Energy Dispersive X-ray Analysis in the TEM

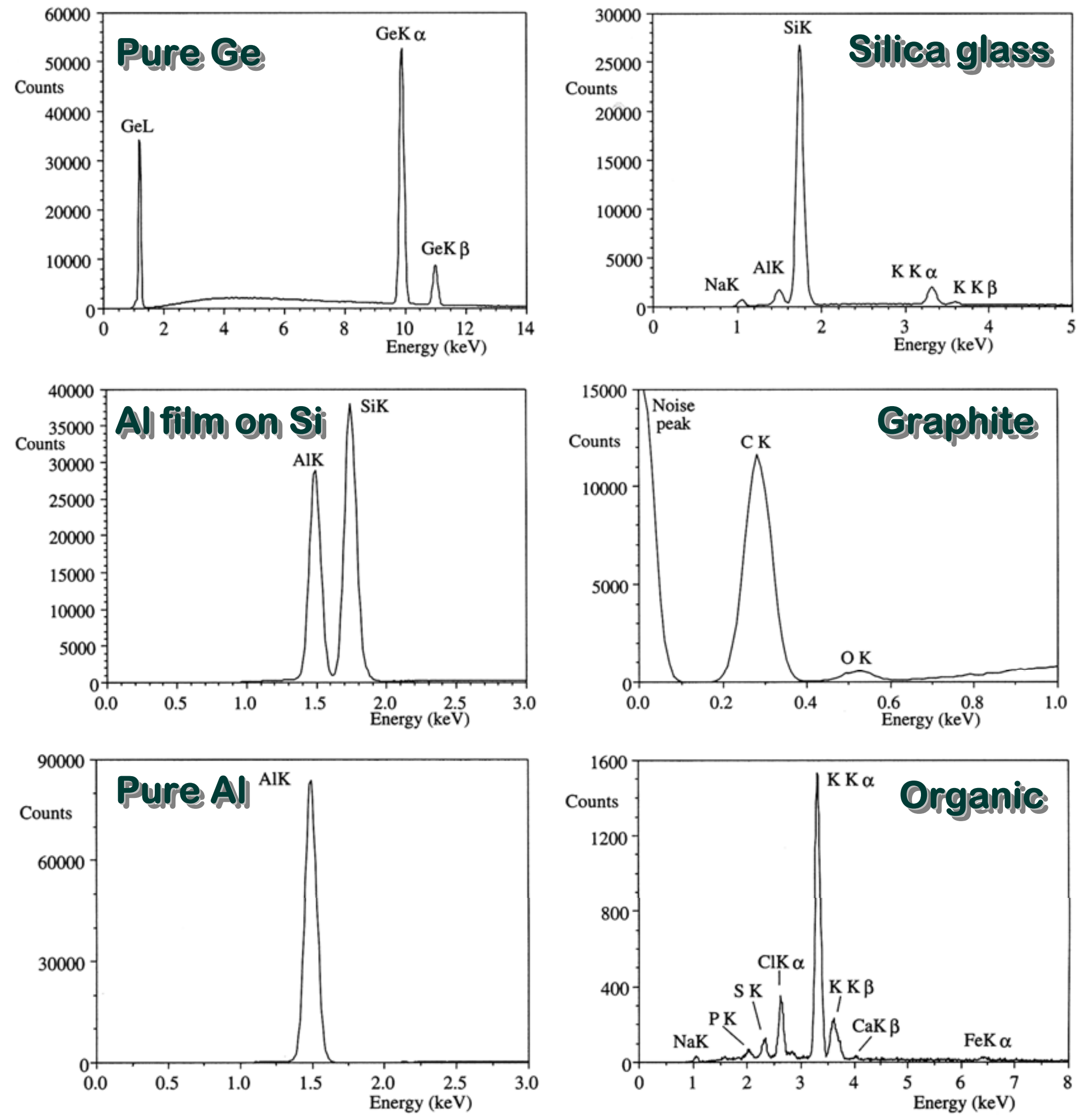
Lecture 19

Example x-ray spectra (EDS)

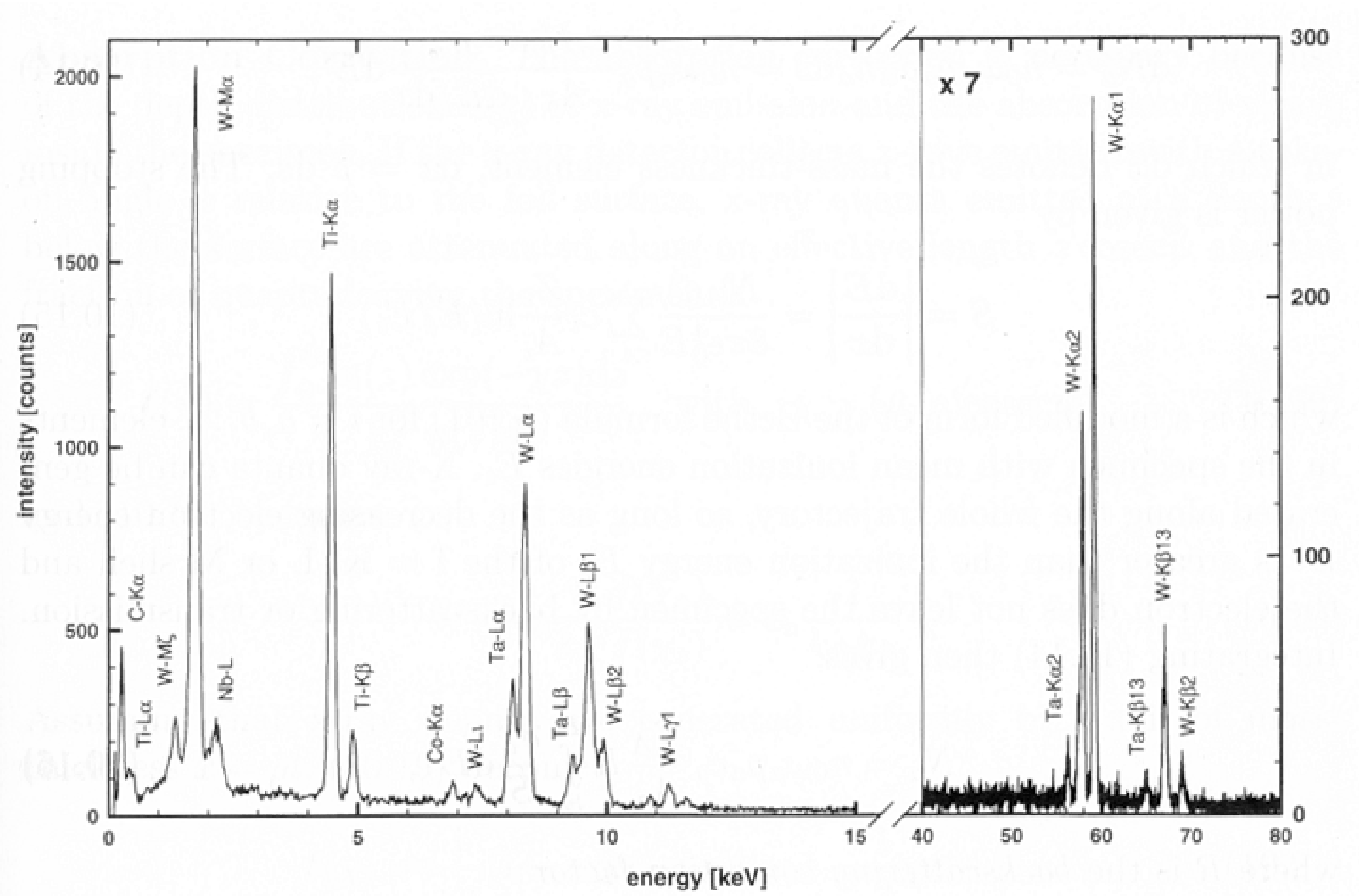
Several examples of EDS spectra

Note:

- Relative # of counts
- Energy range of each spectrum



EDS Example



intensity [counts]
energy [keV]
x 7
C-Kα
Ti-Lα
W-Mζ
W-Mα
Nb-L
Ti-Kα
Ti-Kβ
Co-Kα
W-Lι
Ta-Lα
W-Lα
Ta-Lβ
W-Lβ1
W-Lβ2
W-Lγ1
Ta-Kα2
W-Kα2
W-Kα1
Ta-Kβ13
W-Kβ13
W-Kβ2
0
500
1000
1500
2000
5
10
15
40
50
60
70
80
100
200
300

