

# Other Spectroscopic Techniques

Using electrons, x-rays and ions

# Basic Idea

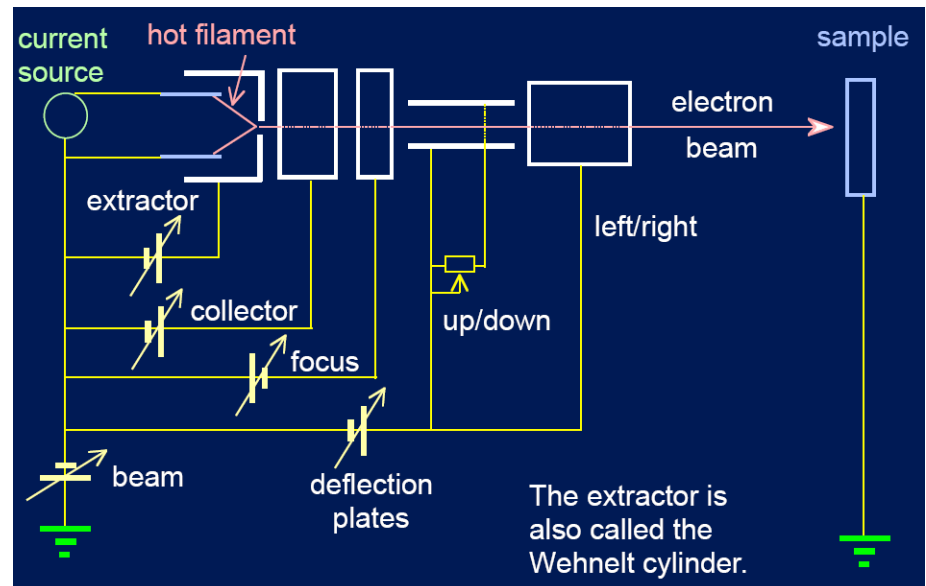
- The concept is similar to optical spectroscopy.
- Send in an excitation (sources).
- Collect and resolve the emission (analyze).
- Detect the emission (detectors).
- The particular excitation-collection pair determines what aspect of the thin film you are measuring.

# Inputs - Outputs

- Sources
  - Optical (UV, VIS, IR)
  - X-rays
  - Electrons
  - Ions
- Emissions
  - Optical
  - X-rays
  - Electrons
    - Backscattered
    - Secondary
    - Auger
  - Ions
    - Backscattered
    - Sputtered

# Electron Sources

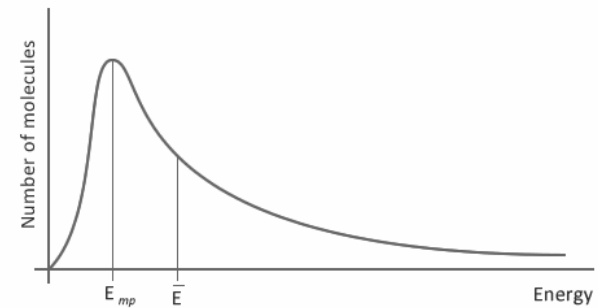
- Electrons can be emitted from a metal by **thermionic emission**.
- A high enough electric field applied to the metal pulls electrons off the metal surface.
- The number of electrons emitted is proportional to the temperature of the metal and inversely proportional to its work function.



# Issues

- Thermionic emission sources are not narrow-band.
- The thermal heating results in a Boltzmann distribution of emitted electron energies.
- Some filament designs require less heating and therefore result in a narrower electron energy distribution.
- There is an upper limit to the electron density due to electron repulsion.

