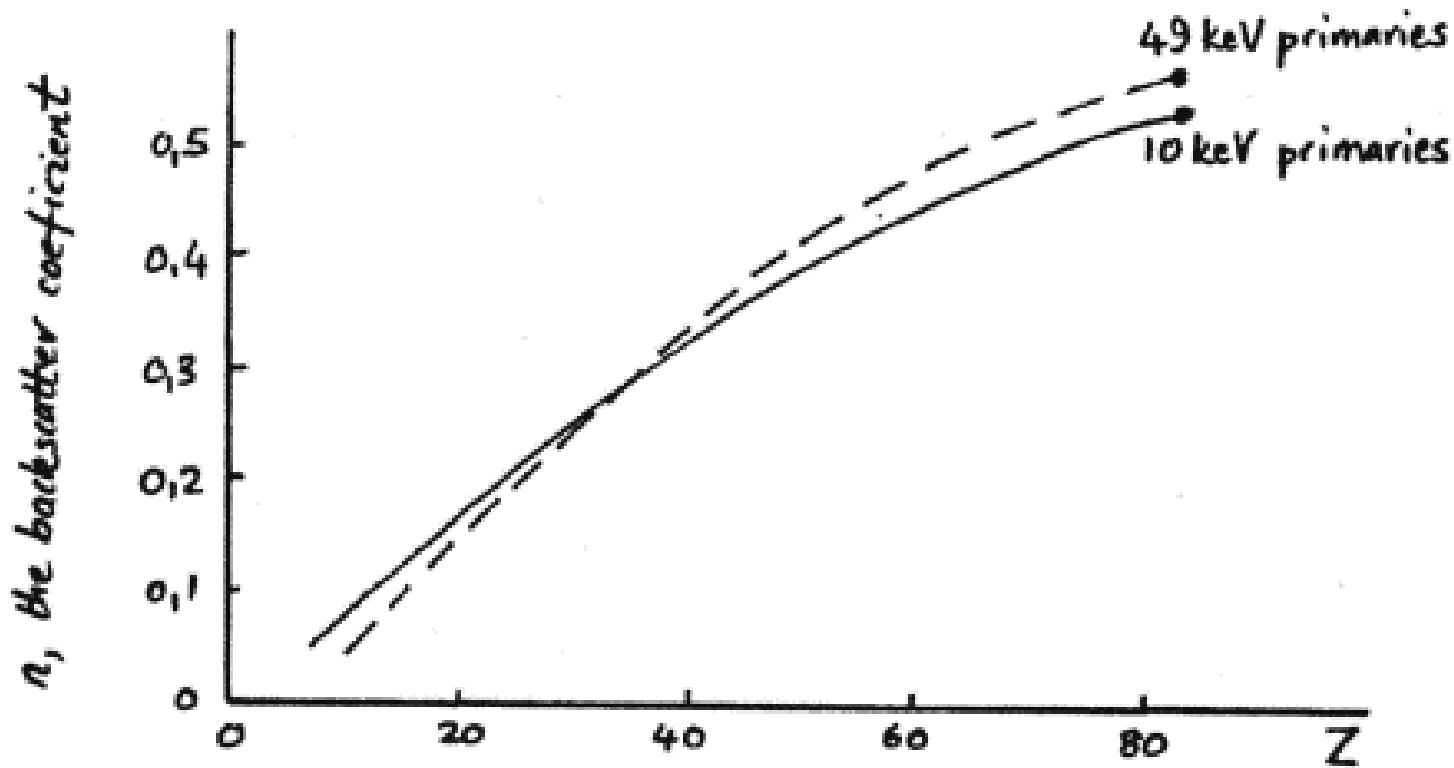
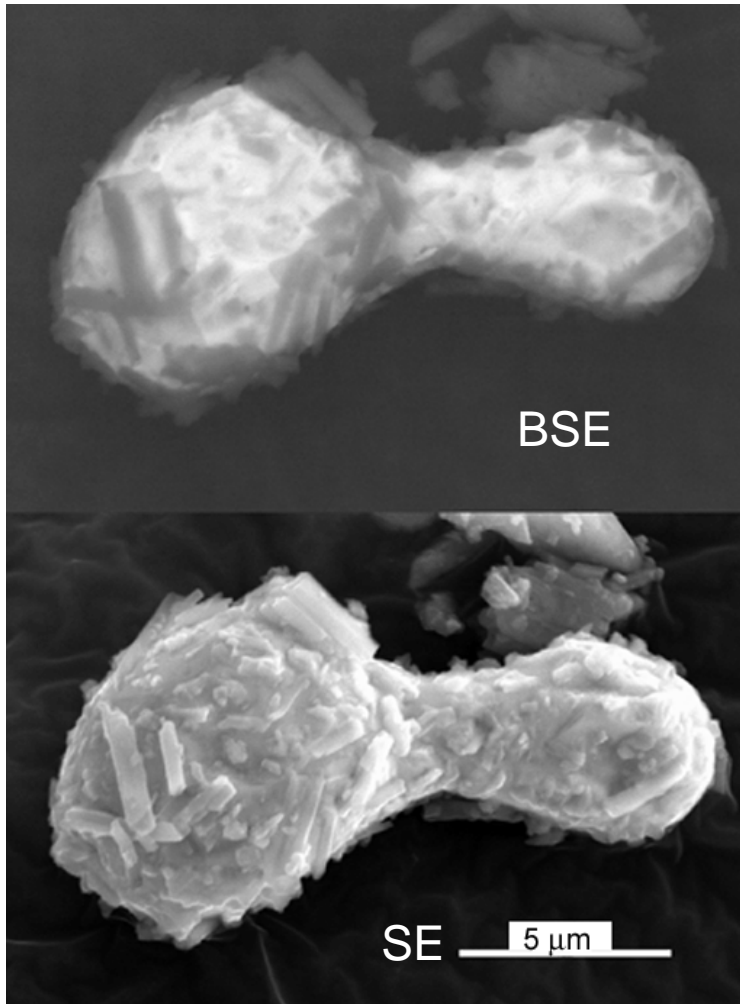


Image: University of Cape Town

Factors that affect BSE emission

- Direction of the irritated surface
 - more electrons will hit the BSE detector when the surface is aligned towards the BSE detector
- Average atomic number
- When you want to study differences in atomic numbers the sample should be as levelled as possible (sample preparation is an issue!)