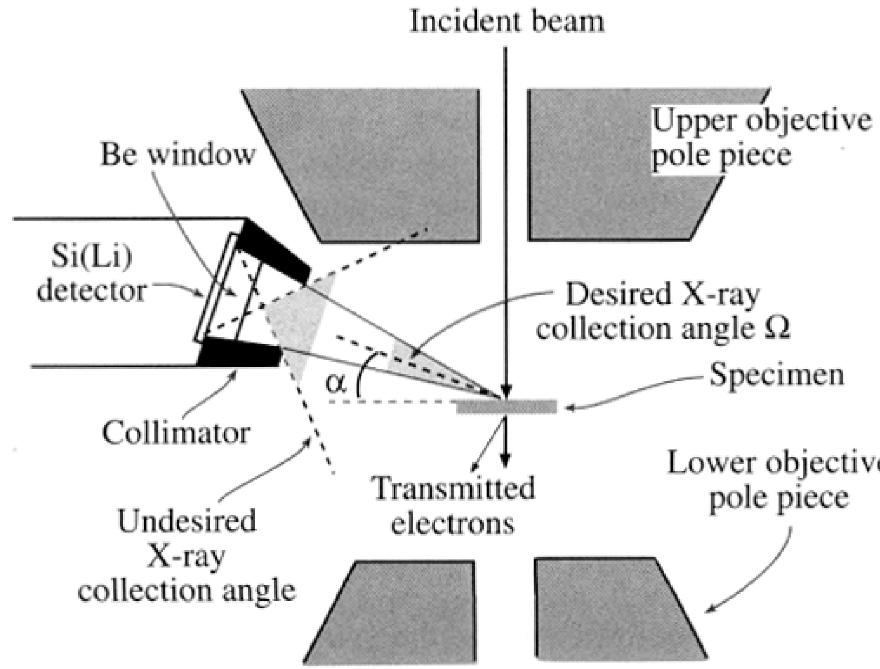
EDS geometry

X-rays produced from all angles

The detector is a small crystal, and subtends only a small angle

EDS is not efficient

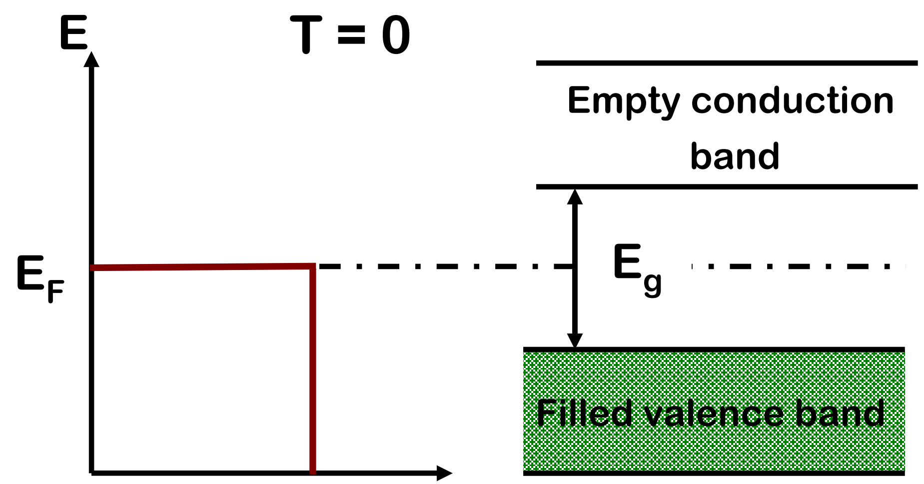
Specimen tilted to the appropriate angle to maximize collection efficiency

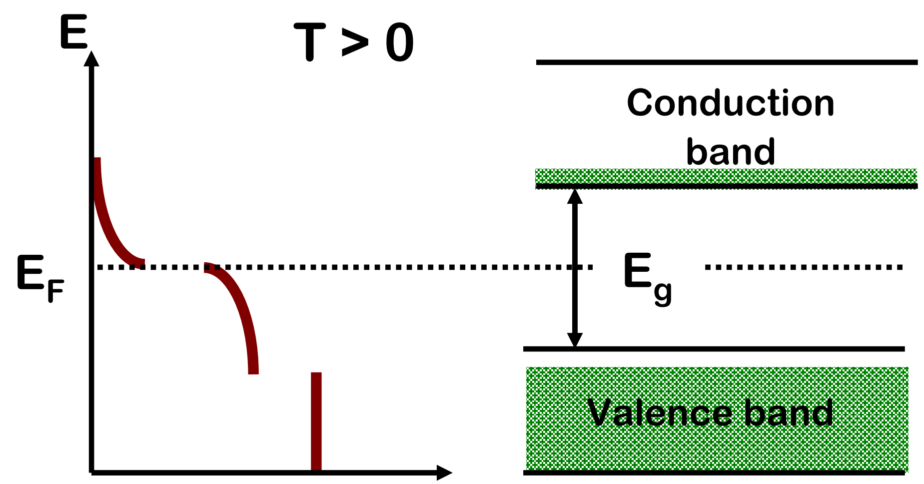


Reminder: Semiconductors

Intrinsic semiconductors

- Pure materials
- Require "excitation" of electrons to get conduction
- This energy input can come from heat or from other forms of energy input
  - e.g. radiation …

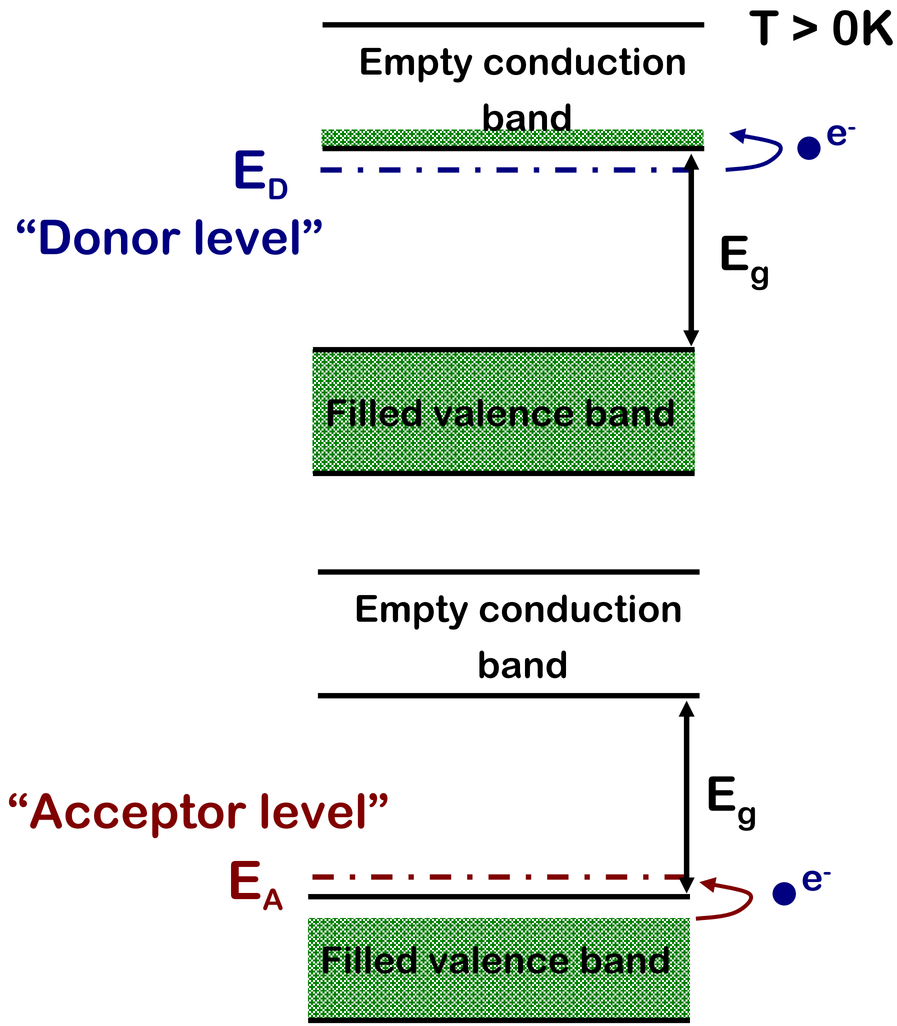




Reminder: Semiconductors

Extrinsic semiconductors

- Ones that have intentionally added impurities
- Allow room temperature conductivity



EDS Detector

Based on a p-i-n junction

- Thick "intrinsic" region
  - Li doped Si - Li fills acceptor states
  - Intrinic Ge - can make Ge more pure
- p-layer on top
- n-layer on bottom
- Two thin ohmic Au contacts on outside