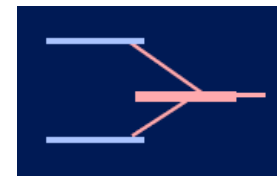
THE MAXWELL-BOLTZMANN DISTRIBUTION



Hairpin filament

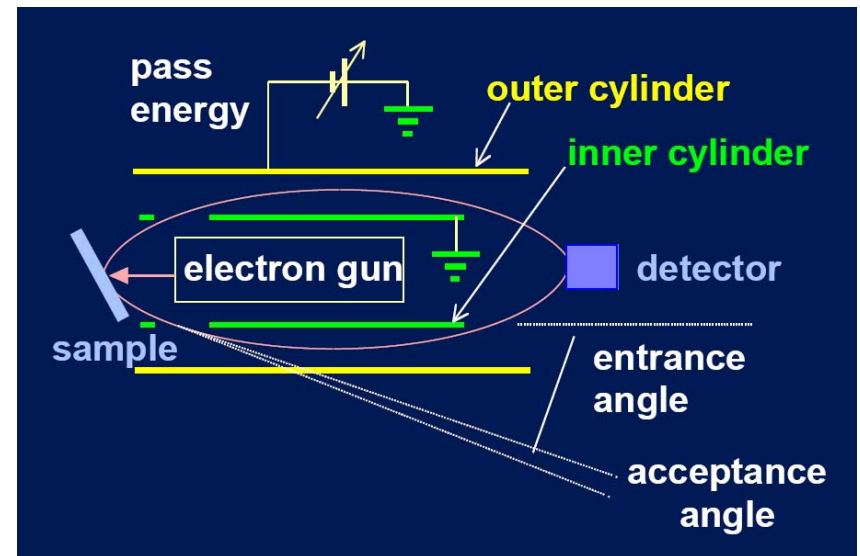


Field emitter tip



# Electron Analyzers

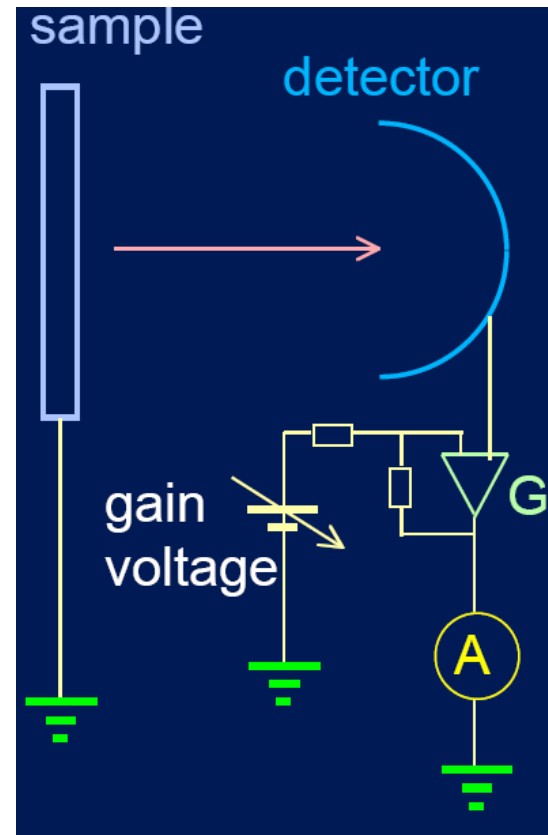
- They use electrostatic or electromagnetic fields to deflect electrons and sort them according to their initial kinetic energy.
- Some types are:
  - Cylindrical Mirror Analyzer (CMA)
  - Hemispherical Sector Analyzer (HSA)
  - Retarding Field Analyzer (RFA)
  - Cylindrical Sector Analyzer (CSA)



CMA

# Electron Detectors

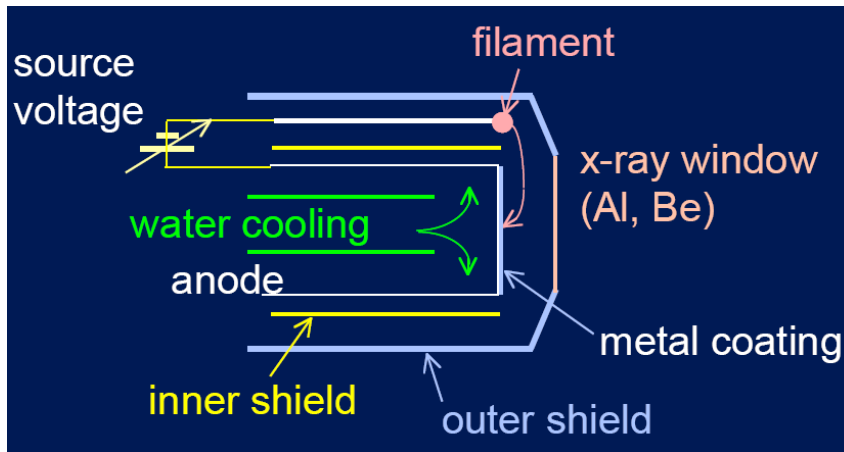
- The detector receives electrons.
- Each electron contributes to a current that is measured.
- An amplification scheme is usually incorporated.
- Some types are:
  - Electron multiplier
  - Channeltron
  - Channel plate



