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Electron Microprobe Analysis

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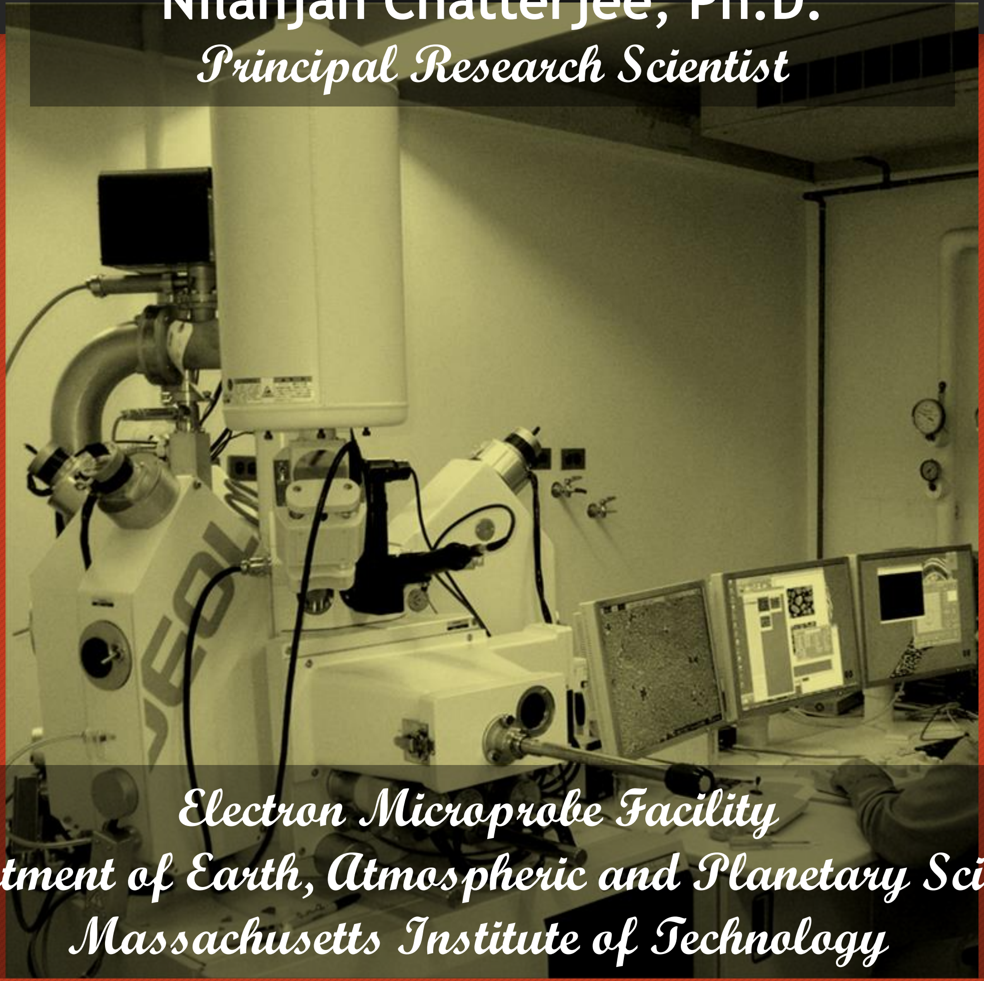
Principal Research Scientist



Electron Microprobe Facility
Department of Earth, Atmospheric and Planetary Sciences
Massachusetts Institute of Technology

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Uses of the EPMA

Complete **quantitative chemical analysis at micron-scale spatial resolution:**

- *Be to U (10-50 ppm minimum detection limit)*

High resolution imaging:

- *compositional contrast (back-scattered electron)*
- *surface relief (secondary electron)*
- *spatial distribution of elements (x-ray)*
- *trace elements, defects (light)*

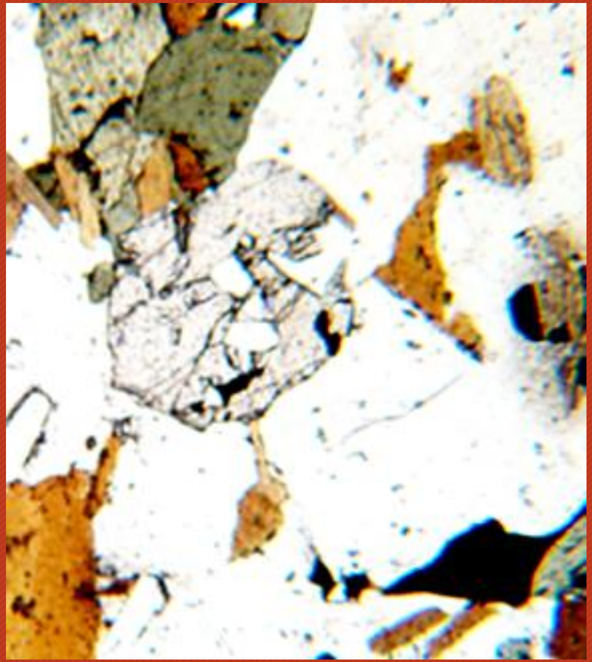
An example: Compositional imaging with back-scattered electrons

Back-scattered electron

Polished surface

Function of composition

Plane polarized transmitted light



Thin section

Function of optical properties

Types of analysis

Qualitative analysis

- Visual characterization (shape, size, surface relief, etc.)
- Identification of elements in each phase

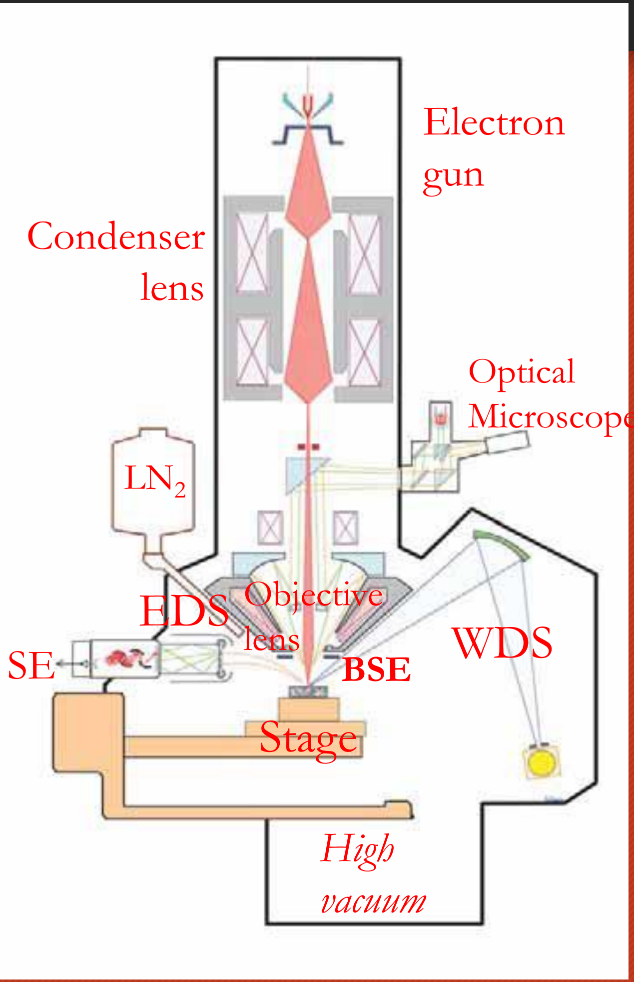
Semi-quantitative analysis

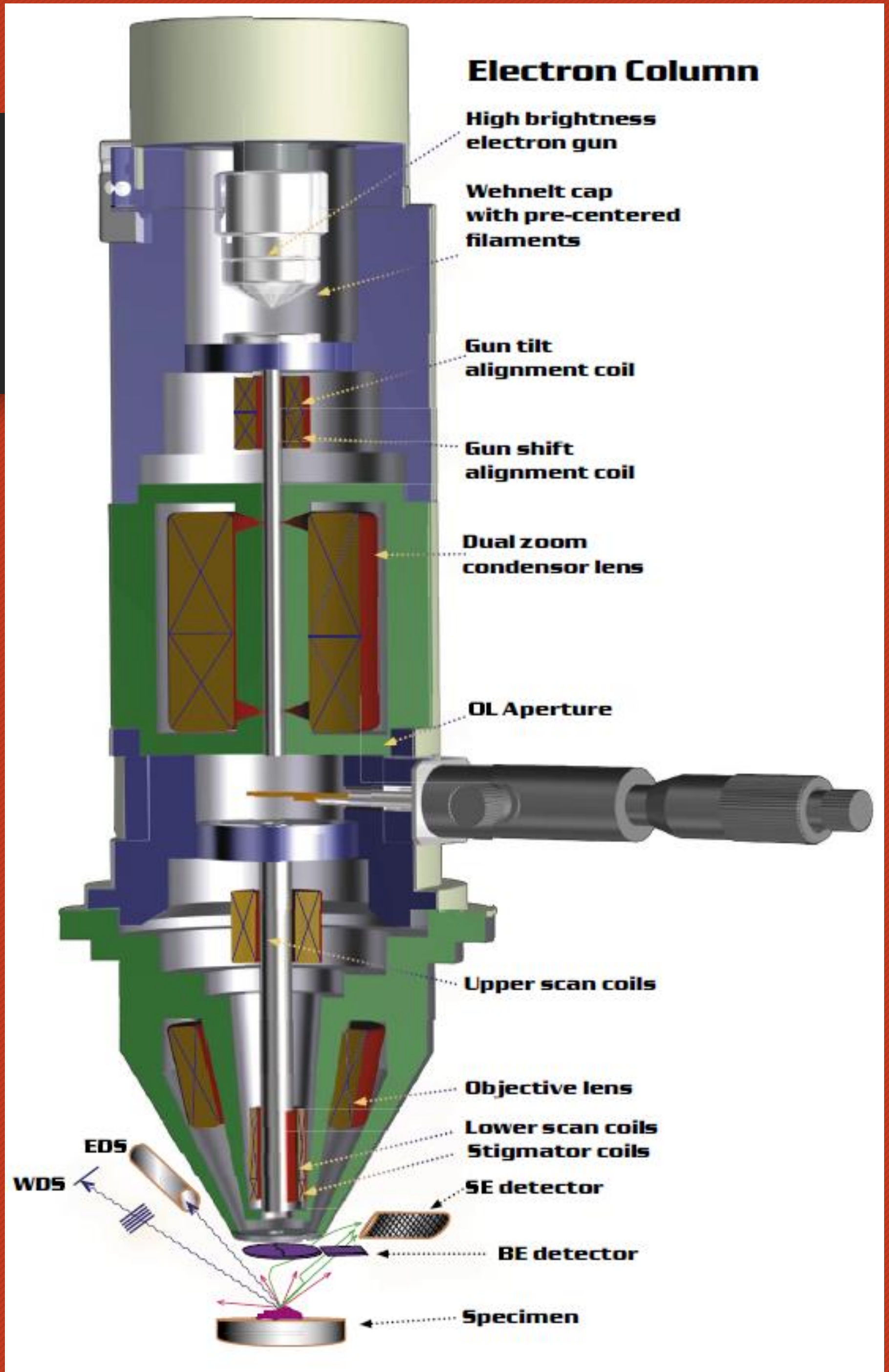
- Quick and approximate concentration measurement of a spot
- Elemental mapping (spatial distribution of elements)