X-rays penetrate Au contact & p-region

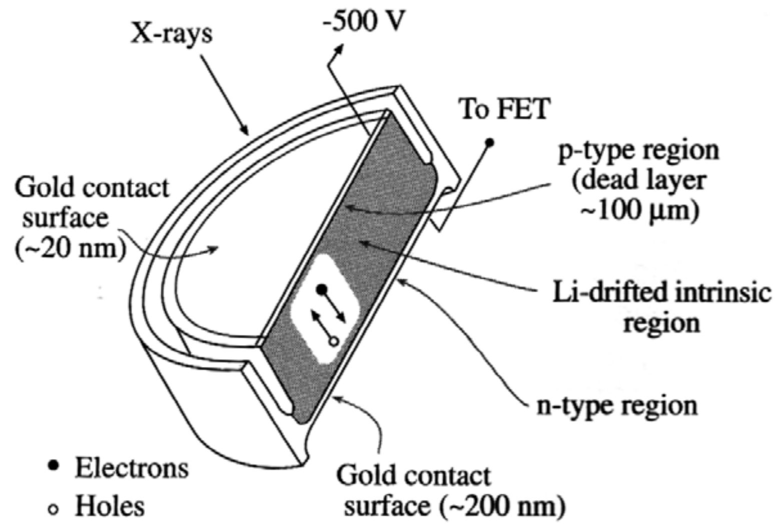
- Sufficient energy

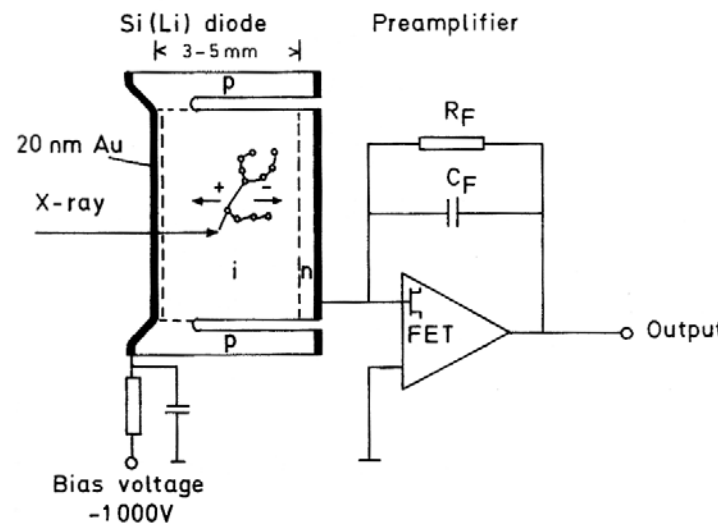
Create electron-hole pairs in the intrinsic region

- Photoelectrons
- Same idea as a solar cell …

p-i-n junction is under bias

- Electron-hole pairs are swept to the contacts
  - Electrons to p, holes to n



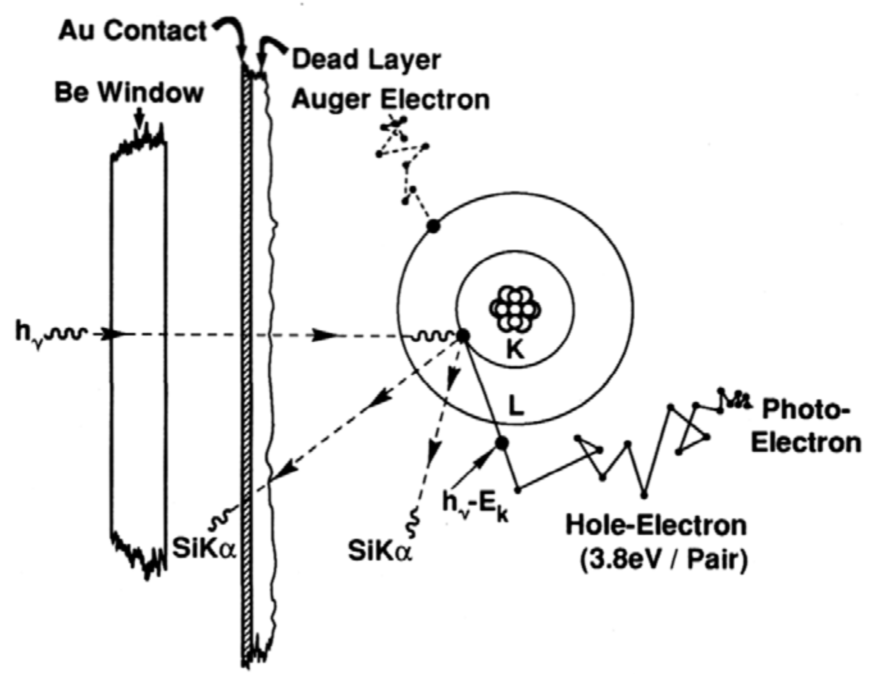


EDS Detector

A bit more to this …

Incident x-rays can:

- Create electron-hole pairs
  - Requires 3.8 eV / pair
- Cause Si x-ray production
  - If Si atom is excited by incident x-ray, can relax by outer shell to inner shell filling and x-ray production
- Cause Auger electron production



Net result, incident x-ray <u>eventually</u> deposits all it's energy into the detector

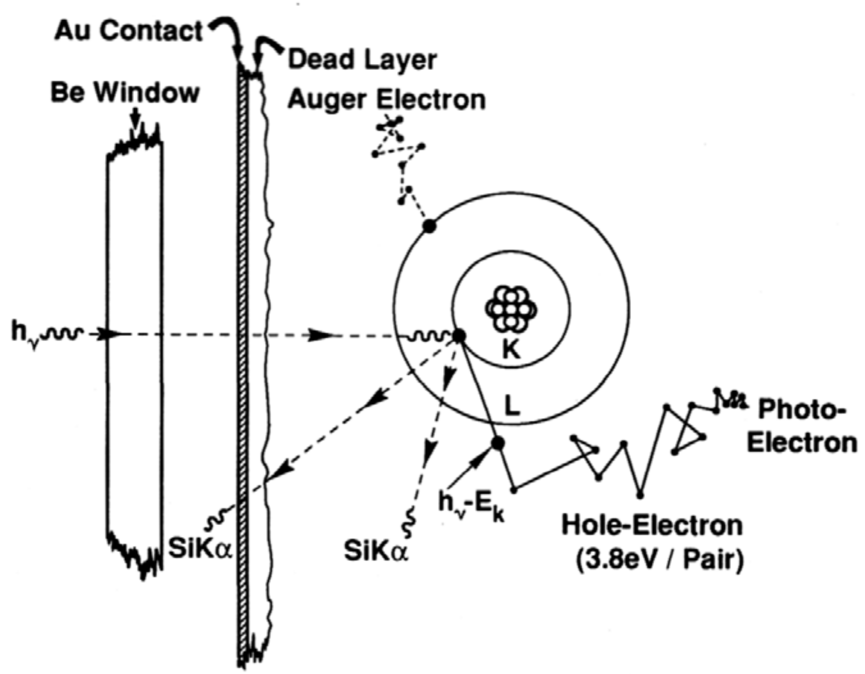
EDS Detector

Ideal # of charges (n):

$$n = \frac{E}{\varepsilon}$$

E: Incident x-ray energy

ε: Energy req'ed to create electron-hole pair



n is thus proportional to E

As an example:

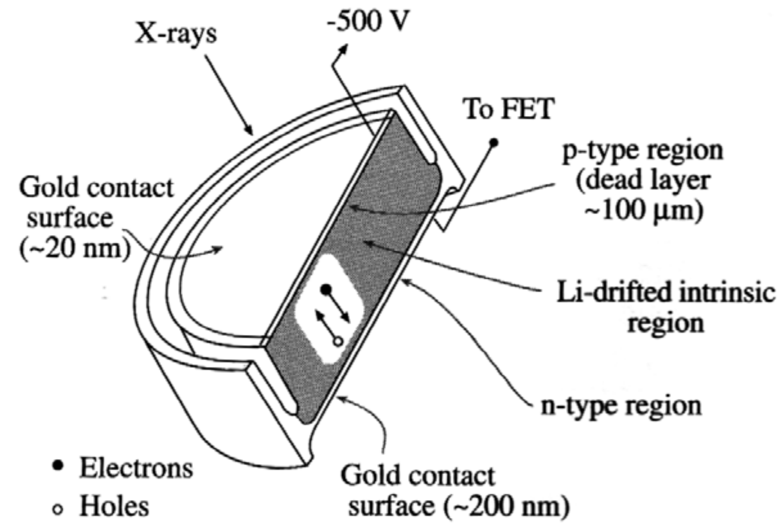
- If x-ray has 5 keV
- n = 1300
- Total charge: 2×10^{-16} C