BSE vs SE



- SE produces higher resolution images than BSE

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- Resolution of 1 –2 nm is possible

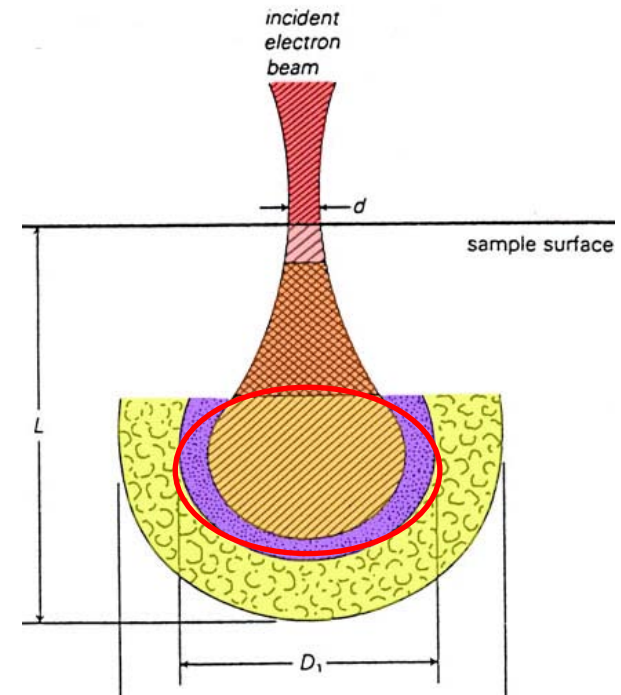
Images: Greg Meeker, USGS

SUMMARY

- Signals:
 - Secondary electrons (SE): mainly topography
 - Low energy electrons, high resolution
 - Surface signal dependent on curvature
 - Backscattered electrons (BSE): mainly chemistry
 - High energy electrons
 - "Bulk" signal dependent on atomic number
 - X-rays: chemistry
 - Longer recording times are needed

X-rays

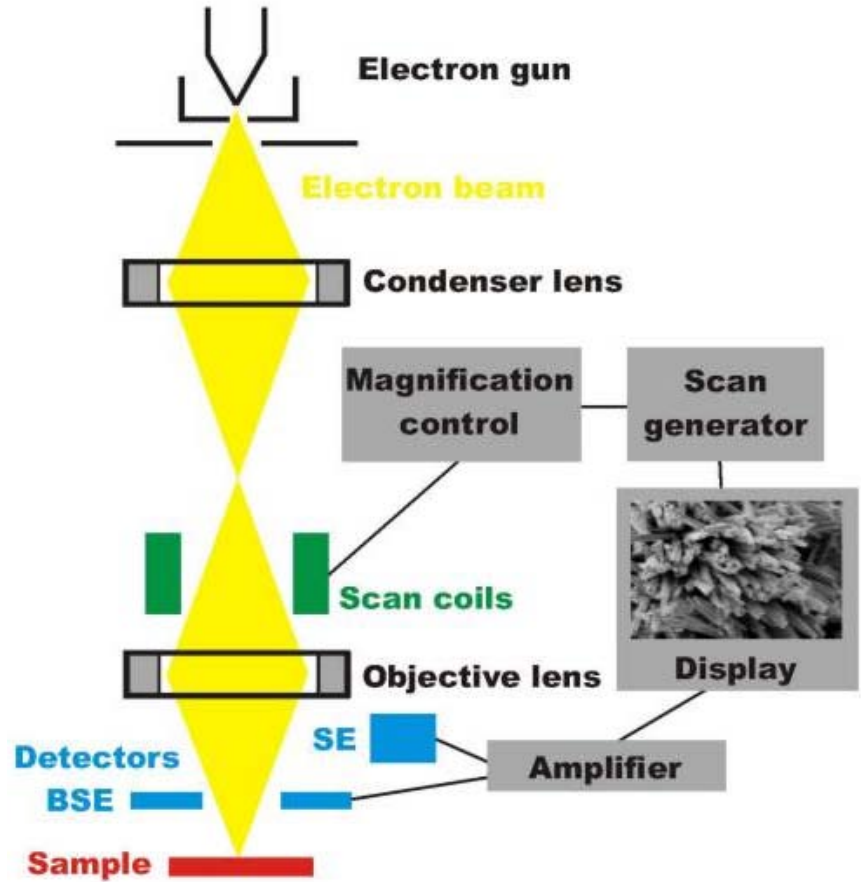
- *Photons* not electrons
- Each element has a *fingerprint* X-ray signal
- Poorer spatial resolution than BSE and SE
- Relatively few X-ray signals are emitted and the detector is inefficient
→ relatively long signal collecting times are needed