Quantitative analysis

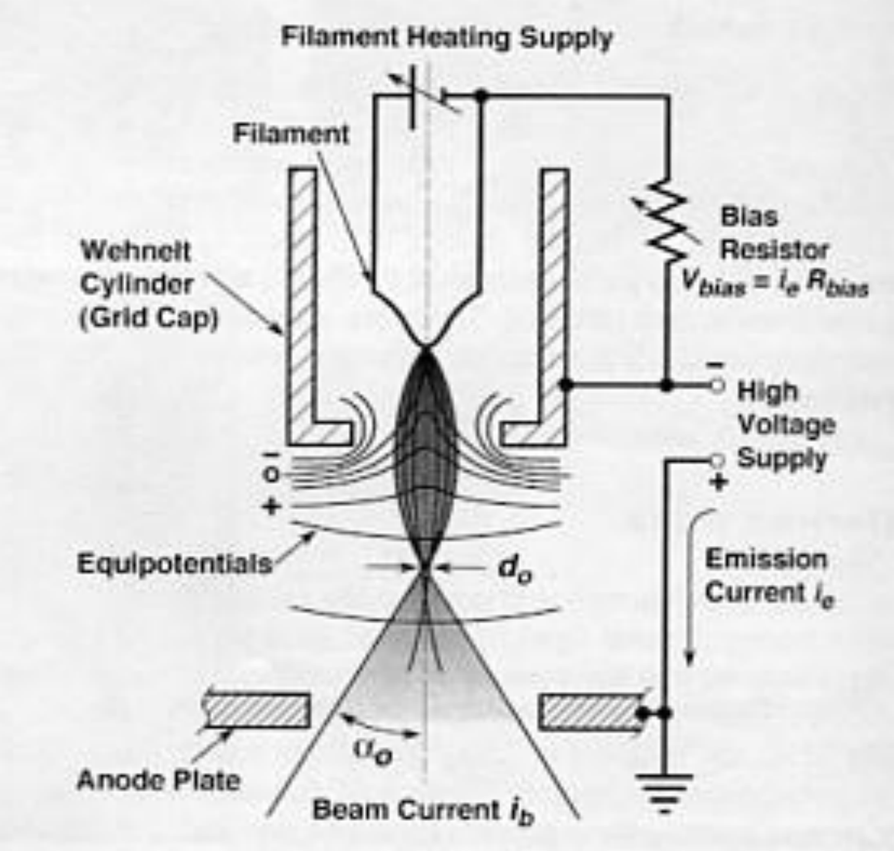
- Complete chemical analysis of a micron-sized spot
- Concentration mapping of all elements

JEOL JXA-8200 Superprobe





Electron emitting source: Tungsten hairpin



Self-biased thermionic electron gun

- **Cathode: Filament** *at negative potential*

  Tungsten has a high melting point and a low work-function energy barrier; heated by filament current, i_f, until electrons overcome the barrier

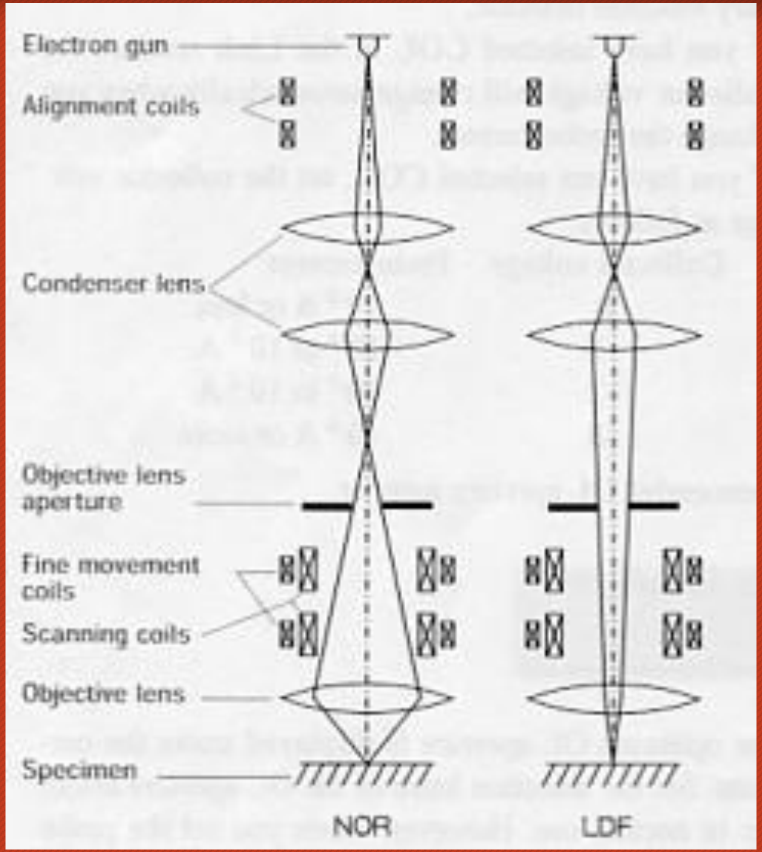
- **Wehnelt Cylinder** *at a slightly higher negative potential than the filament because of the Bias Resistor*

  Bias voltage (V_{bias}) automatically adjusts with changes in i_e to stabilize emission; the grid cap also focuses the electron beam

- **Anode: Plate** *at ground potential*

  Potential difference (accelerating voltage, V_0) causes electron emission (current, i_e)