This is a very small charge

EDS Detector

Based on a p-i-n junction

- Thick “intrinsic” region
  - Li doped Si - Li fills acceptor states
  - Intrinic Ge - can make Ge more pure
- p-layer on top
- n-layer on bottom
- Two thin ohmic Au contacts on outside

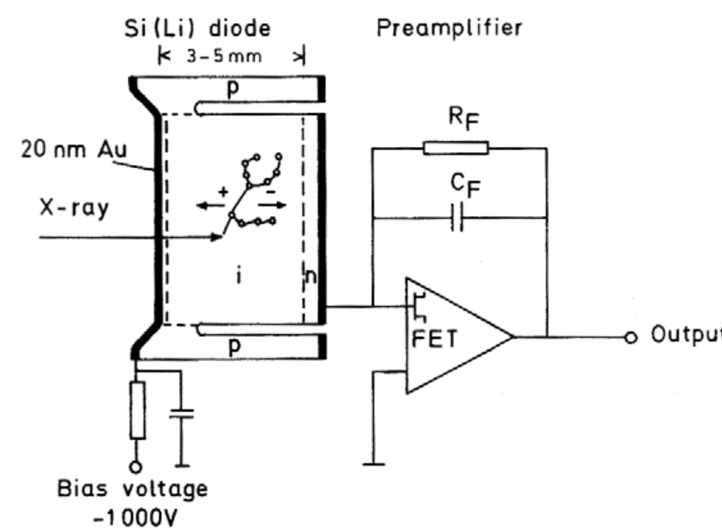


X-rays penetrate Au contact & p-region

- Sufficient energy

Create electron-hole pairs in the intrinsic region

- Photoelectrons
- Same idea as a solar cell …



p-i-n junction is under bias

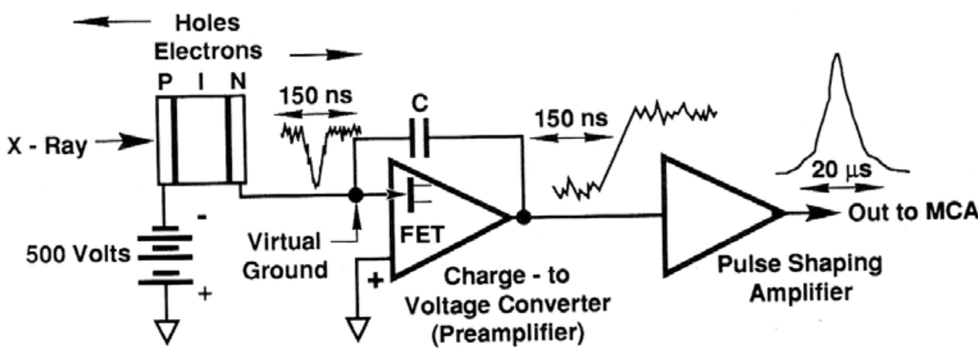
- Electron-hole pairs are swept to the contacts
  - Electrons to p, holes to n

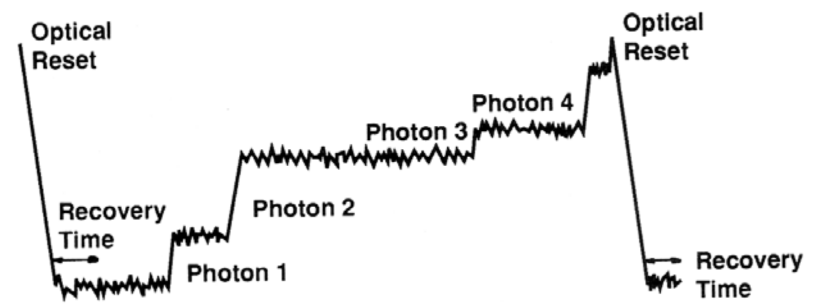
EDS Detector

Because this is a small charge, sensitive electronics are used

n-FET in parallel with a capacitor is used to amplify charge

- To minimize noise, this is kept at LN_2 temperature
- Output is a voltage step that is proportional to the incident energy

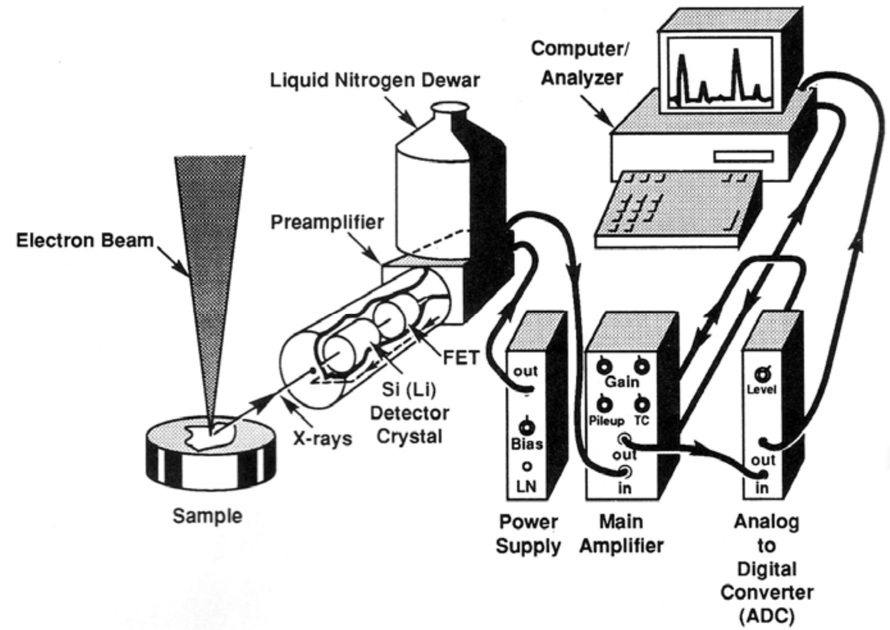




EDS Detector

Back to the electronics

1. X-ray comes in, creates an e- / h+ pair
2. Charge pulse enters FET, converted to voltage pulse
3. Voltage pulse amplified several thousand times
4. Analog-to-digital converter used to assign pulse to specific energy (improves on original assignment)
    1. All done digitally in newer systems - “digital pulse processor”
5. Computer assigns x-ray as a ‘count’ in a multi-channel analyzer



EDS Detector

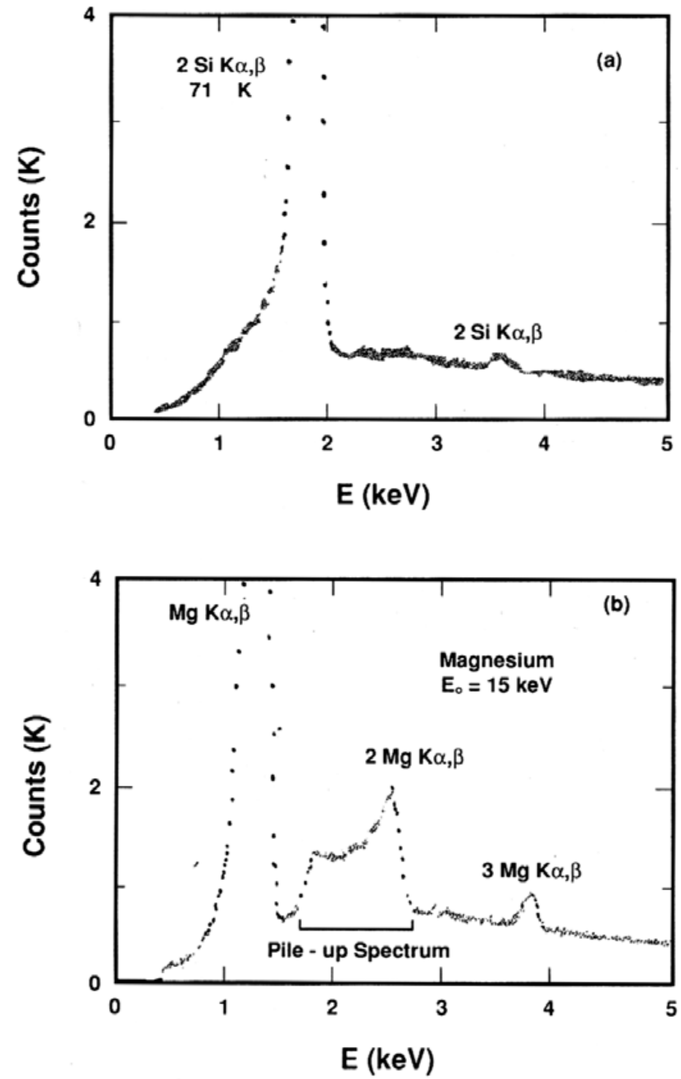
Two parameters under your control

Time constant

- ♦ ~ 10-50 μs
- – Time for the pulse processor to analyze a pulse.
- – Longer means better energy resolution but lower count rate

Dead Time

- – Time pulse processor is shut off to process a pulse
- – Dead Time(%) = $(1-R_{out}/R_{in})*100$
- – In the TEM, below 50-60%
- – If higher than this, too many x-rays are coming into the detector for it to process
- – Results in 'sum peaks'
  - An undesirable artifact ...