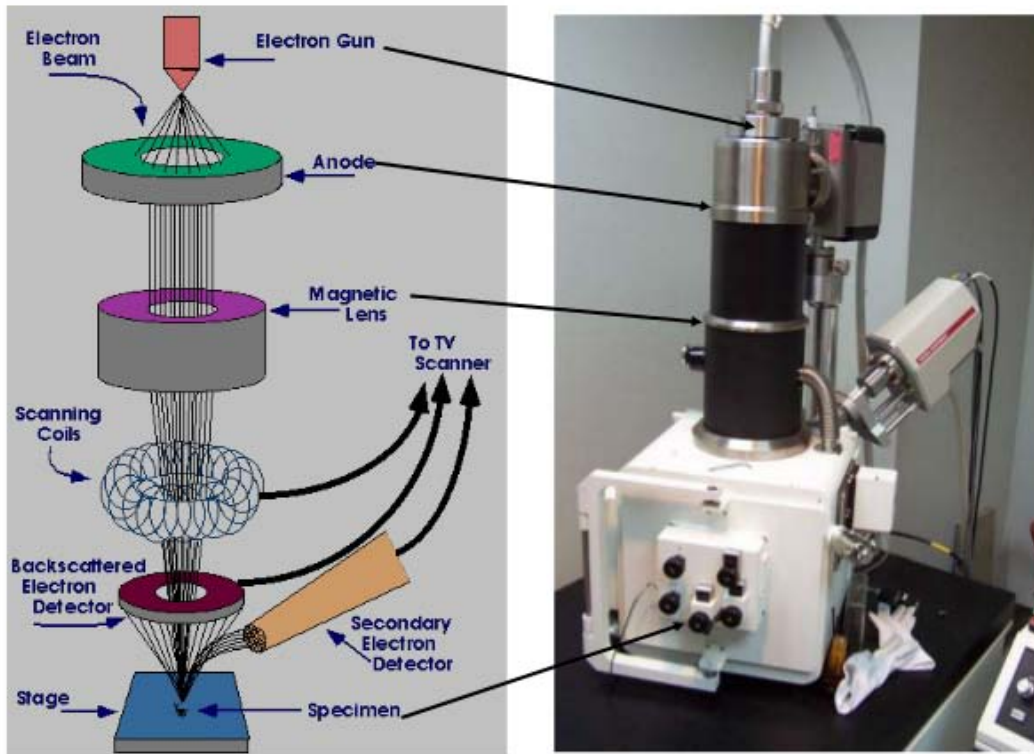
X-rays

- Most common spectrometer: EDS (energy-dispersive spectrometer)
- Signal overlap *can* be a problem
- We can analyze our sample in different modes
 - spot analysis
 - line scan
 - chemical concentration map (elemental mapping)

The instrument in brief



Components of the instrument



8/30/2016

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- electron gun (filament)
- electromagnetic optics
- scan coils
- sample stage
- detectors
- vacuum system
- computer hardware and software (not trivial!!)



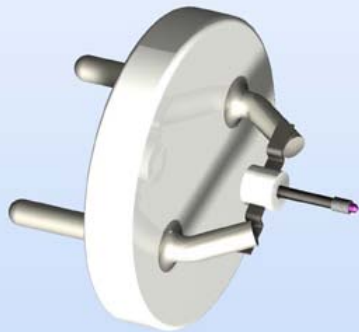
Electron guns:

- We want many electrons per time unit per area (high current density) and as small electron spot as possible
- Traditional guns:
 - thermionic electron gun (electrons are emitted when a solid is heated)
 - W-wire, LaB₆-crystal
- Modern electron guns:
 - field emission guns (FEG) (cold guns, a strong electric field is used to extract electrons)
 - Single crystal of W, etched to a thin tip

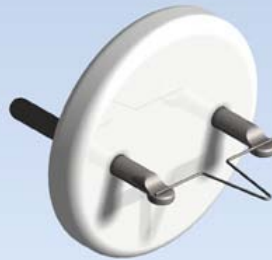


Electron guns:

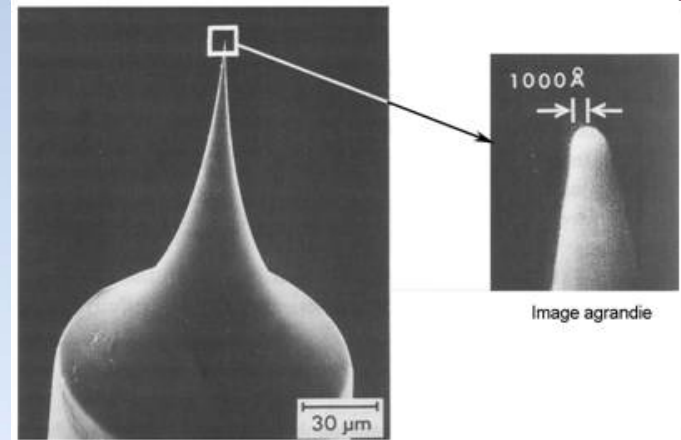
- With field emission guns we get a smaller spot and higher current densities compared to thermionic guns
- Vacuum requirements are tougher for a field emission guns



Single crystal of LaB₆



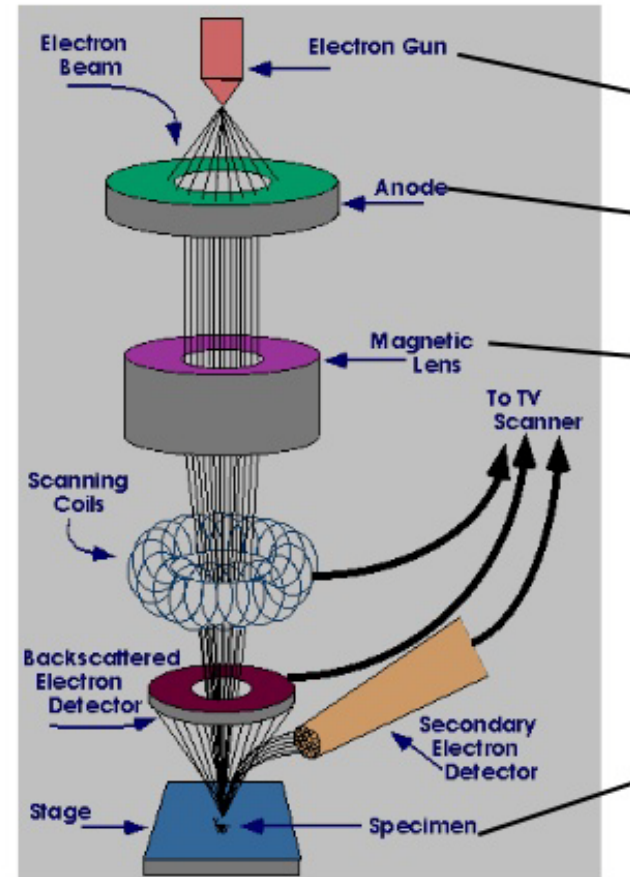
Tungsten wire



Field emission tip

Magnetic Lens System:

- Condenser lens is a lens placed right below the electron gun and is used to adjust the width of the electron beam as per requirement.
 - The condenser lens controls the intensity of the electron beam reaching the specimen.
 - The objective lens brings the electron beam into focus on the specimen.
 - The scanning coils deflect the electron beam horizontally and vertically over the specimen surface. This is also called rastering.
- A fine e- beam is required for SEM, for better performance

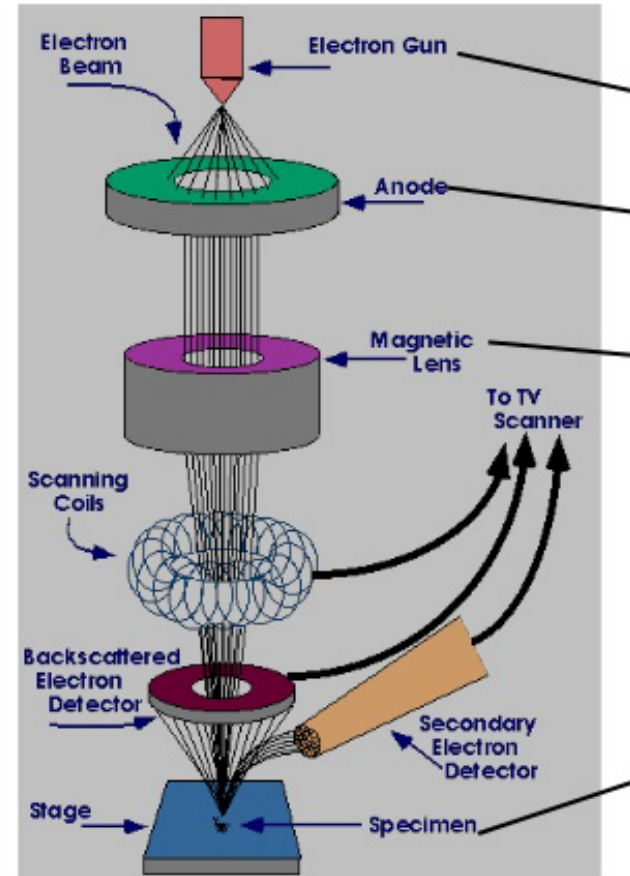


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Specimen Stage/Chamber

- It receives and supports the specimen.
- Specimen stage should be able to perform the horizontal and vertical movements smoothly.
- The horizontal movement is used for selection of the field while the vertical movement is used to change the image resolution
- The operating environment of a standard scanning electron microscope dictates that special preparation techniques are used.
- Typically, a biological specimen is chemically fixed, dehydrated through an acetone or ethanol series and then dried at the critical point - a method used to minimize specimen distortion due to drying tensions.
- For dry samples, this process is not necessary.
- SEM can also be used to investigate smooth surfaces of industrial samples.
- The samples are mounted on a stub of metal with adhesive, coated with 40 - 60 nm of metal such as Gold/Palladium and then observed in the microscope.



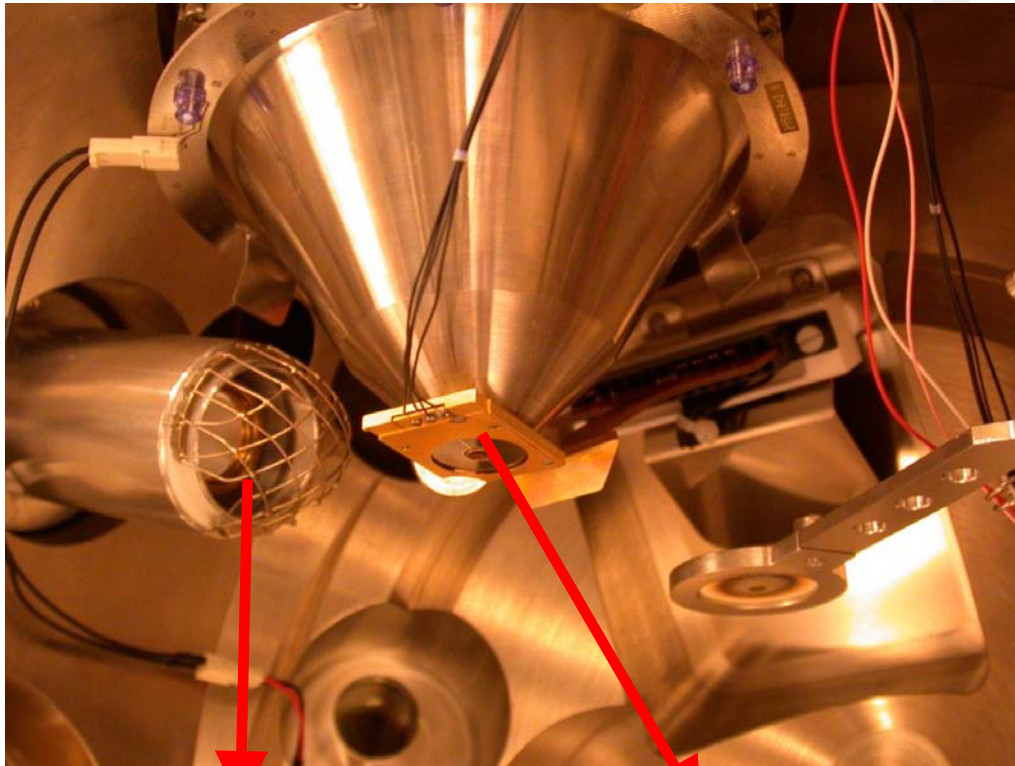
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Detectors:

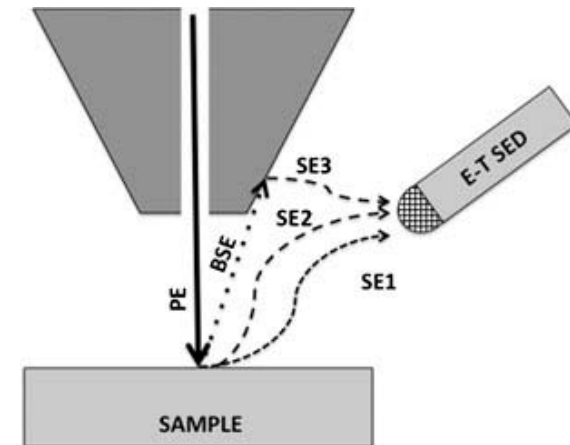
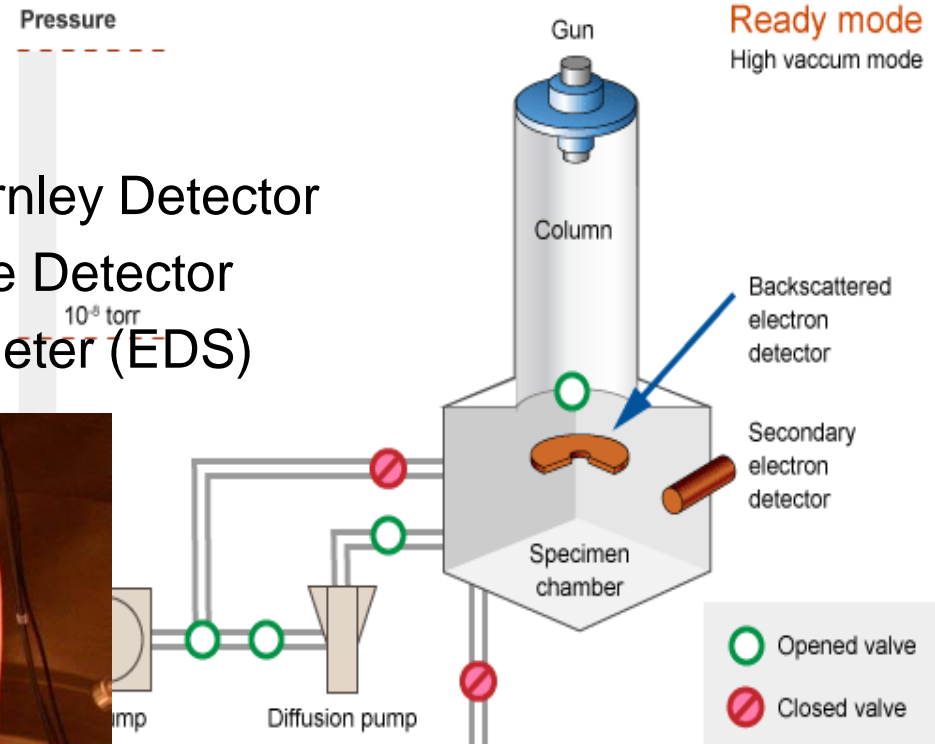
Traditional detectors

- Secondary electrons: Everhart-Thornley Detector
- Backscattered electrons: Solid State Detector
- X-rays: Energy dispersive spectrometer (EDS)



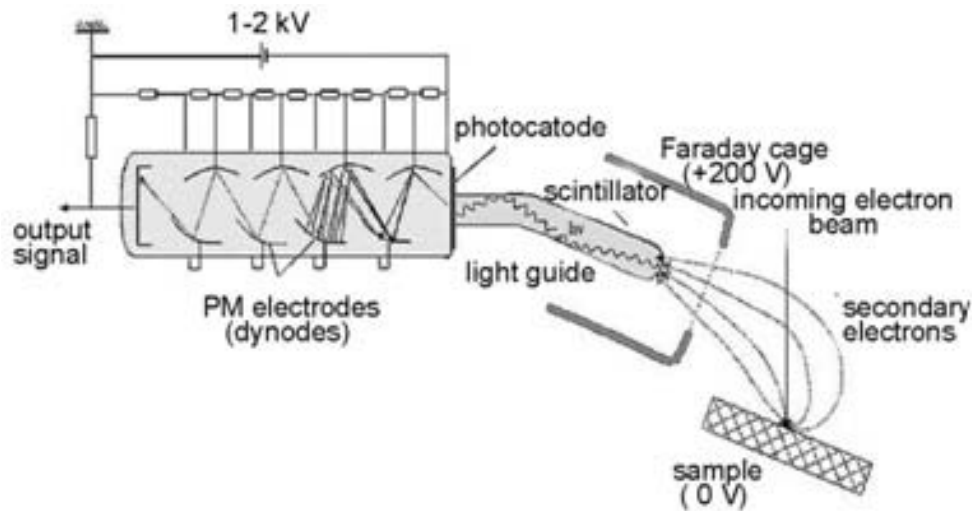
Secondary electron detector:
(Everhart-Thornley)

Backscattered electron detector:
(Solid-State Detector)



electron trajectories

The secondary electron detector: **Everhart-Thornley detector:**



- The detector consists primarily of a [scintillator](#) inside a [Faraday cage](#).
- A low positive [voltage](#) is applied to the Faraday cage to attract the relatively low energy (less than 50 [eV](#) by definition) secondary electrons.