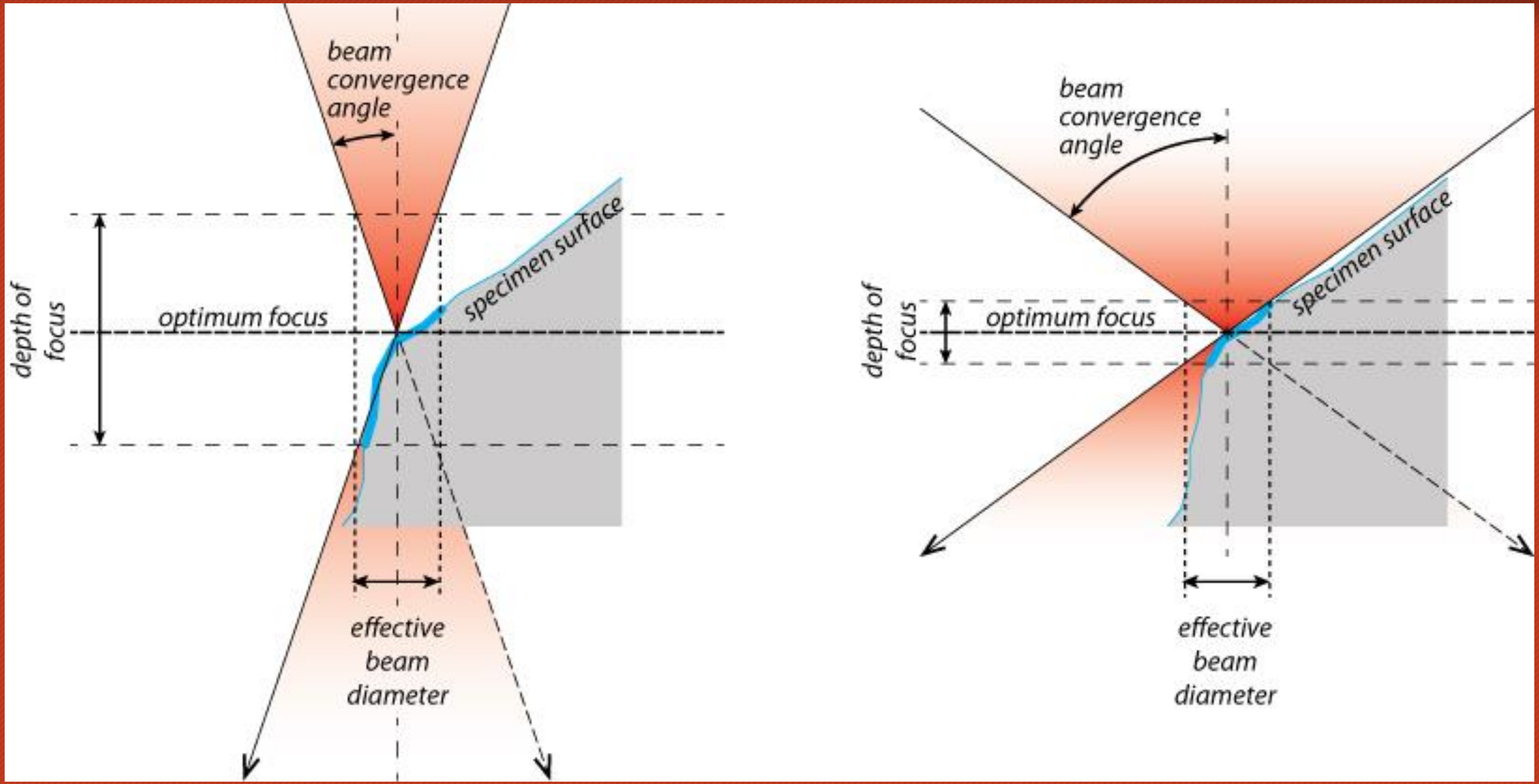
Lens modes



Normal

Large depth of focus for rough surfaces

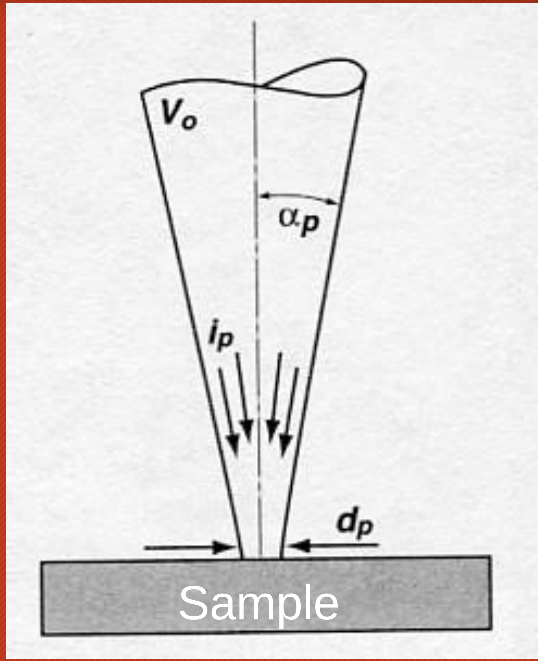
Depth of focus



Large depth of focus

Small depth of focus

Electron probe parameters



Accelerating voltage, V_0

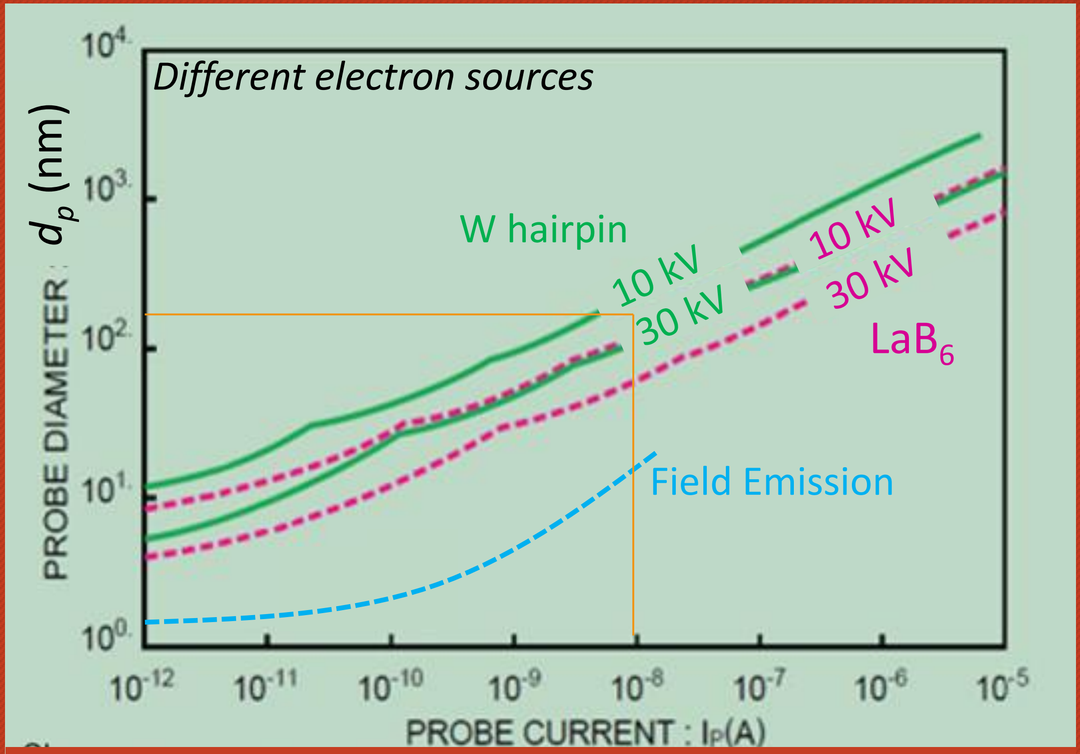
(V_0 of 15 kV generates electron beam with 15 keV energy)

Final beam current, or probe current, i_p

Final beam diameter, or probe diameter, d_p

Final beam convergence angle, or probe convergence angle, α_p

Electron probe diameter

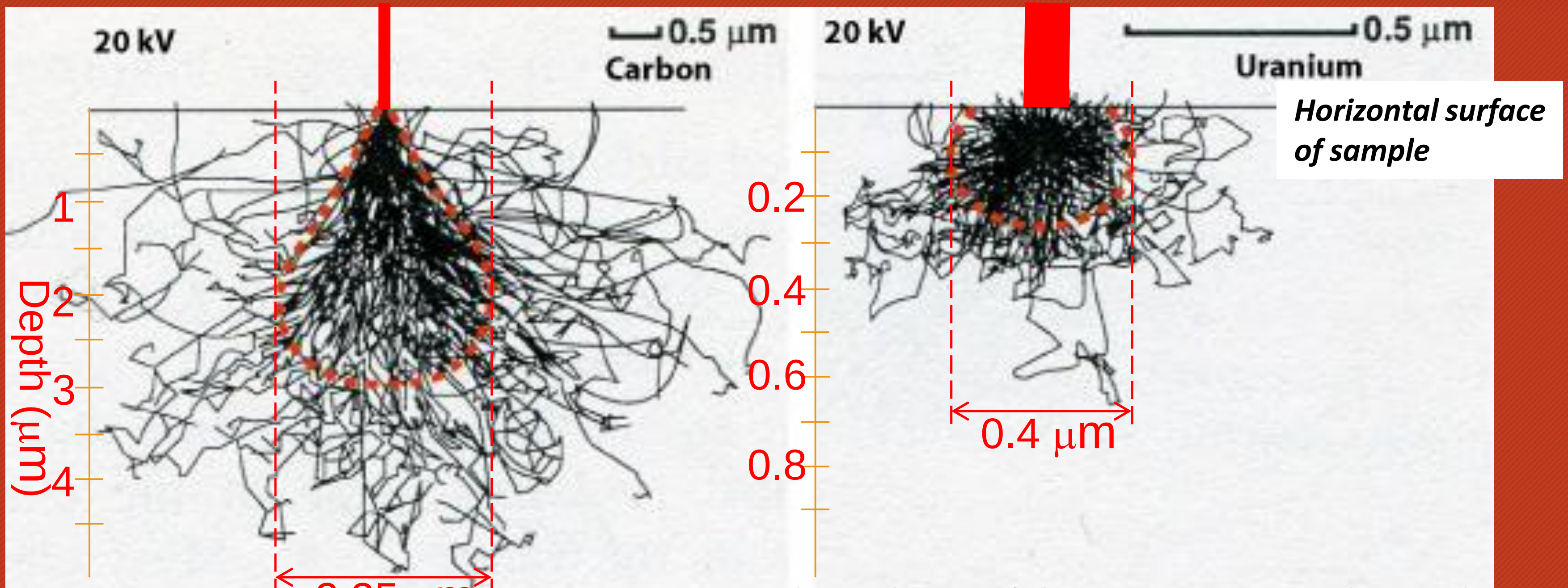


- *At a fixed Probe current, Probe diameter increases*
  - *with source as Field emission < LaB_6 < W*
  - *with decreasing Accelerating voltage*
- *As Probe current increases, Probe diameter also increases (signal improves, but image resolution degrades)*

At 10 nA and 15 kV, a Tungsten hairpin filament produces a beam with $d_p \approx 100$ nm

Spatial resolution: electron interaction volume

Vertical electron beam, probe diameter = 0.1 μm



Monte Carlo simulations of electron trajectories in the sample

Low atomic number: large tear-drop *High atomic number: small hemisphere*

Width of interaction volume >> probe diameter

Spatial resolution can be improved by using a lower accelerating voltage that reduces the interaction volume

Electron interaction depth (range)

$$R = 0.0276\ E^{1.67} \frac{A}{\rho Z^{0.889}}$$

R : Kanaya-Okayama electron range

E : beam energy

A : atomic weight

ρ : density

Z : atomic number

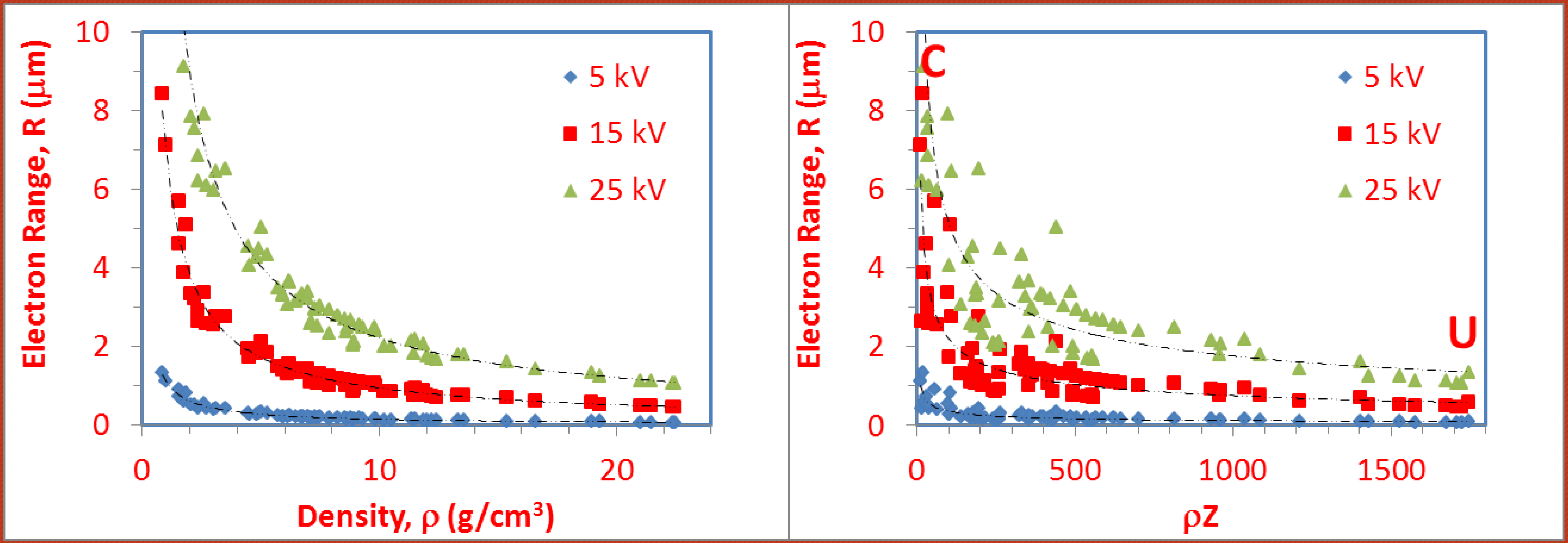
Electron range increases with increasing E, and decreasing ρ and ρZ

E.g., at 20 kV,

R = 4.29 μm in Carbon (Z = 6, A = 12.01, ρ = 2.26 g/cc)

R = 0.93 μm in Uranium (Z = 92, A = 238.03, ρ = 19.07 g/cc)

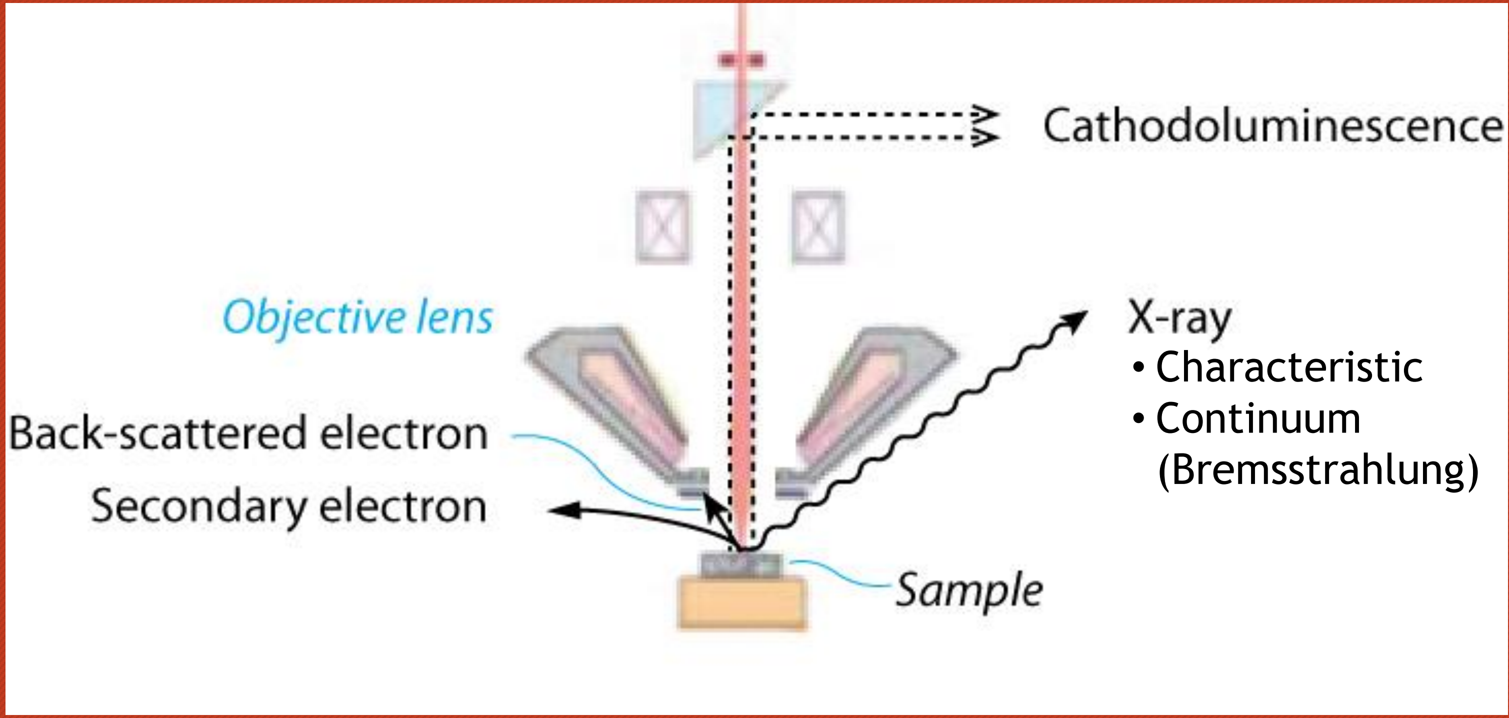
Electron interaction depth (range)