Examples of "sum peaks"

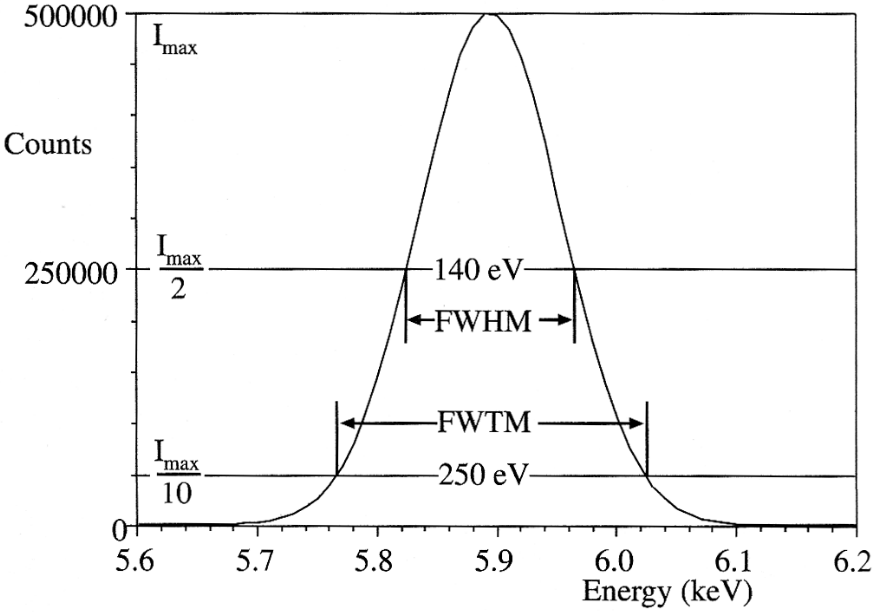
EDS Detectors

Resolution of the detector is (obviously) an important parameter

Usually quoted as a "Full Width at Half Maximum" value (FWHM)

Measured on the Mn Kα peak (standard)

Most detectors these days quote 129eV, get about 140 eV when installed

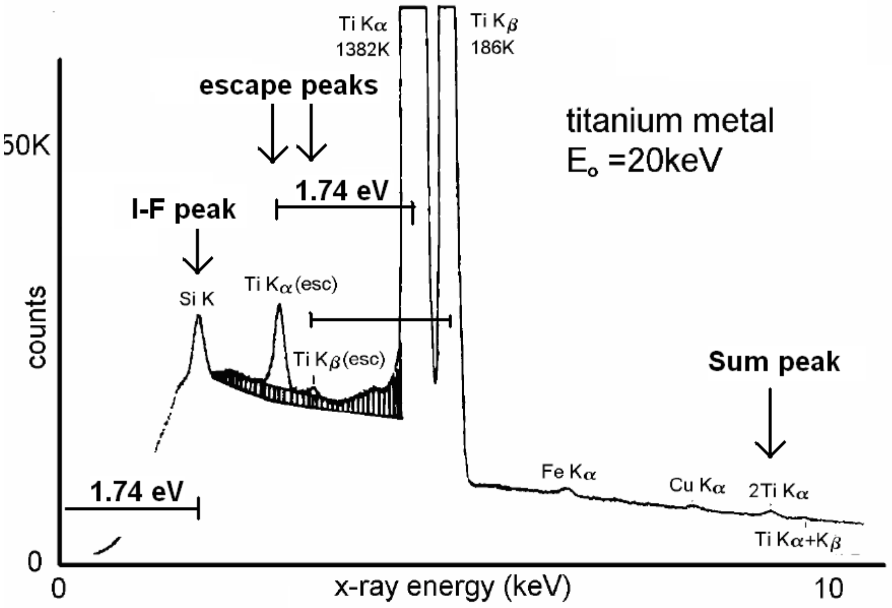


EDS Detector

Two more artifacts

Escape peak:

- Peak corresponding to decreased energy due to "escaping" detector X-ray
  - Si Kα in case of Si(Li) detector
- Result: $$n = \frac{E - E_{Si\ K\alpha}}{\varepsilon}$$



Internal-Fluorescence peak

- Incoming photons fluoresce atoms in dead layer

EDS Detector

Three reasons to keep the detector cold

1. LN_2 keeps the intrinsic layer intrinsic
2. LN_2 prevents Li atom diffusion
3. LN_2 keeps the pre-amplifier FET cold and thus reduces electronic noise

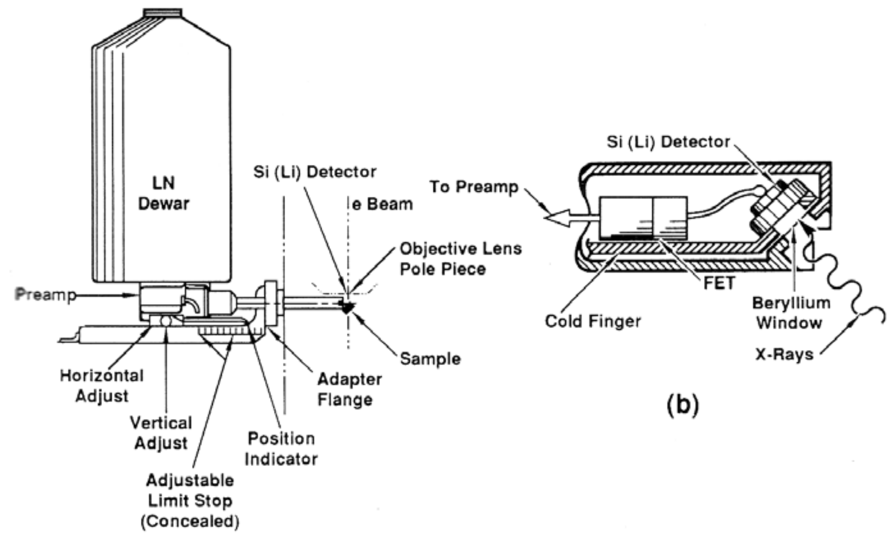
Problem:

– Cold attracts junk in the vacuum

– Leads to film on the detector that x-rays must penetrate

Solution:

– A “window” to protect the detector from vacuum

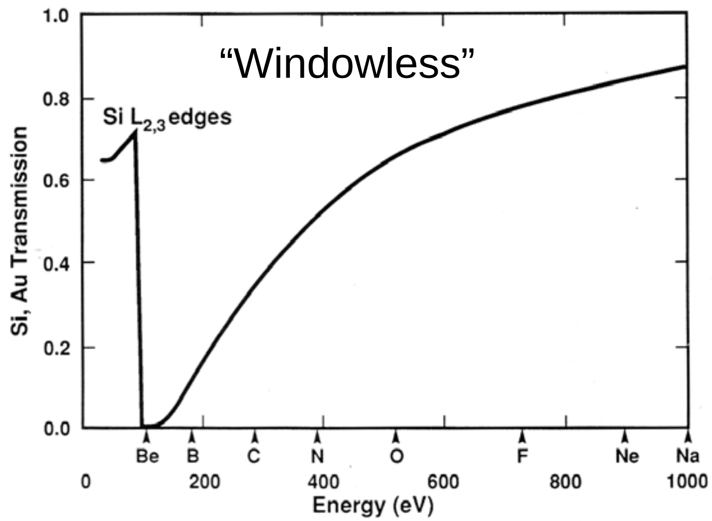


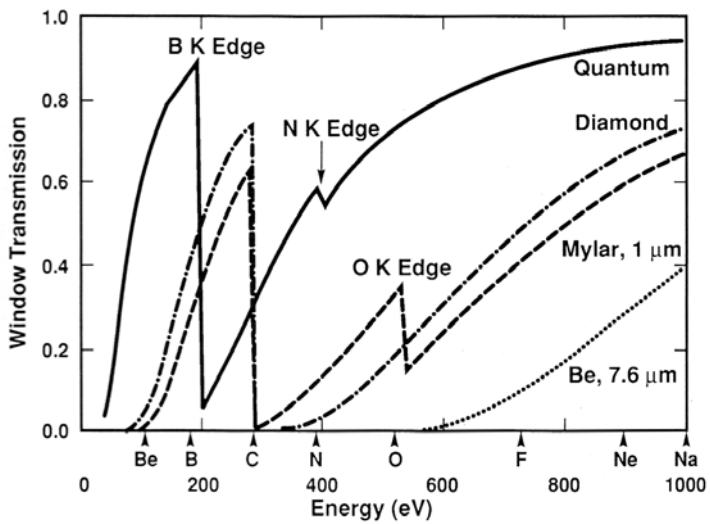
EDS Detector

The idea is to use a thin, strong light element 'window' to protect the detector from crap

This works OK in practice, but limits the ability to detect light elements …

The window on your detector is a characteristic of the detector and will affect the output





Spurious x-rays

Recall, x-rays generated at all angles.