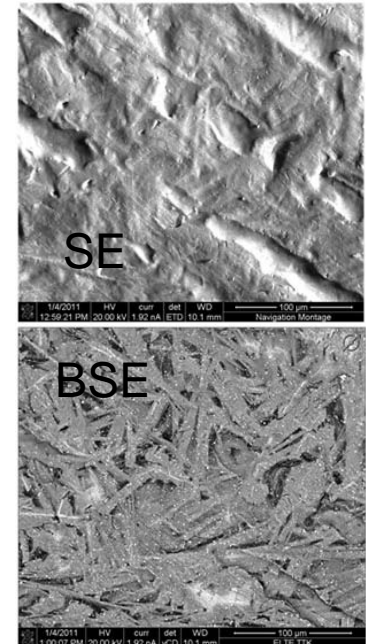
- Other electrons within the specimen chamber are not attracted by this low voltage and will only reach the detector if their direction of travel takes them to it.
- The scintillator has a high positive voltage (in the nature of 10,000 eV) to accelerate the incoming electrons to it where they can be converted to light photons.
- The direction of their travel is focused to the lightguide by a metal coating on the scintillator acting as a mirror.
- In the light pipe the photons travel outside of the microscope's vacuum chamber to a photomultiplier tube for amplification.

The BSE detector :solid state semiconductor diode

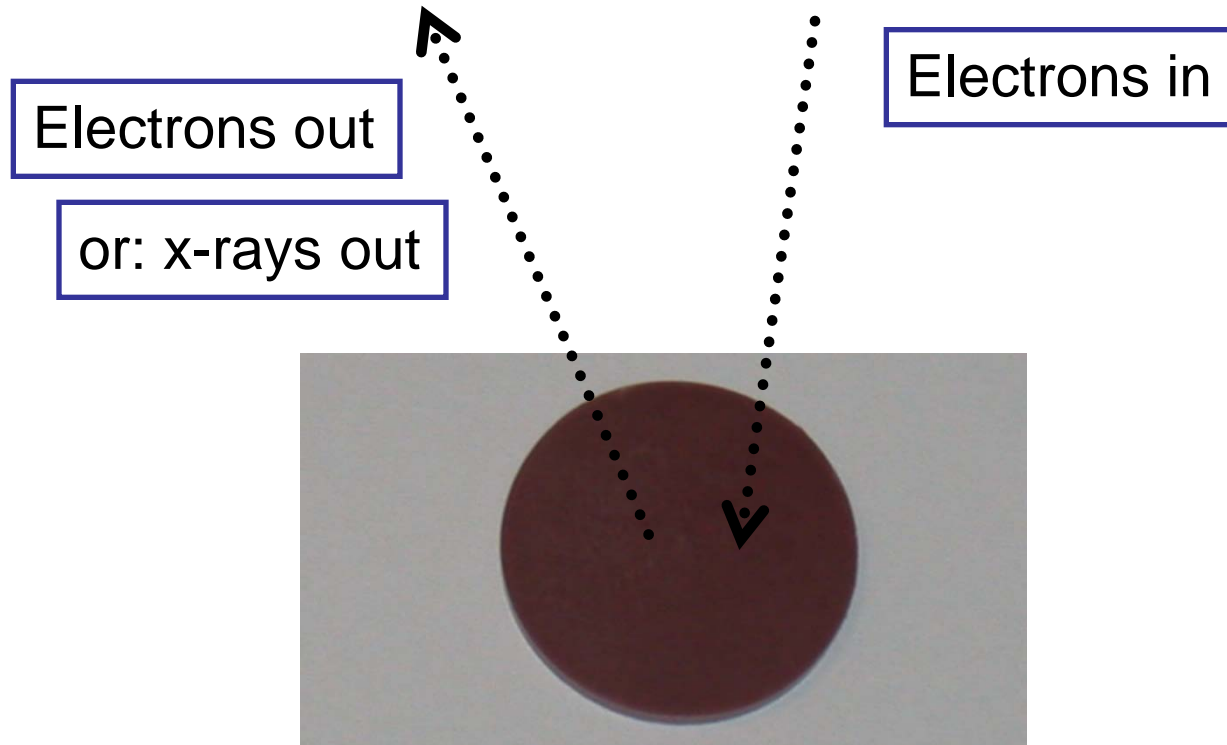


- The backscattered electron detector is usually a solid state semiconductor diode operating on the principle of electron-hole production induced by energetic electrons. It has the form of a flat, thin plate with an annular opening in the middle.
- Solid state BSE detectors are positioned between the sample and the objective lens. The electron beam passes through a hole in the centre of the detector and backscattered electrons are collected as they are returned from the sample.

- The resulting image has greyscales based on the contrast produced by the sample.
- The contrast of the image depends on various factors like the atomic number (Z) of the sample material, the acceleration voltage of the primary beam, and the specimen angle (tilt) with relation to the primary beam.
- Backscattered electrons therefore give us useful information about the composition and surface topography of the sample. Material with a high atomic number (Z), like gold (Au) will generate more BSEs than material with a lower atomic number, like silicon (Si). Because of these differences in backscatter electron yield the detector can be used to identify different phases or inclusions.