Electron range increases with increasing E, and decreasing ρ and ρZ

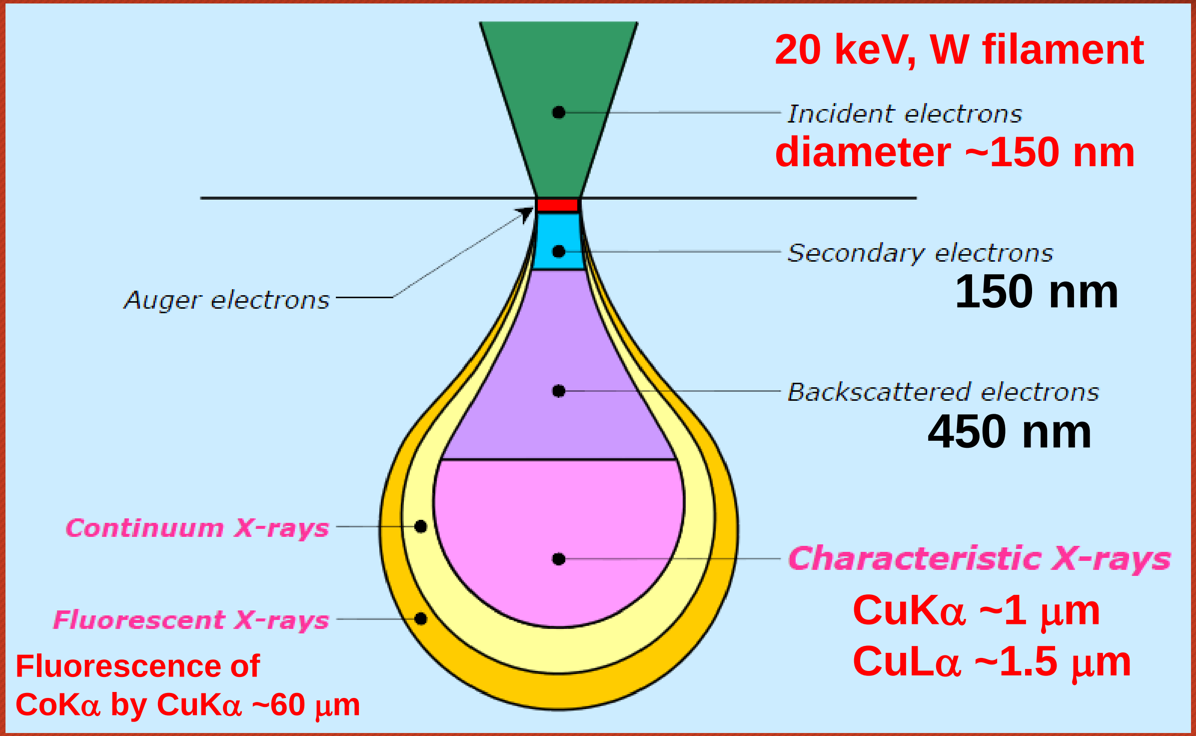
Signal types

Electron beam



Other signals include phonon excitation (manifested by heating), plasmon excitation (generated by moving electrons in metals), and auger electron (ejected from atom by internally absorbed x-ray)

Spatial resolution for different signals (production volume)

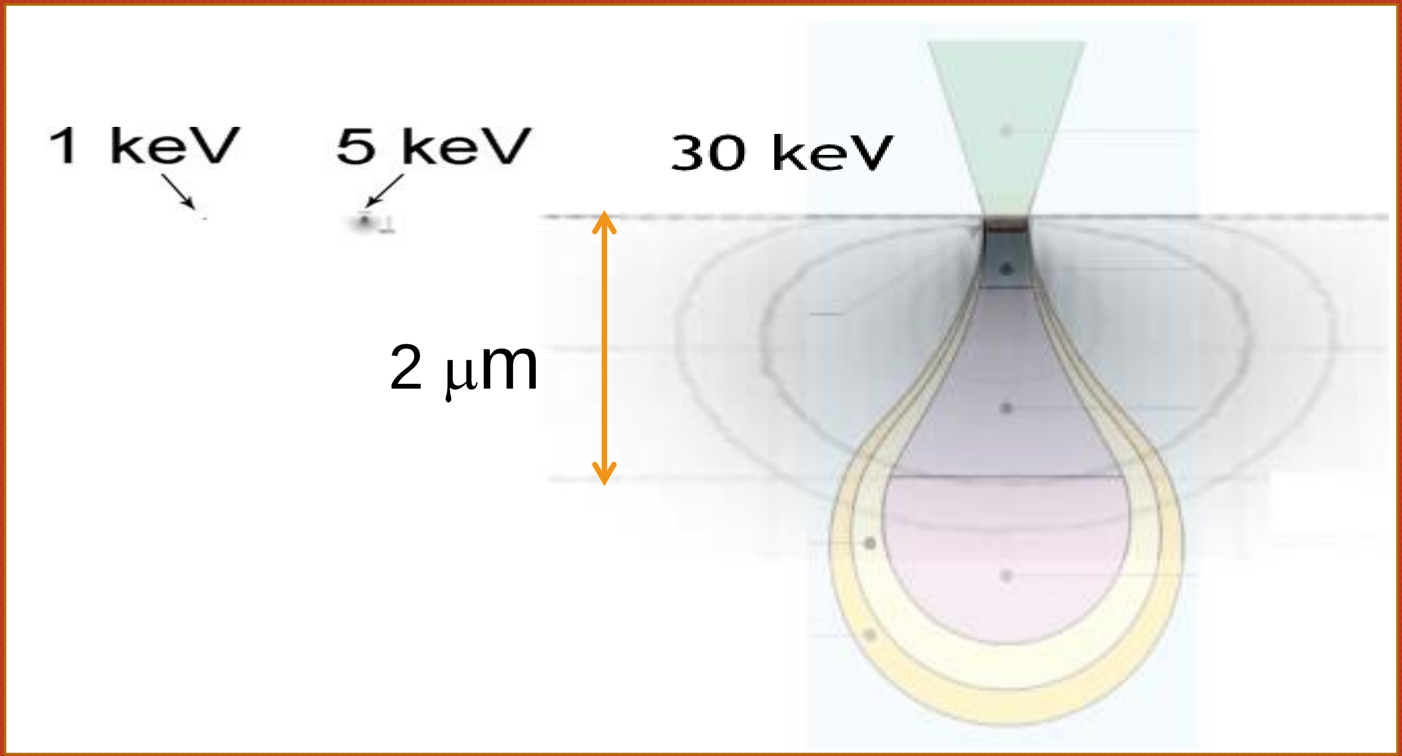


Production volume is different for each signal

(not to scale)

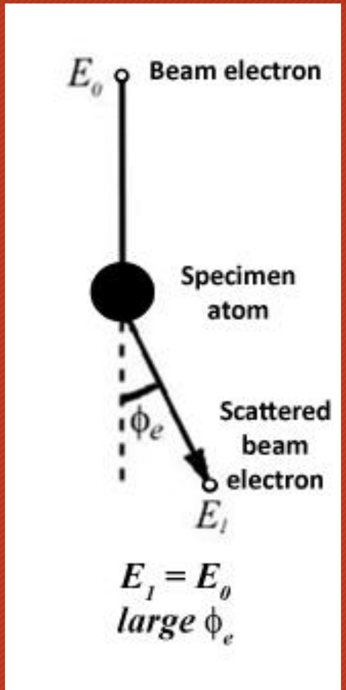
The "onion shell" model:
Cu-10%Co alloy

Production volume for cathodoluminescence



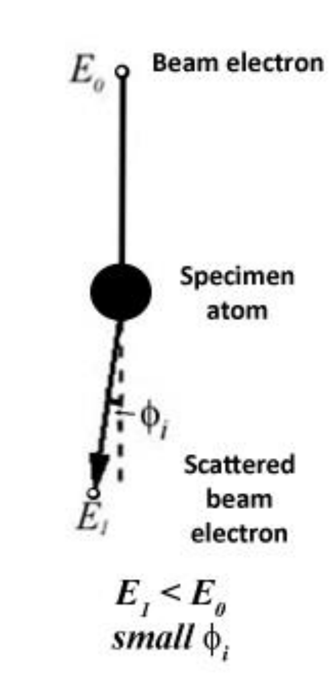
Gallium Nitride

Electron-specimen interactions: Elastic scattering



Back-scattered electron (BSE)

Electron-specimen interactions: Inelastic scattering



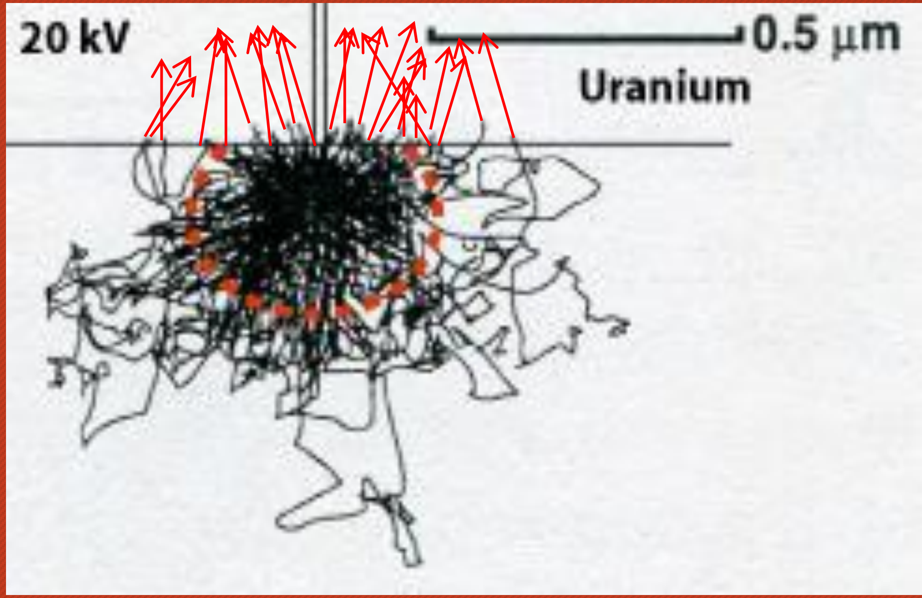
Inner shell interactions:

- Characteristic X-rays
- Secondary electron (SE)

Outer shell interactions:

- Continuum X-rays
- Secondary electron (SE)
- Cathodoluminescence (CL)

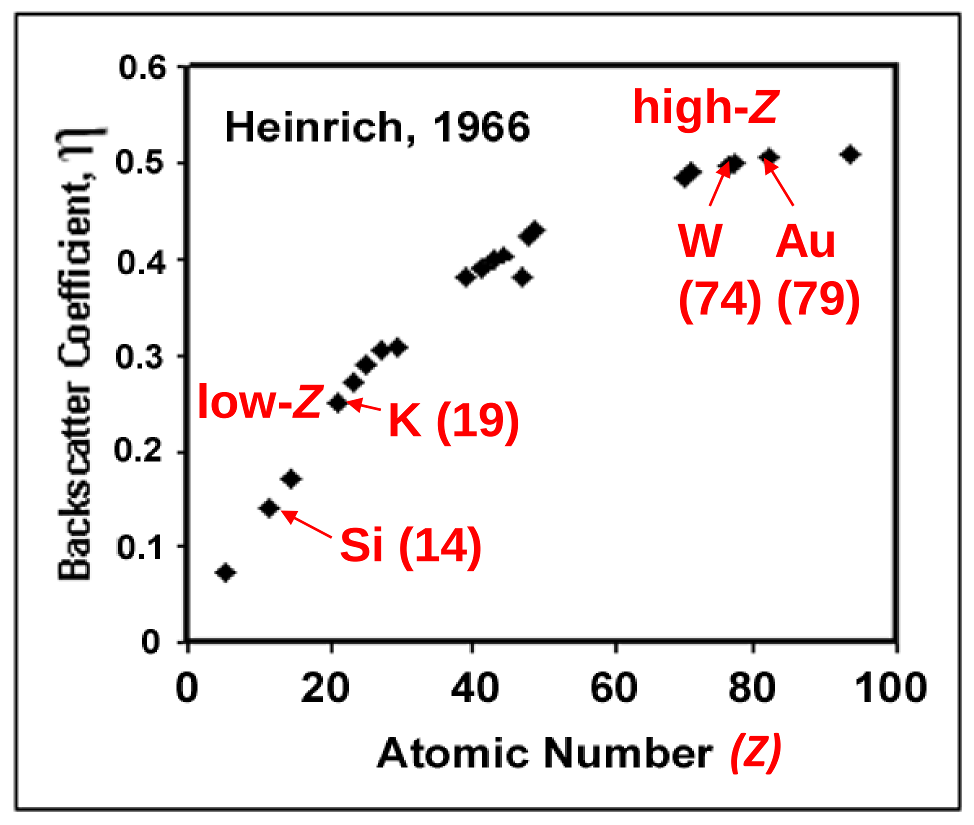
Back-scattered electron (BSE)



- *Beam electrons scattered elastically at high angles*
- *Commonly scattered multiple times, so energy of BSE ≤ beam energy*

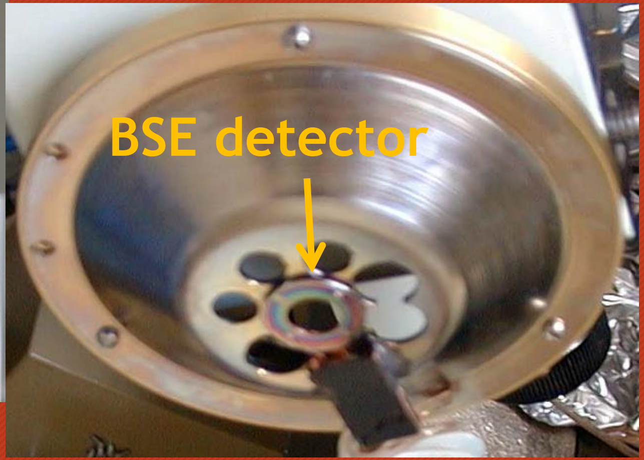
Electron backscatter coefficient

Fraction of beam electrons scattered backward

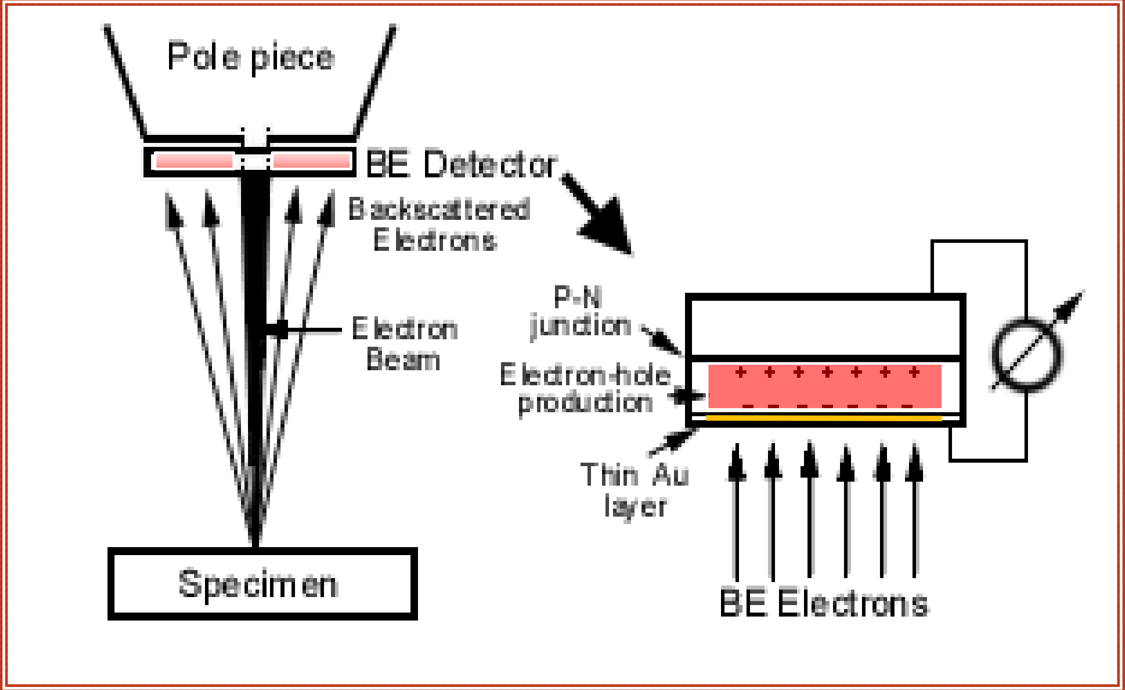


- *Large differences between high- and low-atomic number elements*
- *Larger differences among low-Z elements than among high-Z elements*

Back-scattered electron detector

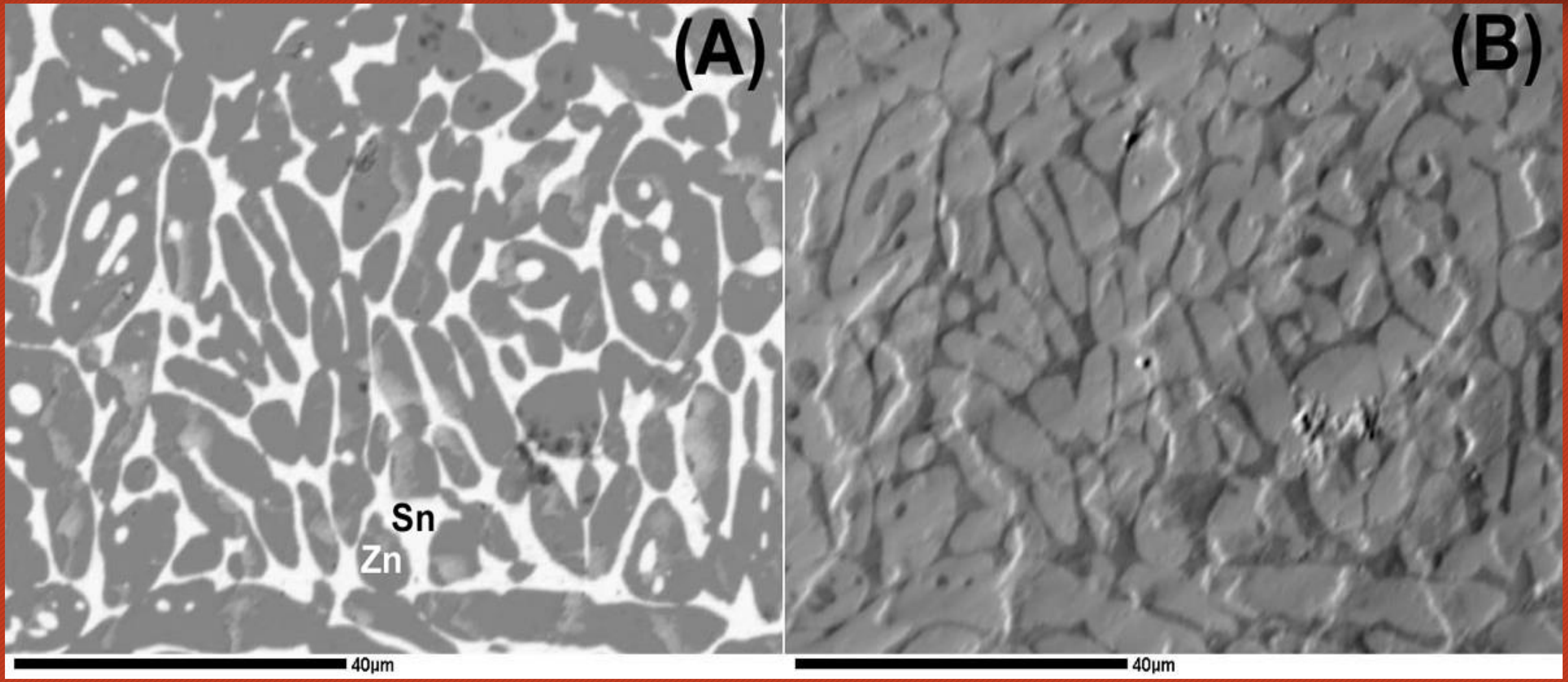


Back-scattered electron detector



Solid-state diode

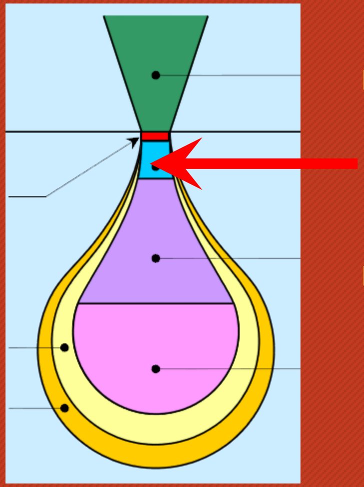
Compositional and topographic imaging with BSE