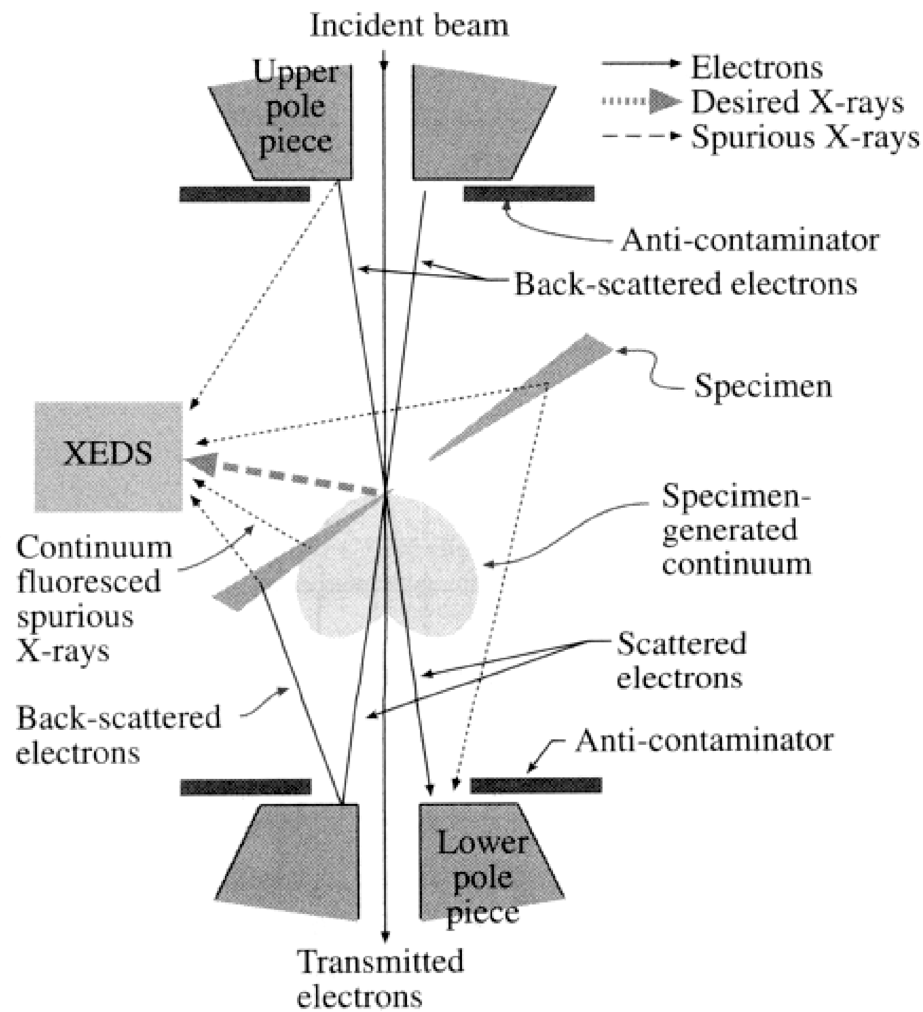
They are high energy.

Can excite further x-ray production from:

- Microscope parts
- Sample holder
- Other regions of sample

Be careful!

- Do not modify microscope without working w/ radiation safety technicians

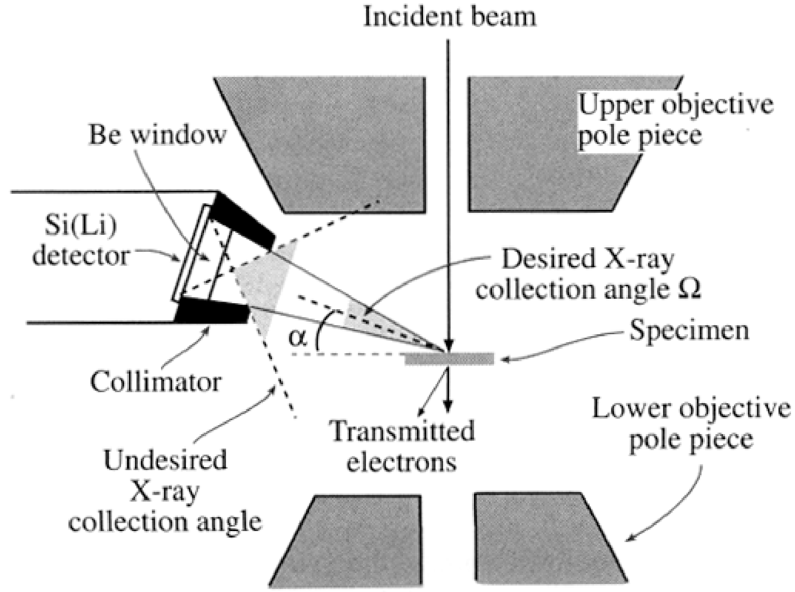


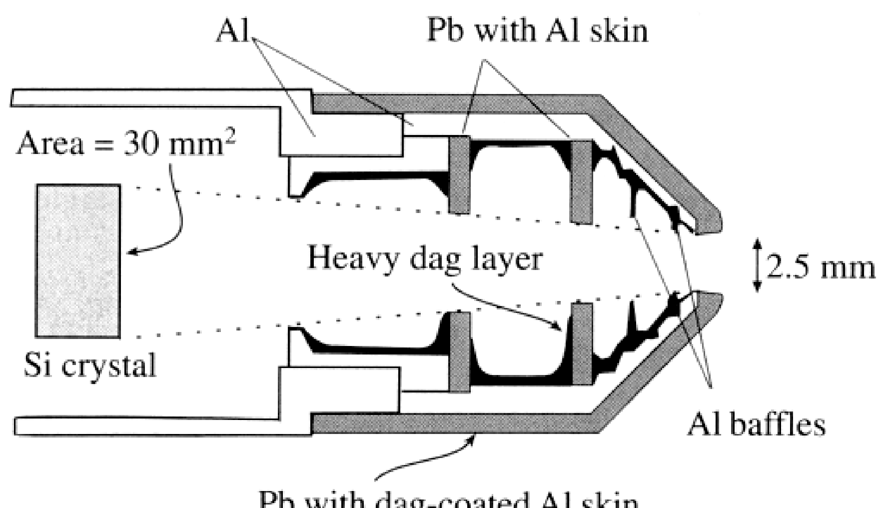
Collimator

- Role of the collimator is to prevent collection of spurious x-rays
- X-rays coming in from 'wrong' angles (i.e. not from the specimen!) are absorbed by heavy Pb layer / baffles
- Defines the 'collection angle' (Ω):

$$\Omega = \frac{A\cos\delta}{S^2}$$

  - A: detector area
  - S: distance from analysis point to detector face
  - d: angle between detector face normal and specimen (often 0°)





Qualitative XEDS Analysis

Qualitative analysis

- Quick look of sample without going through laborious quantitative analysis
- Useful in identifying the right data for quantitative analysis

Data acquisition

- maximize the X-ray count rate to give you the most intensity in the spectrum in shortest time and minimal artifacts

Peak Identification

- Understand peaks based on their ‘family’
- Requires every peak to be identified unambiguously and statistical certainty

Artifact corrections

- adsorption and fluorescence

Acquiring a Spectrum

Have a general sense for what's in the sample and what you are looking for

How to get a good spectrum:

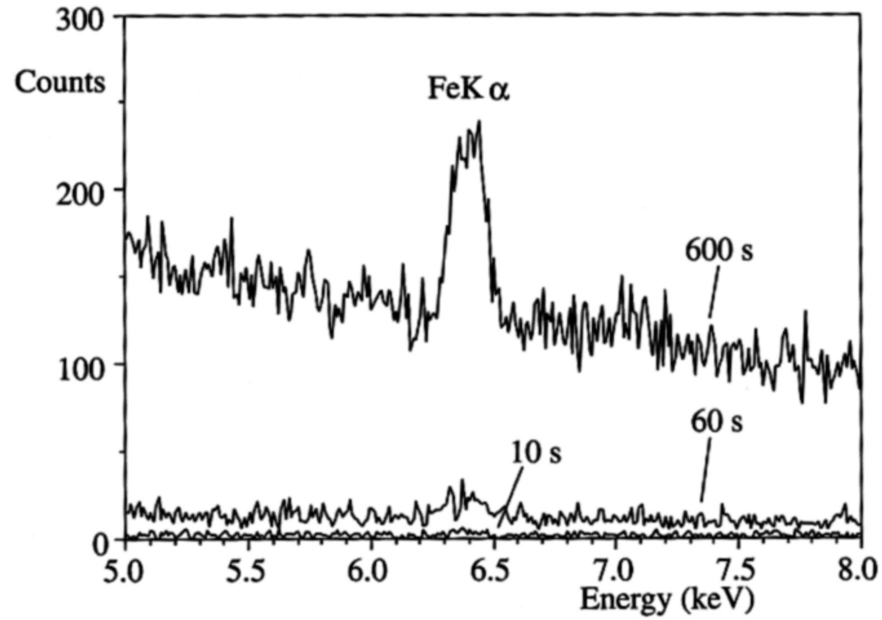
- Chose the energy range carefully
- Higher voltage increases brightness which increases P/B ratio
- Sample thickness – balance counts versus absorption and spatial resolution
- Long collection time – spread beam over large area to reduce sample knock-on damage
- Detector time constant – to maximize throughput of counts
- Dead time – below 50-60% with output rate of 5,000-10,000 cps

Peak visibility – collect for longer time if in doubt of small peaks or intensity fluctuation

Peak Visibility

With increasing counting time, a clear characteristic Fe Ka peak develops above the background in a spectrum of Si-0.2% Fe

This demonstrates the need to acquire statistically significant counts before deciding if a small peak is present or absent



Statistical Criterion:

If $I_A > 3\sqrt{I_B}$, then the peak is statistically significant

If $I_A > 3\sqrt{I_B}$, then the peak is not significant and should be ignored

IA: Intensity in peak of interest over a fixed range

IB: Intensity in background over the same fixed range increment

Identification of the Peaks

- Be suspicious, look for the unexpected peaks
- Look for family of peaks, the presence in the spectrum of all possible members of a family of lines increases the confidence for the identification of that element
- Consider the appearance of the K, L, and M families in EDS spectra as a function of position in the energy range of 0 to 10 keV
- Beware of artifacts, such as escape peaks, systems peaks, and pathological overlaps
  - "Pathological overlaps": a fancy way of saying that the energy value of two peaks of interest (or artifact) overlap

Quantification
background subtraction

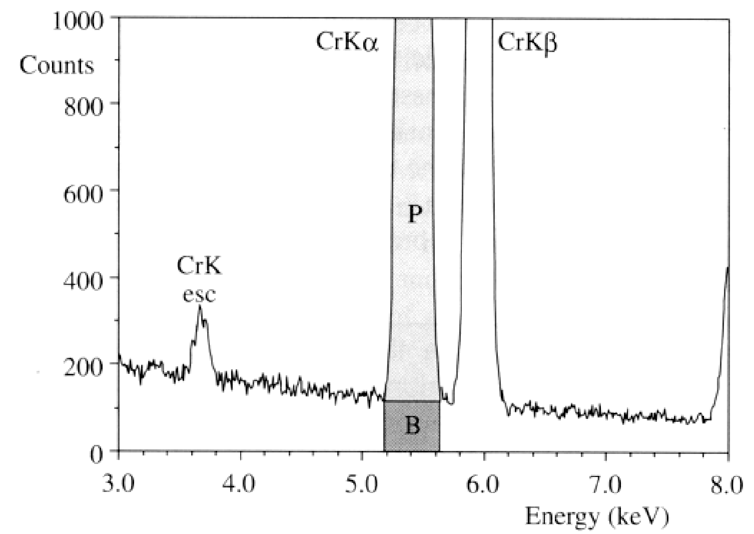
EDS is readily *quantifiable*

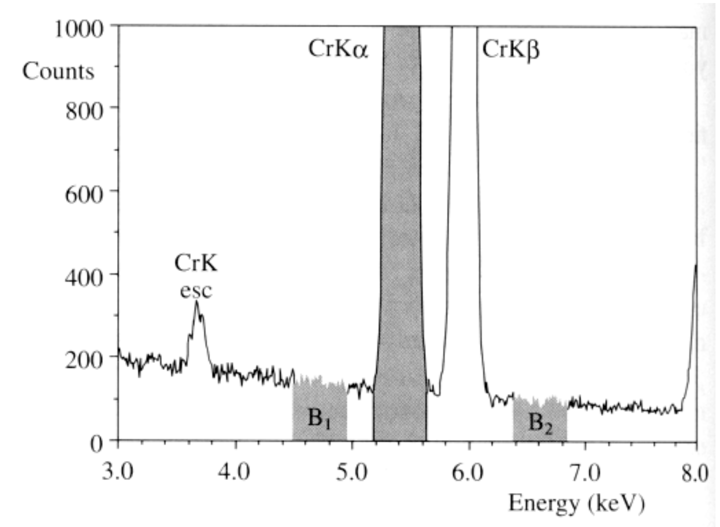
- i.e. can determine the relative proportion of one element to another

Need to subtract the Bremsstrahlung background to find real number of counts

Most modern software does this for you

- Details on methods found in the text





Quantification
Cliff-Lorimer method

Relatively simple idea - it works!

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}$$

But this means you have to have a standard.

Standards:

- Ideally, well characterized single phase
- Thin sample that is representative, stable
- Want very high counts: 104 above background

kAB is a function of the EDS / TEM combination.

- It is NOT a constant (but can be theoretically estimated)
  - Check your results for logical consistency
- Best if experimentally determined for a given system
  - TEM + Detector + Geometry

Quantification
Cliff-Lorimer method

General notes:

1. **A detailed description of how to statistically account for errors is given in W&C, Chap. 35**
   - Tedious and detailed, but necessary for 'best results'
2. **If you have a new detector / fix a detector / change configuration a new k-factor determination is necessary**
3. **Because TEM samples are thin, often not necessary to include 'fluorescence and 'absorption corrections**
   - This is different than in SEM where these effects are often significant

X-Ray Absorption & Fluorescence

Idea: x-ray produced elsewhere in sample causes:

1. Ejection of inner shell electron
2. Higher level electron transitions down to fill hole
3. New x-ray is produced

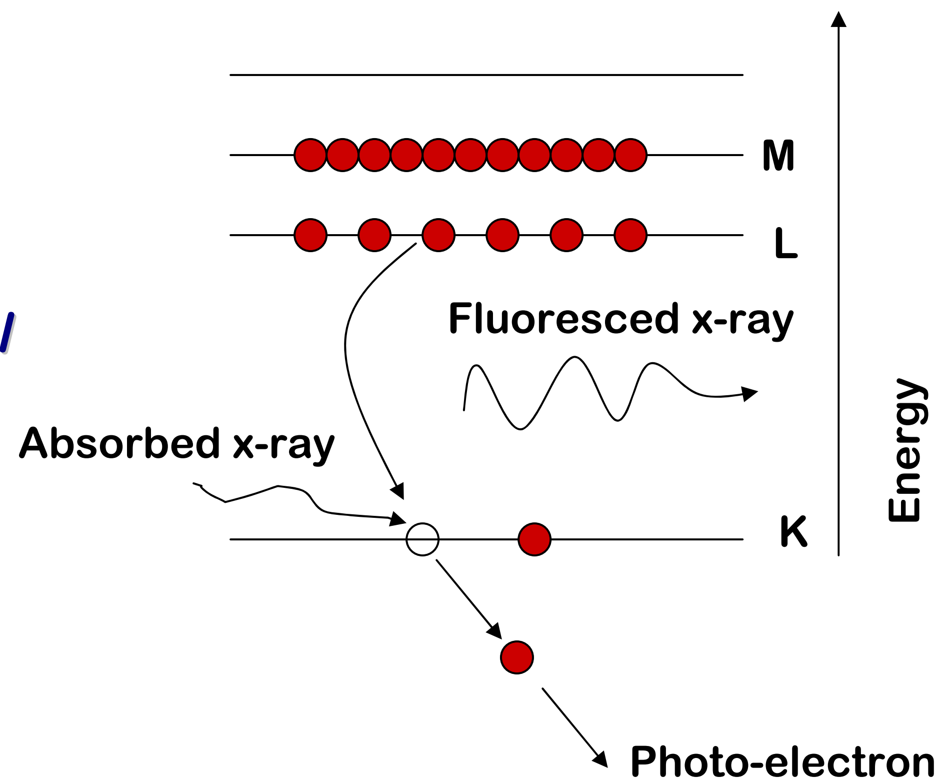
Can cause fluoresence peaks from the detector / support grid / sample