**Basic design of an electron detector**

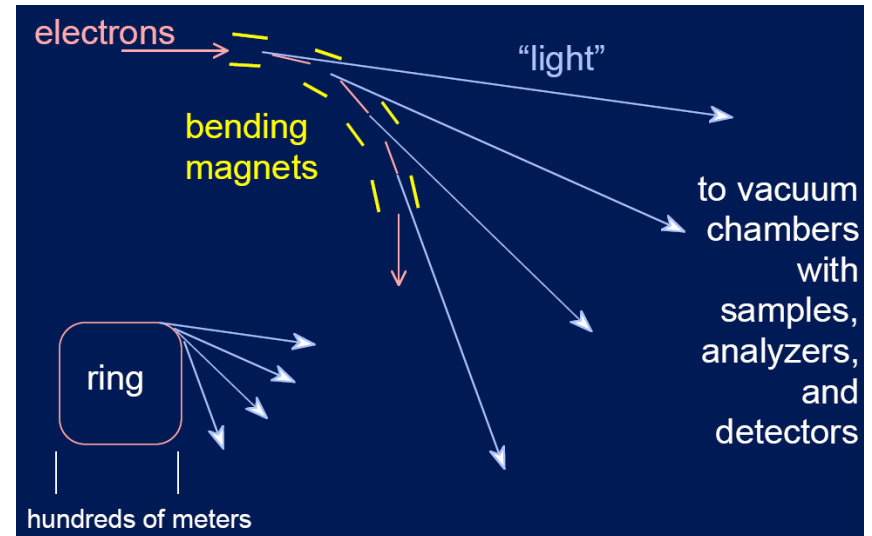
# X-Ray Sources

## Bremmstrahlung



- Created by sudden stopping of electrons
- Suitable for small labs
- Low maintenance
- Complex emission spectrum
- Subject to contamination

## Synchrotron



- Created by accelerated electrons
- National lab type facility
- High brilliance source
- Narrow, tunable lineshape

# X-Ray Analyzers

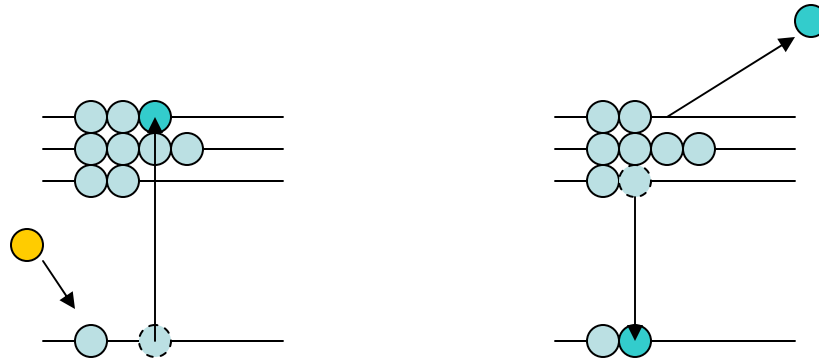
- Wavelength Dispersive
  - Use a crystal and x-ray diffraction just ;like an optical spectrometer.
  - Very sensitive and precise but expensive and slow.
- Energy Dispersive
  - Use absorption in Si or Ge , generate multiple electron-hole pairs and separate them with an applied voltage.
  - Faster and cheaper but less sensitive.

# X-Ray Detectors

- Scintillators and phosphors
  - X-rays are absorbed as they penetrate the detector and emit visible light.
- Calorimeters
  - X-rays are absorbed and the heat they produce is measured.
- Charge detectors
  - X-rays kick-off electrons from their orbits and the resultant current is measured.

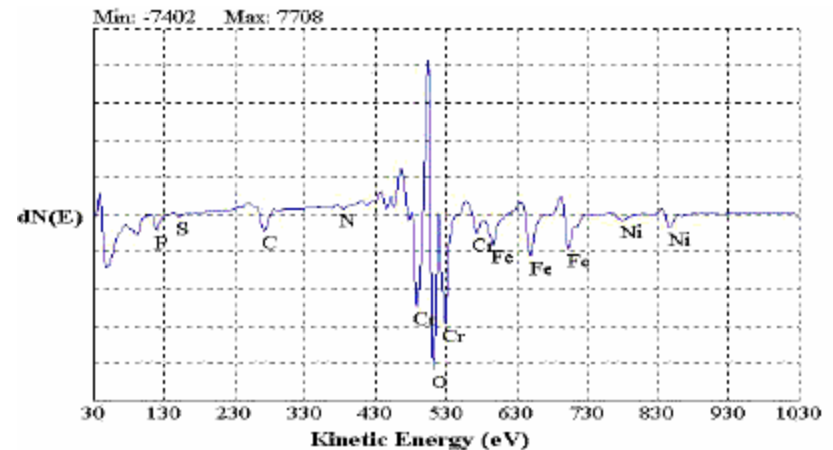
# Auger Electron Spectroscopy

- Electrons with moderate energy ( $\sim 5$  keV) impact the sample and excite electrons from the core levels.
- These electrons release their energy when returning to their ground states either by x-ray fluorescence or electron emission (Auger emission).
- The kinetic energy of the escaped electrons are analyzed.



# AES Uses

- AES is a surface sensitive (~30 Å) technique used for chemical composition and defect analysis.
- Most useful for conductors.
- A relatively small area (10 nm – 1 mm) can be sampled.
- Requires UHV.
- May damage the sample.
- Low sensitivity (0.1 atomic % at best)



Auger electron spectrum of stainless steel.