A+B: Compositional mode

A-B: Topographic mode

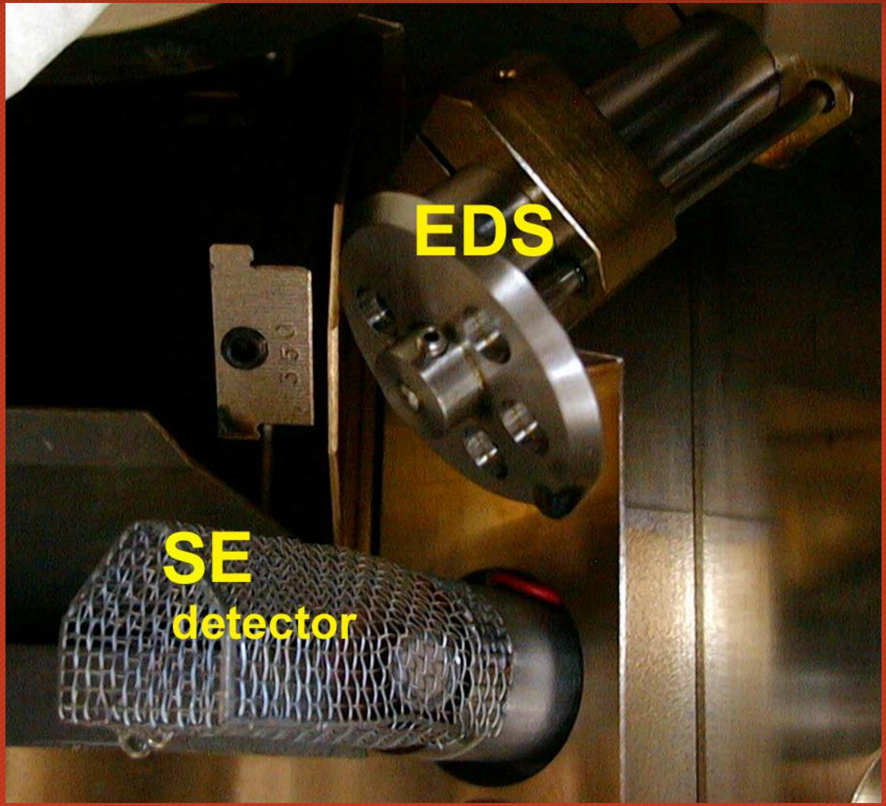
Secondary electron (SE)



- *Specimen electrons mobilized by beam electrons through inelastic scattering (causing outer and inner shell ionizations)*
- *Emitted at low energies (mostly ≤ 10 eV for slow secondaries, less commonly ≤ 50 eV for fast secondaries)*

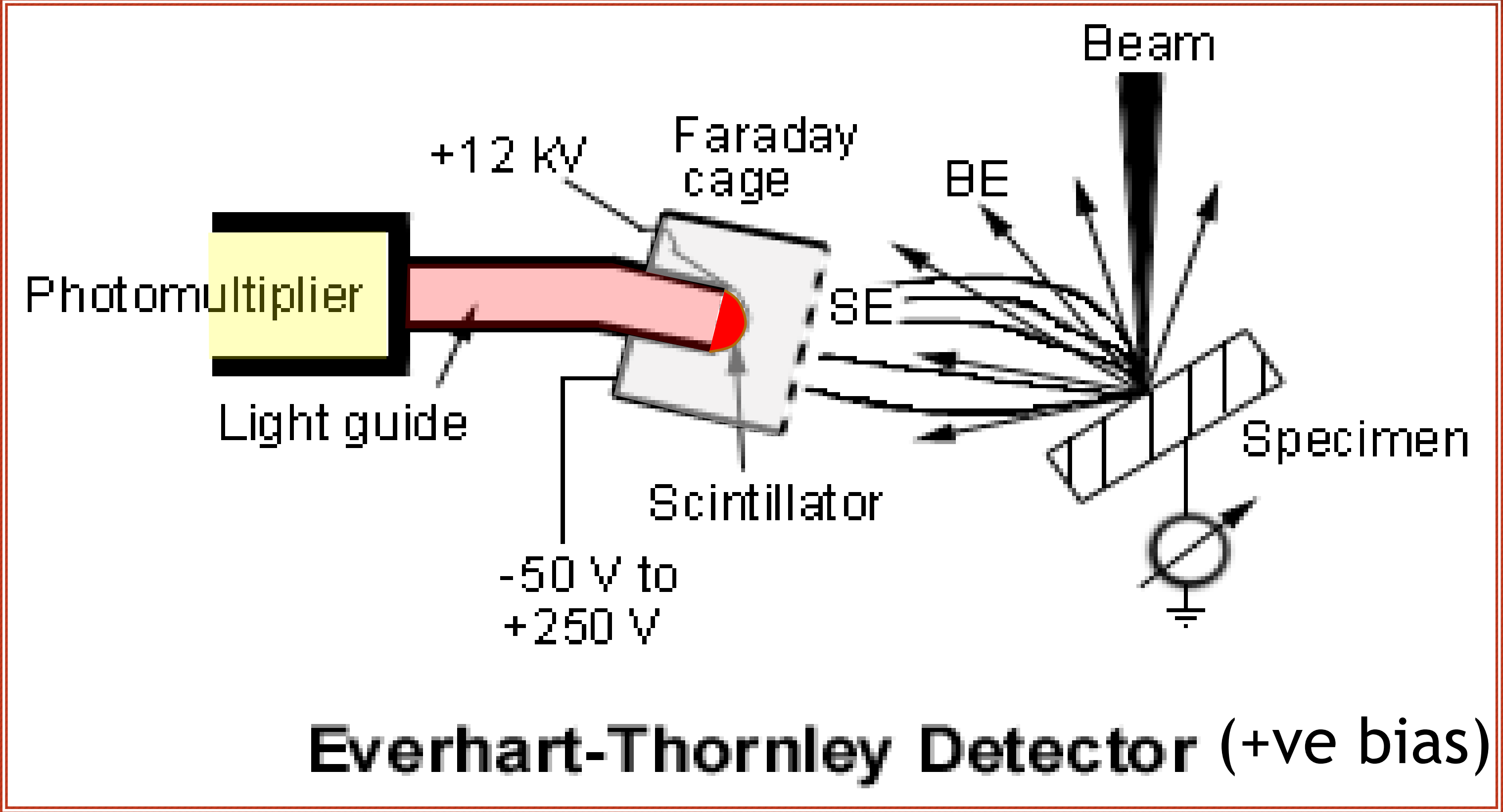
  (recall BSE have high energies up to that of the electron beam)

Secondary electron detector



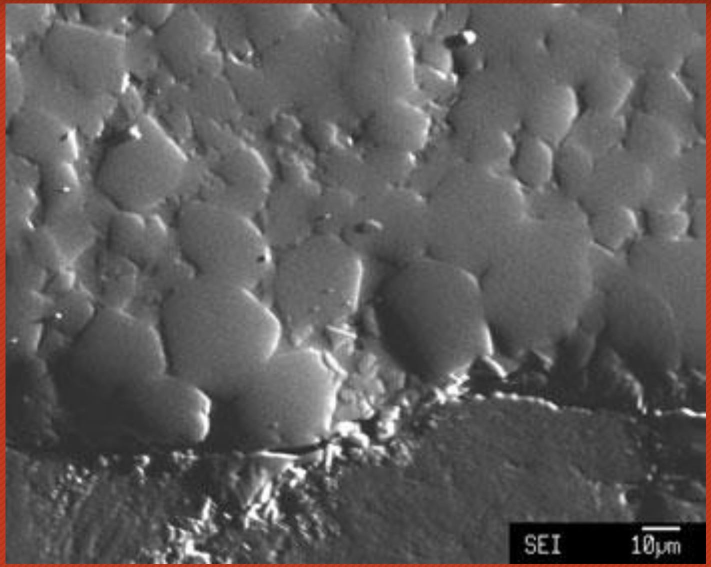
Located on the side wall of the sample chamber

Secondary electron detector



When Faraday cage is positively biased,
secondary electrons are pulled into the detector

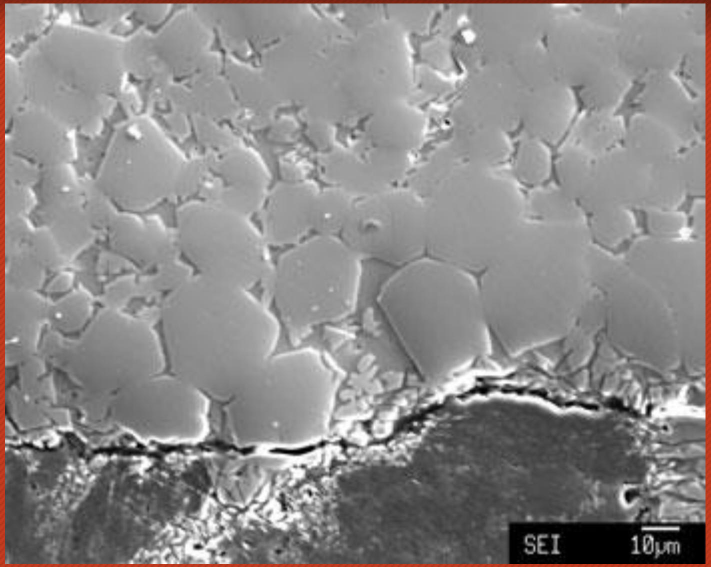
Imaging with the Everhart-Thornley detector



Negative Faraday cage bias

only BSE

Surfaces in direct line of sight are illuminated



Positive Faraday cage bias

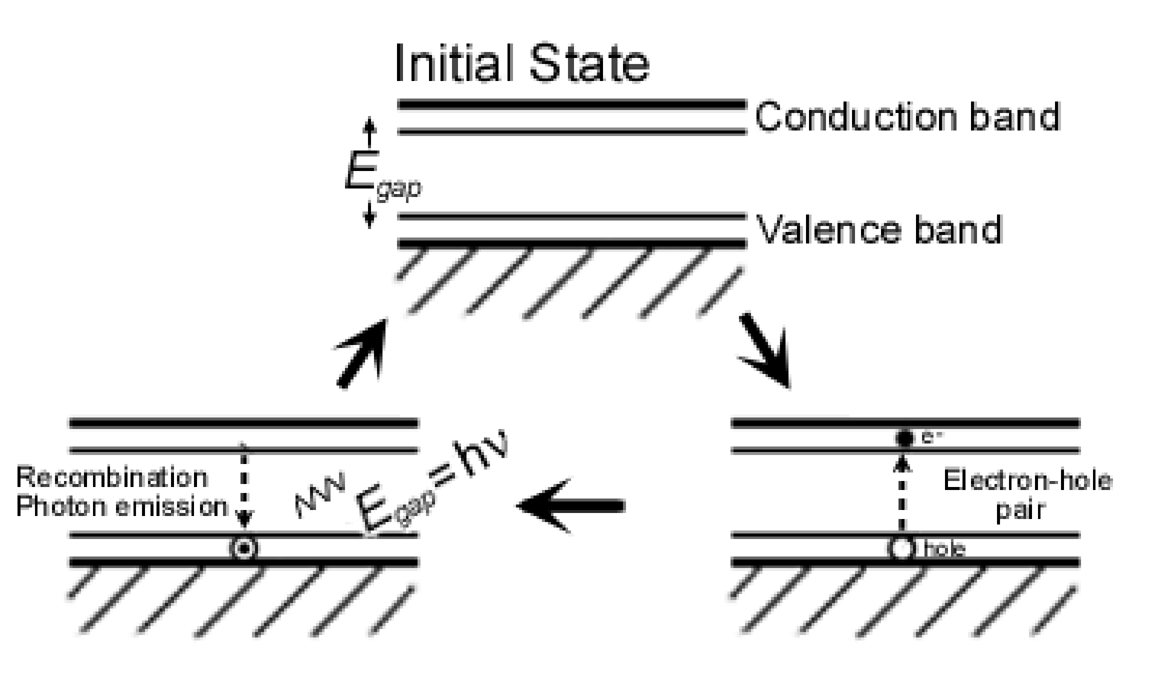
BSE + SE

All surfaces are illuminated

Cathodoluminescence (CL)