- If from sample, can affect quantification

Can cause absorption of x-rays you wish to detect

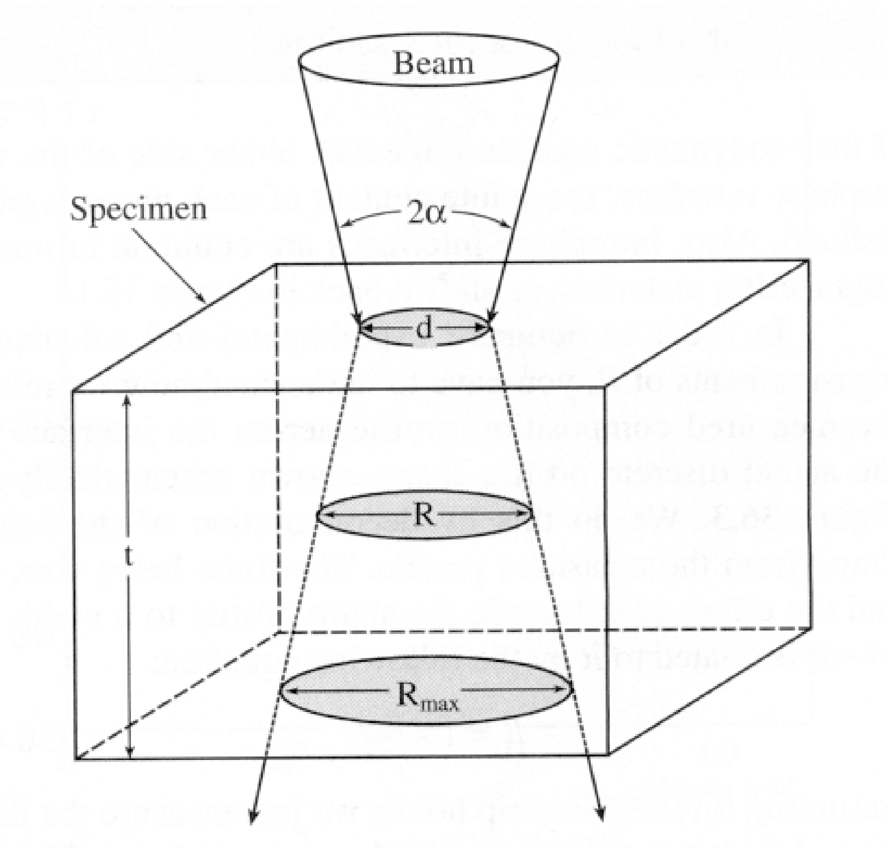
Problematic for thicker samples

- See W&C Chap 35 for more details



Spatial resolution

Spatial resolution determined by both size of incident probe and relative spreading in the sample



Spatial resolution

Spatial resolution determined by both size of incident probe and relative spreading in the sample

Often 'Monte Carlo' simulations are used to find out how much spreading occurs

Program sources available in W&C Chap 1.

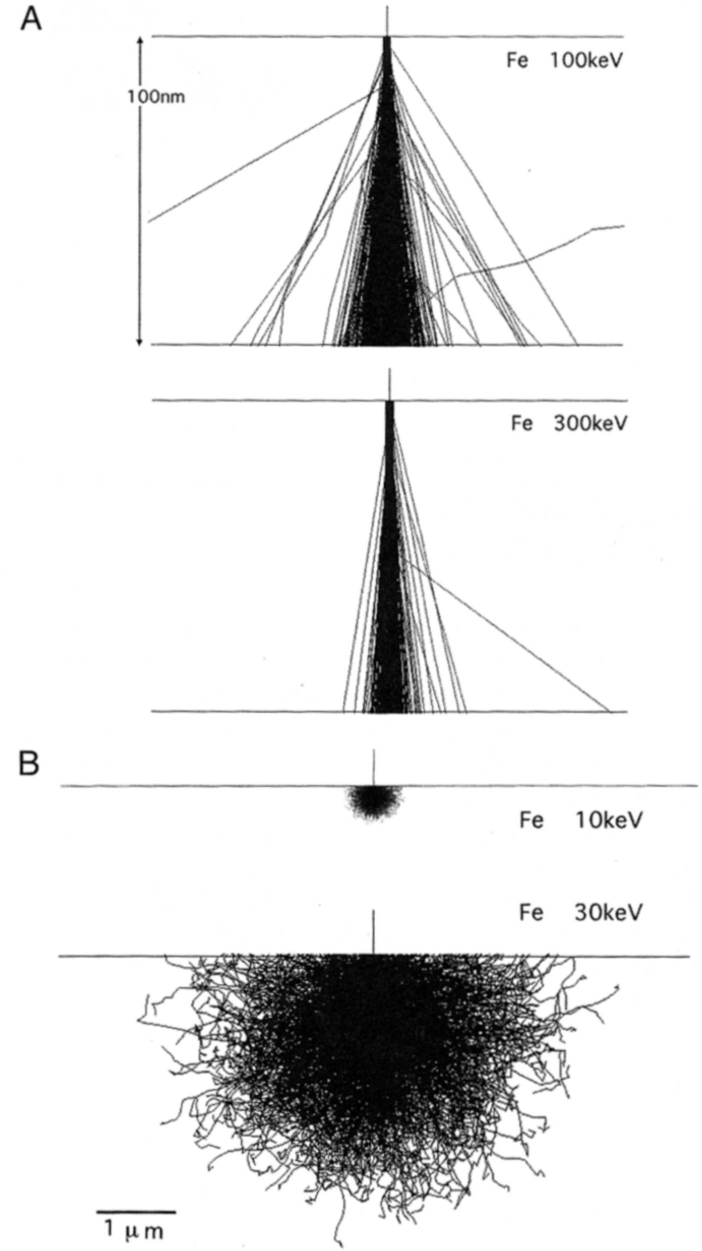
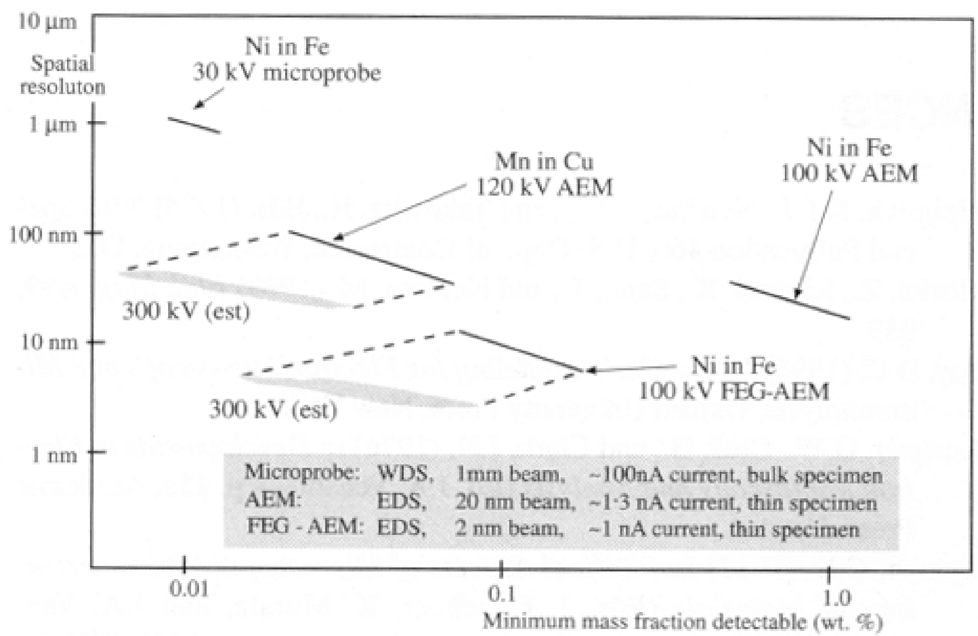


Figure 36.1. (A) Monte Carlo simulations of 10^3 electron trajectories through a 100-nm thin foil of Fe at 100 kV and 300 kV. Note the *improved* spatial resolution at higher kV. (B) Conversely, in a bulk sample the interaction volume at 30 kV is significantly more than at 10 kV, giving *poorer* X-ray spatial resolution at higher kV.

Sensitivity of EDS & EELS



"Minimum Mass Fraction" - minimum detectability

- 0.01% to 1% for EDS & EELS
- Depends on microscope & sample

"Minimum Detectable Mass"

- We're talking about a *small* volume
- 10's to 100's of atoms do-able with EDS
- 100's of atoms with EELS.