# Electron Diffraction Techniques

- Low Energy Electron Diffraction (LEED)
  - Low energy ( $\sim 100$  eV) electrons are sent to the sample and the diffraction pattern is detected.
  - Surface sensitive technique to measure crystal structure.
- Reflection High Energy ED (RHEED)
  - Similar to LEED but uses high energy (1-30 keV) electrons

# X-Ray Electron Spectroscopy

- XES uses electrons for excitation but detects emitted x-rays.
- X-rays come from a greater depth than electrons (1-10 microns).
- Used for chemical composition detection.
- Slightly worse sensitivity than AES.
- Not good for materials that absorb x-rays (such as lead).
- Coupled with SEM, it is known as EDX (energy dispersive x-ray analysis).

# X-Ray Photoelectron Spectroscopy

- Send in x-rays and detect emitted electrons.
- Actually secondary electrons are detected.
- Surface sensitive technique (10-100 Å)
- Does not damage samples like AES.
- Not as good lateral resolution (~1 μm).
- Better chemical sensitivity (chemical bonding information).

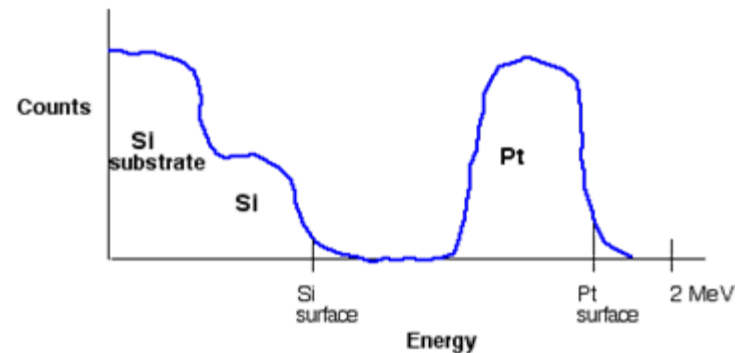
# X-Ray Fluorescence Spectroscopy

- Send in x-rays, detect x-rays
- Low lateral resolution (~150 micron).
- Can explore deeper in to the sample (~10 micron).
- Better than ppb resolution
- Suitable for polymers that might decompose under electron excitation.
- Can be used on liquids as well as solids.

# Rutherford Backscattering Spectroscopy

- Send in He ions (2 MeV), collect back scattered ions.
- The energy of the ions contain information on chemical composition and film thickness.
- Has poor lateral (~1 mm) and depth (>20 Å) resolution.

- Energy of scattered ions depends on
- element (mass)
  - angle
  - location in solid

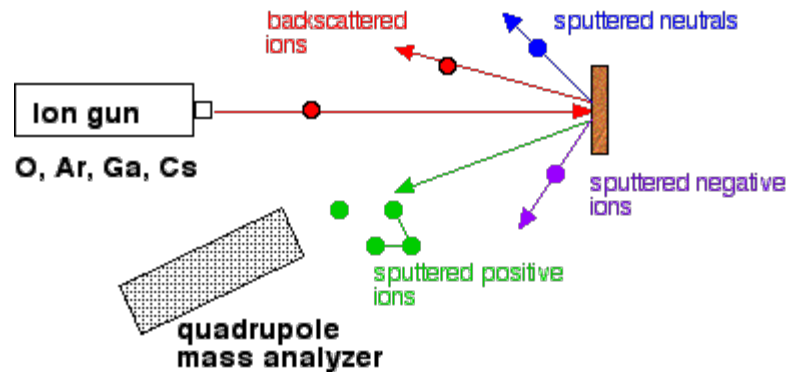


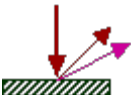
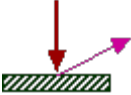
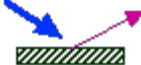


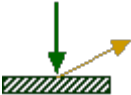

from graph:

- height --> concentration
- width --> layer thickness
- absolute energy value --> element and depth

# Secondary Ion Mass Spectroscopy

- Send in ions, detect secondary ions and analyze their mass or charge-mass ratios.
- Surface sensitive technique for chemical composition and dopant analysis.



IN		DETECT	Technique
high energy electrons (30 keV)		backscattered and secondary electrons	Scanning Electron Microscopy
moderate energy electrons (5 keV)		secondary electrons	Auger Electron Spectroscopy
light (X-rays - 1 keV)		secondary electrons	X-ray Photoelectron Spectroscopy
low energy electrons (100 eV)		diffracted electrons	Low Energy Electron Diffraction
moderate energy electrons (5 keV)		diffracted electrons	Reflection High Energy Electron Diffraction
moderate-high energy ions (2-30 keV)		secondary ions	Secondary Ion Mass Spectrometry
polarized light (2 eV)		polarized light	ellipsometry