Caused by inelastic scattering of beam electrons in semiconductors

Filled valence band is separated from an empty conduction band by E_{gap},



Electron recombines with the valence band to generate light with energy E_{gap}

Electron beam interacts:

Valence electron moves to the conduction band

Trace element impurities expand the conduction band and enable additional electron transitions
Emitted light has additional energy components $E \neq E_{gap}$

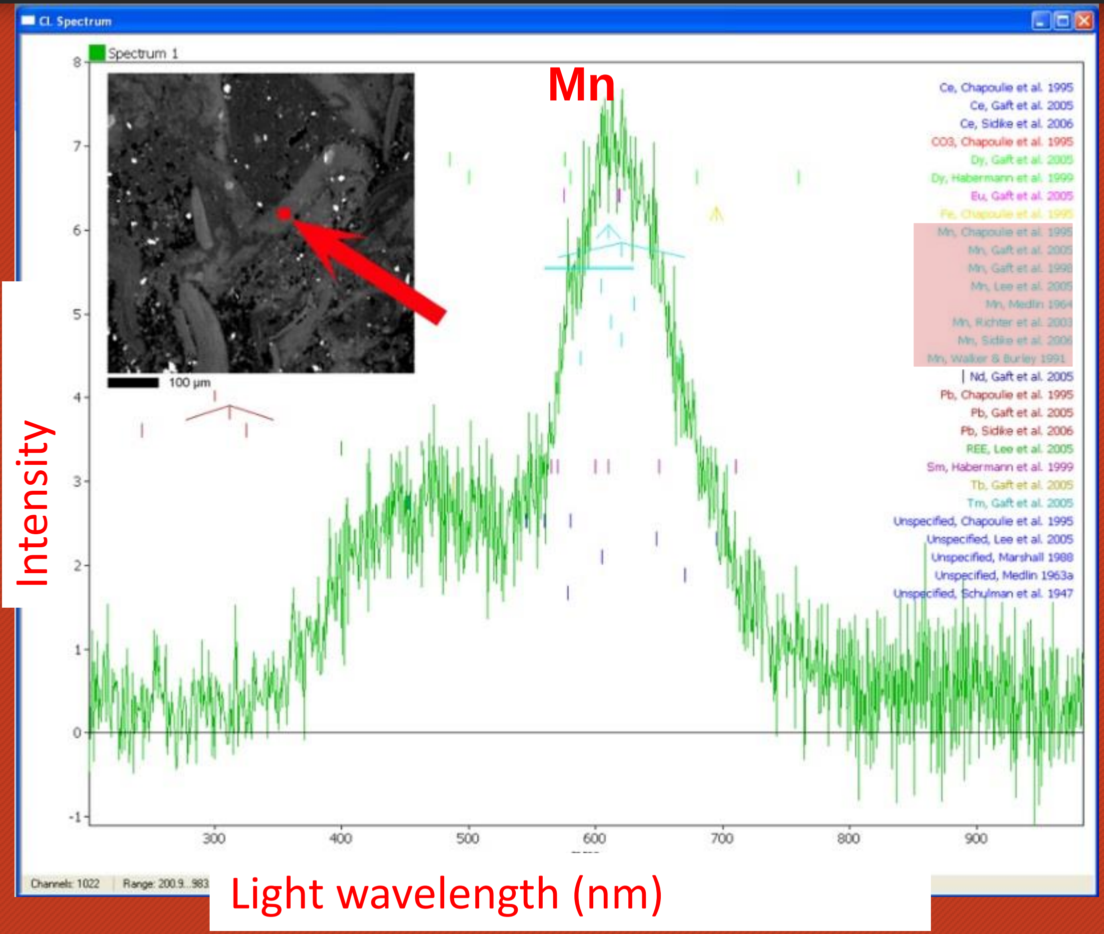
Cathodoluminescence spectrometer

Optical microscope camera (not used)

Optical microscope light (turned off)

Optical spectrometer (CCD array detector)

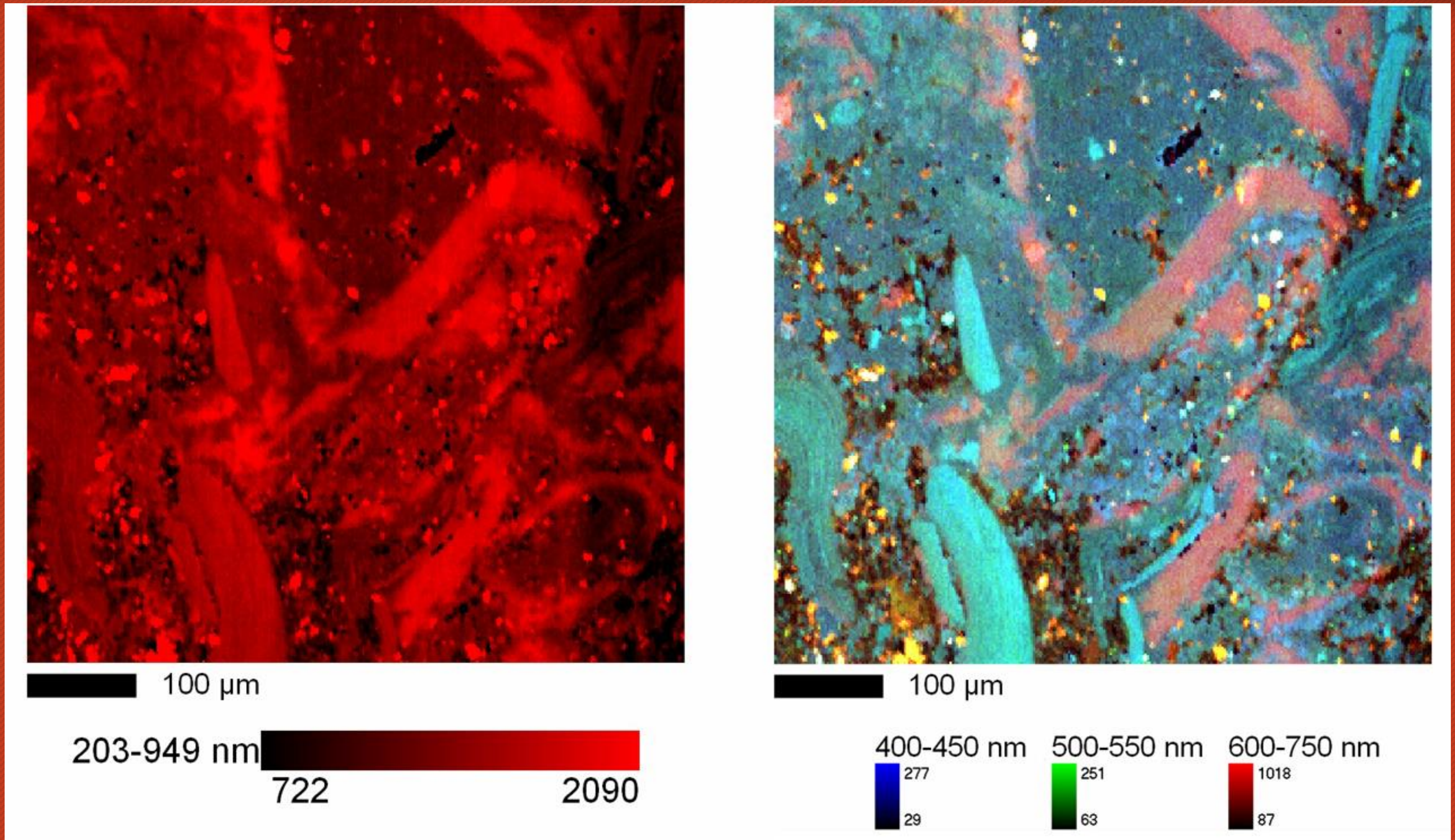
Cathodoluminescence spectrum



$(Ca,Mg)CO_3$ (dolomite) with Mn

Hyperspectral CL imaging

A continuous spectrum covering all light wavelengths is collected at each point of the image area



Total intensities of 200-950 nm light at each pixel (red shades represent 722-2090 counts)

Total intensities of 400-450 nm light (blue shades: 29-277 counts)

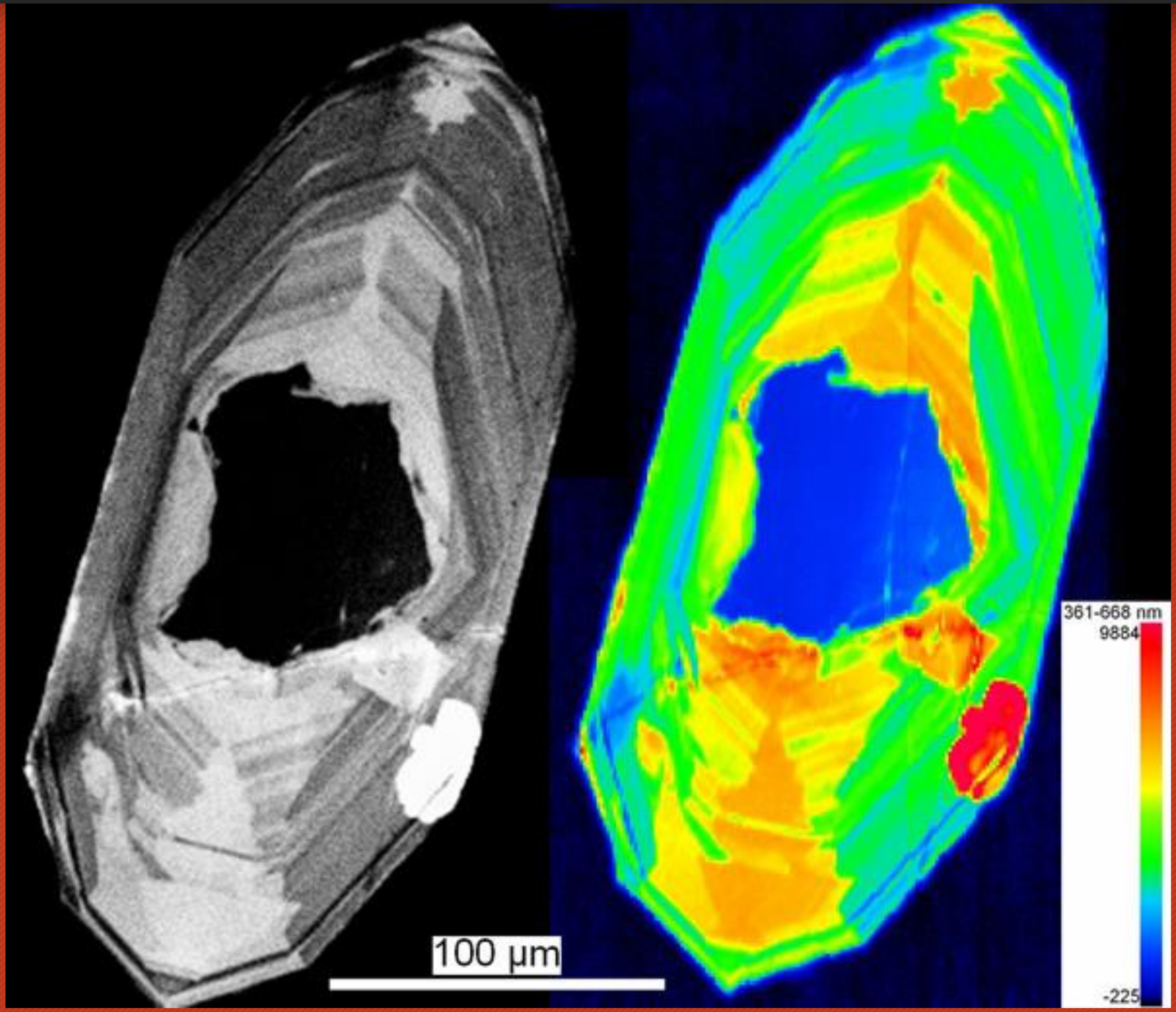
Total intensities of 500-550 nm light (green shades: 63-251 counts)