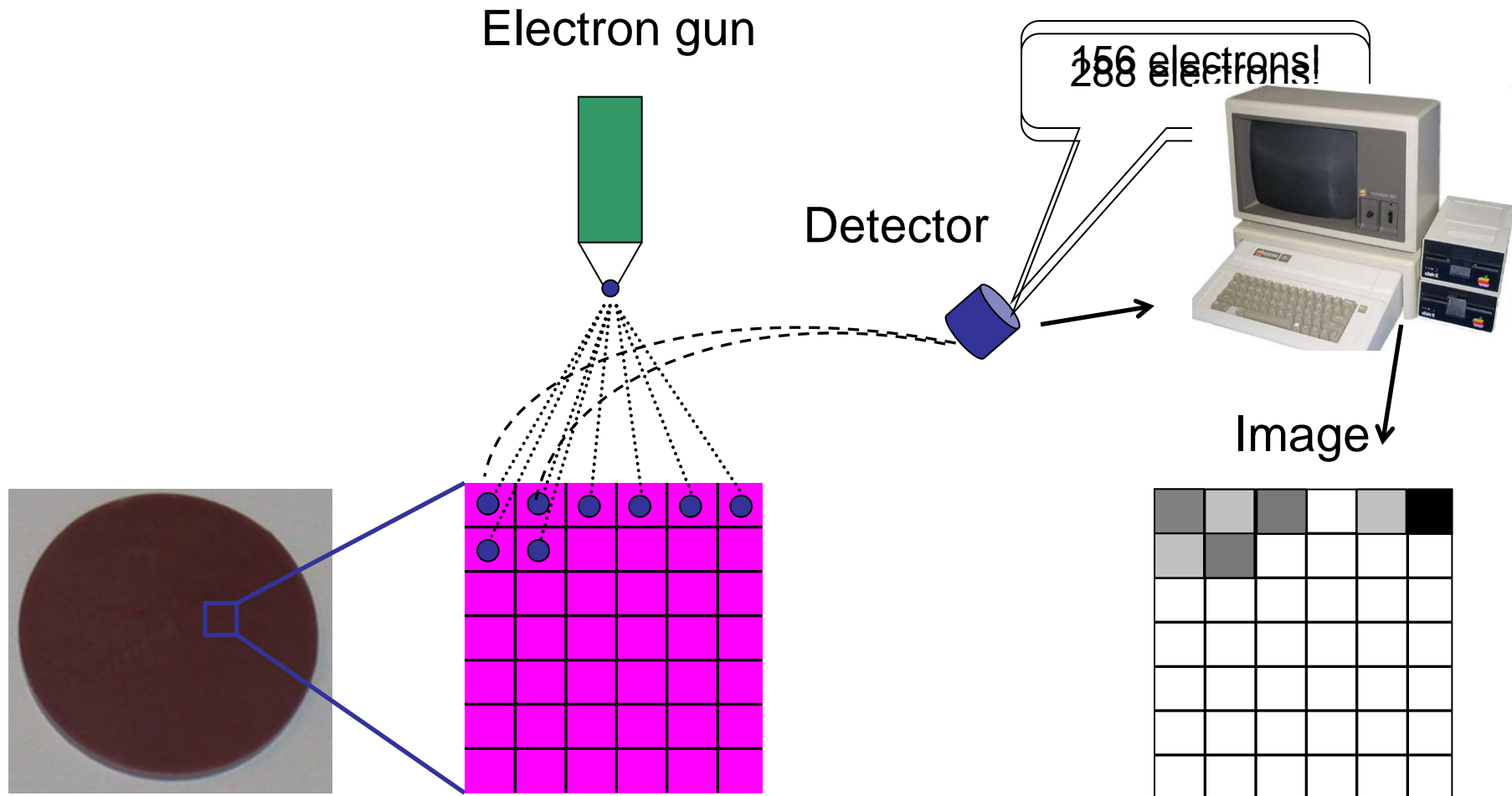


How do we get an image?



- In brief: we shoot high-energy electrons and analyze the outgoing electrons/x-rays
-

How do we get an image?



Why do we need vacuum?

- Chemical (corrosion!!) and thermal stability is necessary for a well-functioning filament (gun pressure)
 - A field emission gun requires $\sim 10^{-10}$ Torr
 - LaB₆: $\sim 10^{-6}$ Torr
- The signal electrons must travel from the sample to the detector (chamber pressure)
 - Vacuum requirements is dependant of the type of detector

Environmental SEM: ESEM

- Traditional SEM chamber pressure: $\sim 10^{-6}$ Torr
 - ESEM: 0.08 – 30 Torr
- Various gases can be used
- Requires different SE detector

Why ESEM?

- To image challenging samples such as:
 - insulating samples
 - vacuum-sensitive samples (e.g. biological samples)
 - irradiation-sensitive samples (e.g. thin organic films)
 - “wet” samples (oily, dirty, greasy)
- To study and image chemical and physical processes in-situ such as:
 - mechanical stress-testing
 - oxidation of metals
 - hydration/dehydration (e.g. watching paint dry)

Some comments on resolution;

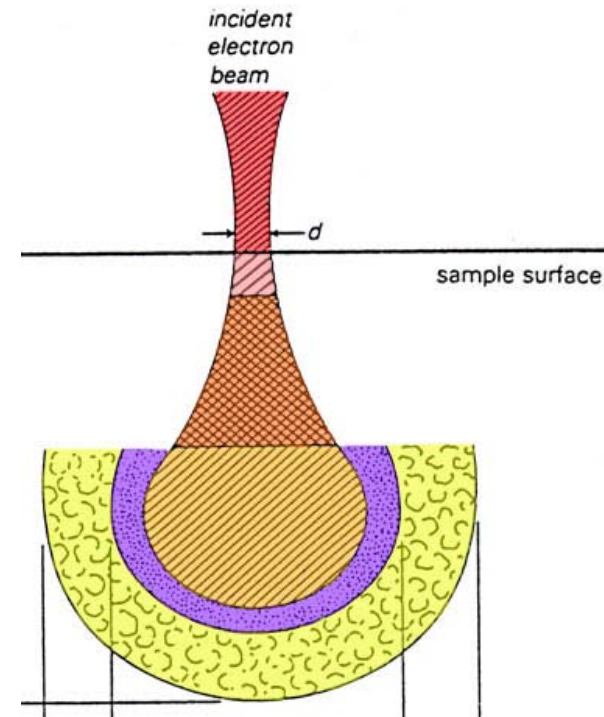
- Best resolution that can be obtained depends on the size of the electron spot on the sample surface
- The introduction of FEG has dramatically improved the resolution of SEM's
- The volume from which the signal electrons are formed defines the resolution
 - SE image has higher resolution than a BSE image
- Scanning speed:
 - a weak signal requires slow speed to improve signal-to-noise ratio
 - when doing a slow scan drift in the electron beam can affect the accuracy of the analysis