Total intensities of 600-750 nm light (red shades: 87-1018 counts)

Hyperspectral CL imaging

Total intensities of light of all wavelengths at each pixel in grey scale:

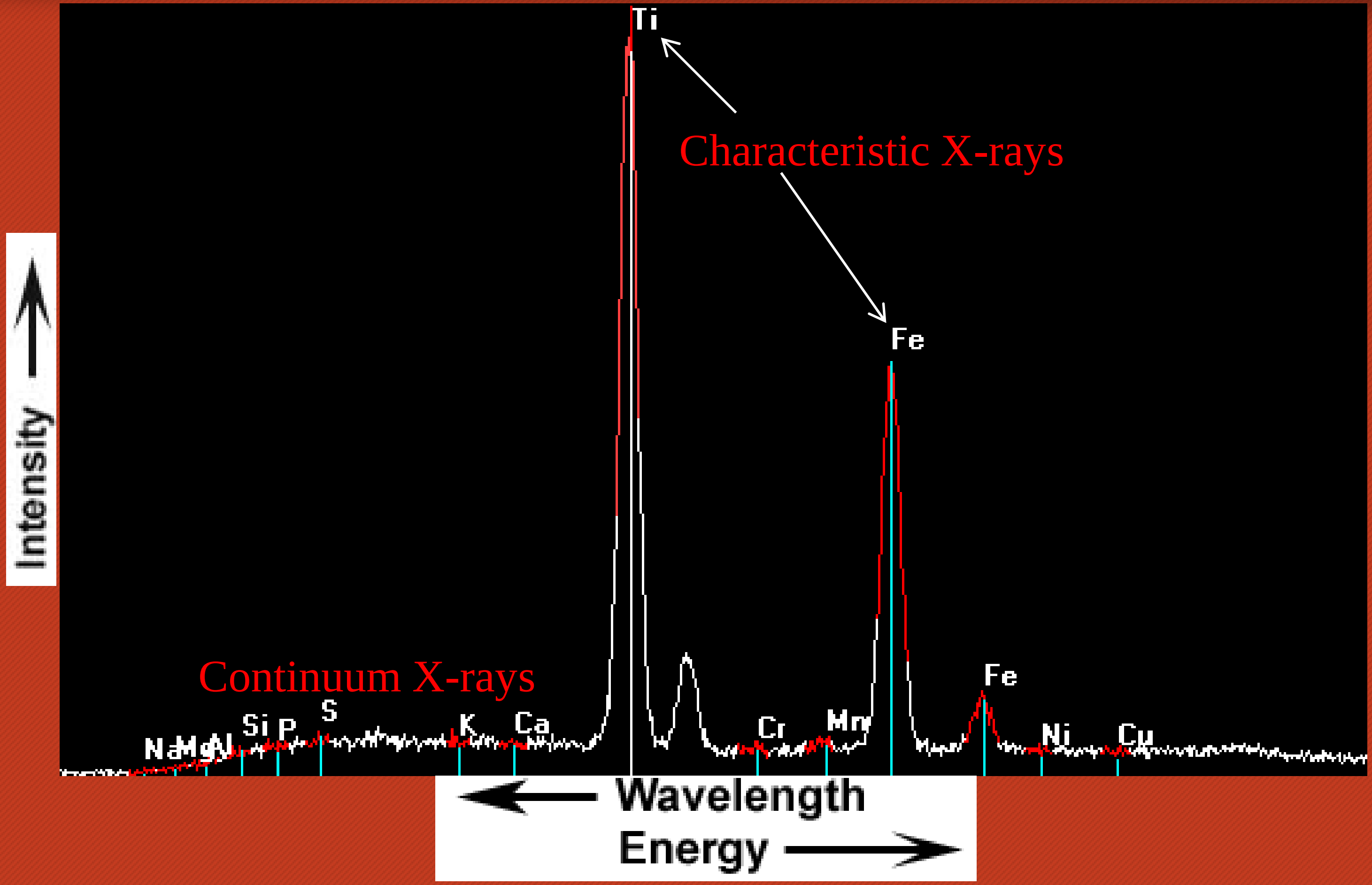
Black: no light
White: maximum intensity



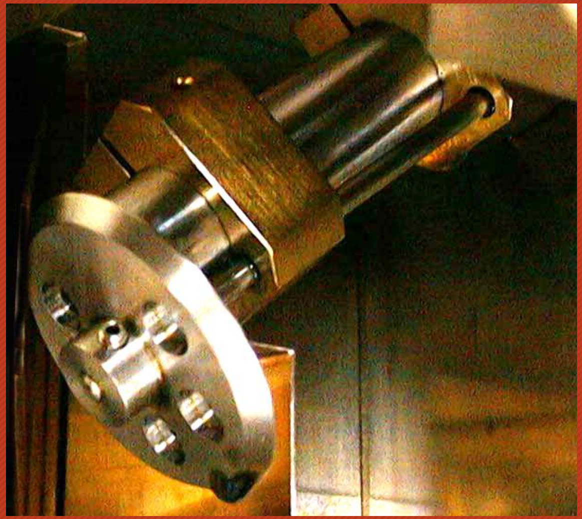
Total intensities of 361-668 nm light at each pixel in multicolor scale:

Blue (≤ 0 counts): no light
Red (9884 counts): maximum intensity

The X-ray spectrum

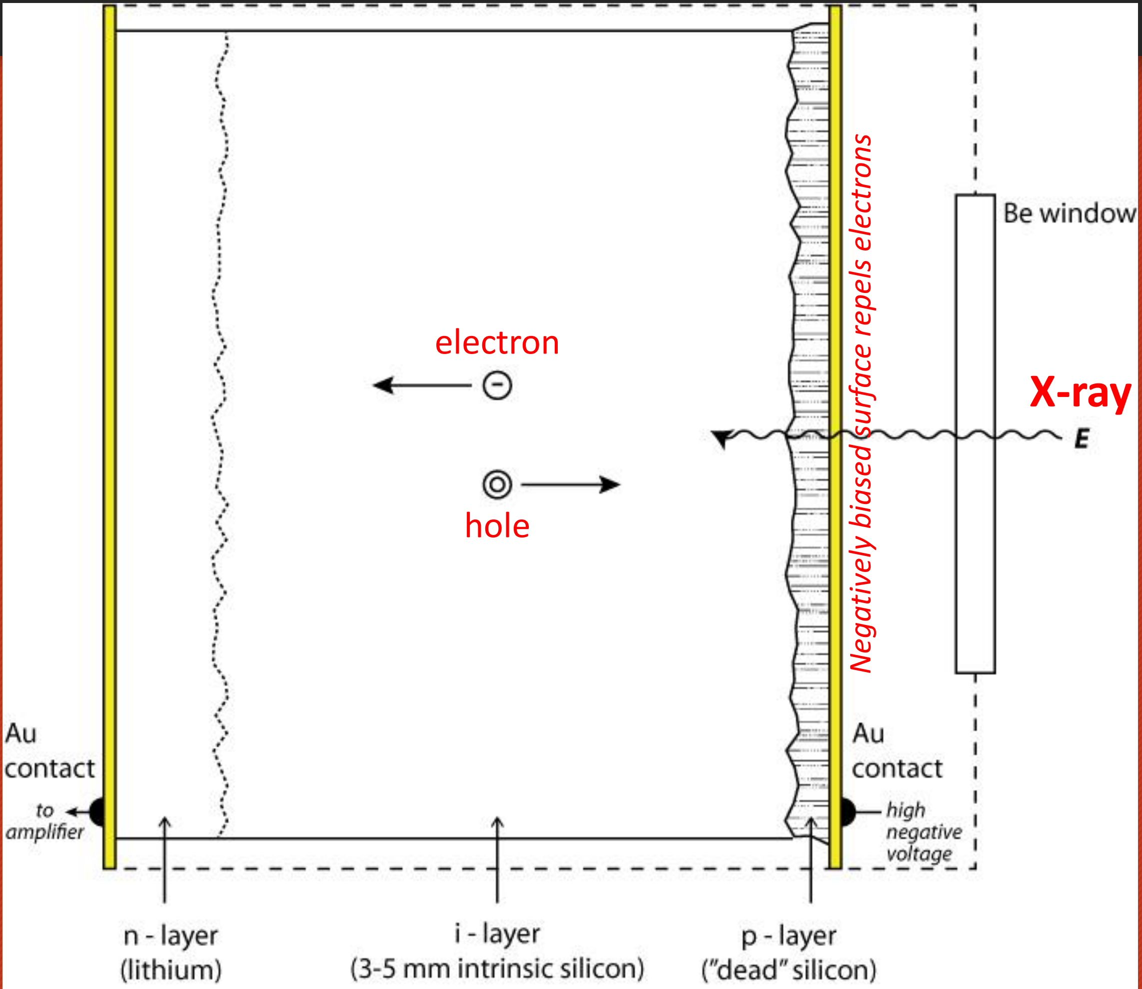


Energy Dispersive Spectrometer (EDS)



- *EDS detector: solid-state semiconductor, window and aperture*
- *Multichannel analyzer (MCA) processes the X-ray signal*

Energy Dispersive Spectrometer (EDS)



Lithium-drifted silicon, or Si(Li), "p-i-n" detector

- *A single crystal of silicon, coated with lithium on one side*
- *Pure silicon is a semiconductor. But impurity of boron, a p-type dopant, makes it a conductor*
- *Lithium, an n-type dopant, counteracts the effect of boron and produces an intrinsic semiconductor*

Qualitative analysis with BSE and EDS