Summary:

- The scanning electron microscope is a versatile instrument that can be used for many purposes and can be equipped with various accessories
- An electron probe is scanned across the surface of the sample and detectors interpret the signal as a function of time
- A resolution of 1 – 2 nm can be obtained when operated in a high resolution setup
- The introduction of ESEM and the field emission gun have simplified the imaging of challenging samples

Summary

- Signals:
 - Secondary electrons (SE): mainly topography
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 - High energy electrons
 - “Bulk” signal dependent on atomic number
 - X-rays: chemistry
 - Longer recording times are needed



SEM

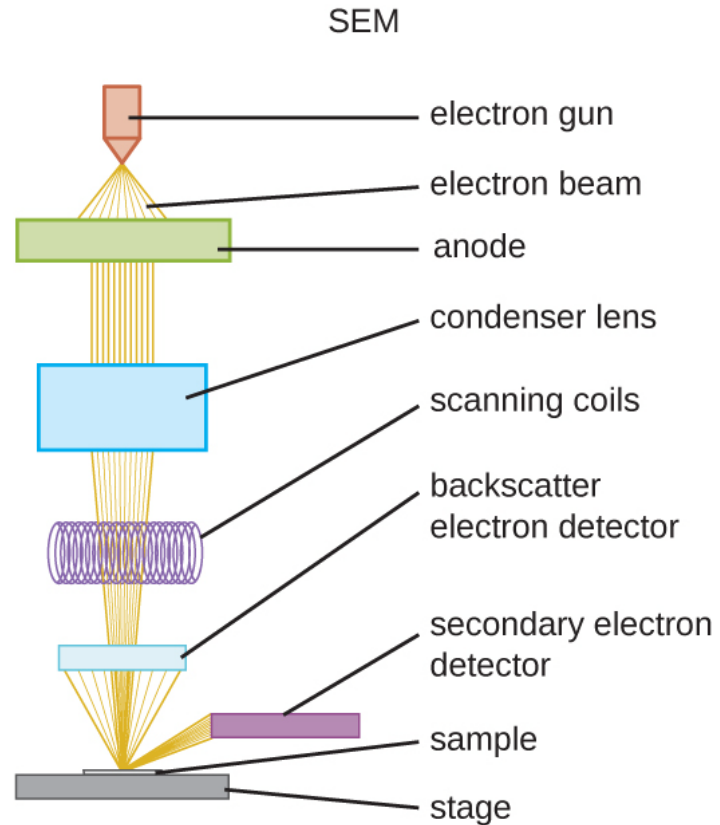
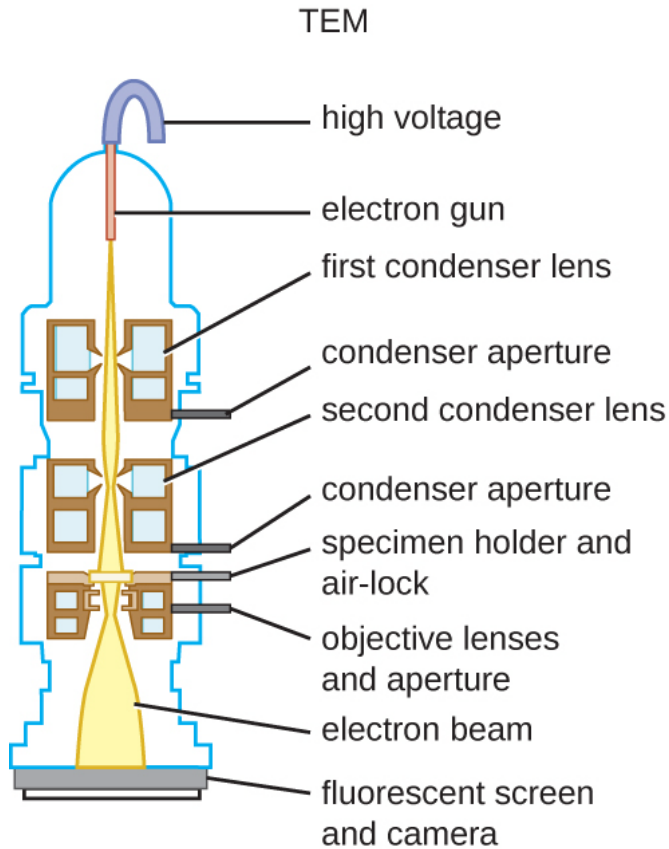
V/S

TEM

- in SEM is based on scattered electrons
- The scattered electrons in SEM produced the image of the sample after the microscope collects and counts the scattered electrons.
- SEM focuses on the sample's surface and its composition.
- SEM shows the sample bit by bit
- SEM provides a three-dimensional image
- SEM only offers 2 million as a maximum level of magnification.
- SEM has 0.4 nanometers.

- TEM is based on transmitted electrons
- In TEM, electrons are directly pointed toward the sample.
- TEM seeks to see what is inside or beyond the surface.
- TEM shows the sample as a whole.
- TEM delivers a two-dimensional picture.
- TEM has up to a 50 million magnification
- The resolution of TEM is 0.5 angstroms

TEM vs SEM



Optical vs. TEM vs. SEM vs. CRT

