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.

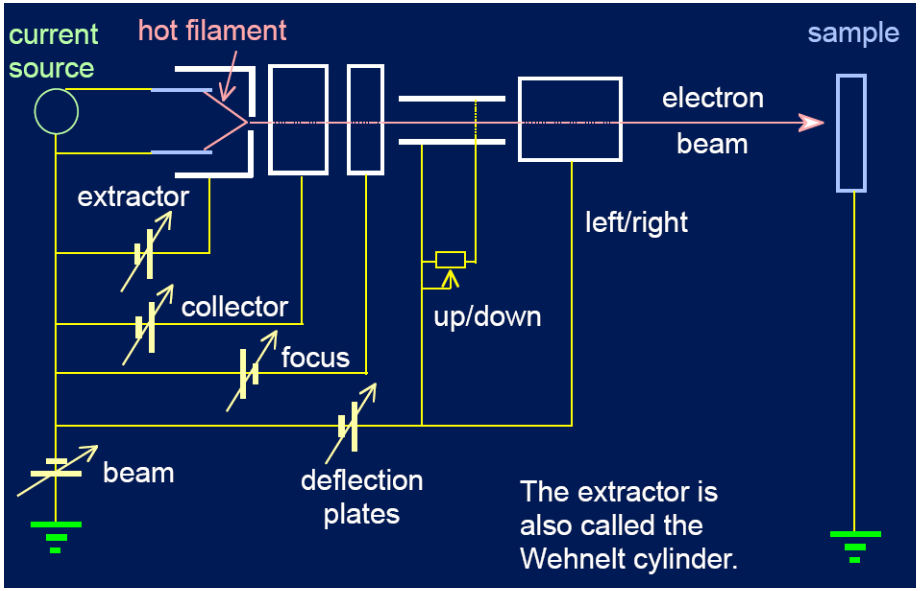
Inputs - Outputs

- Sources
  - Optical (UV, VIS, IR)
  - X-rays
  - Electrons
  - Ions

- Emissions
  - Optical
  - X-rays
  - Electrons
    - Backscattered
    - Secondary
    - Auger
  - Ions
    - Backscattered
    - Sputtered

Electron Sources

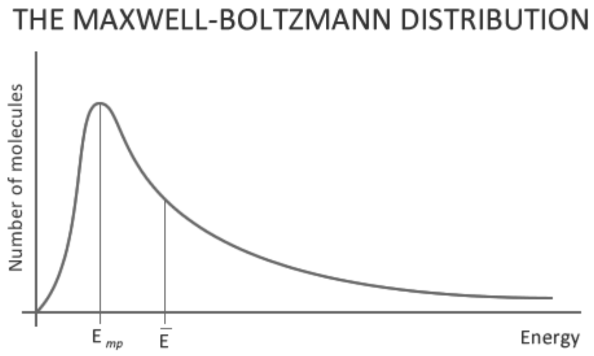
- Electrons can be emitted from a metal by **thermionic emission**.
- A high enough electric field applied to the metal pulls electrons off the metal surface.
- The number of electrons emitted is proportional to the temperature of the metal and inversely proportional to its work function.



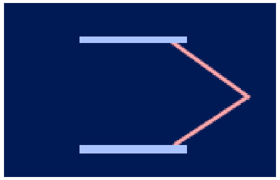
The extractor is also called the Wehnelt cylinder.

Issues

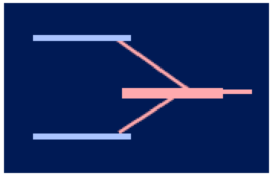
- Thermionic emission sources are not narrow-band.
- The thermal heating results in a Boltzmann distribution of emitted electron energies.
- Some filament designs require less heating and therefore result in a narrower electron energy distribution.
- There is an upper limit to the electron density due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



Hairpin filament

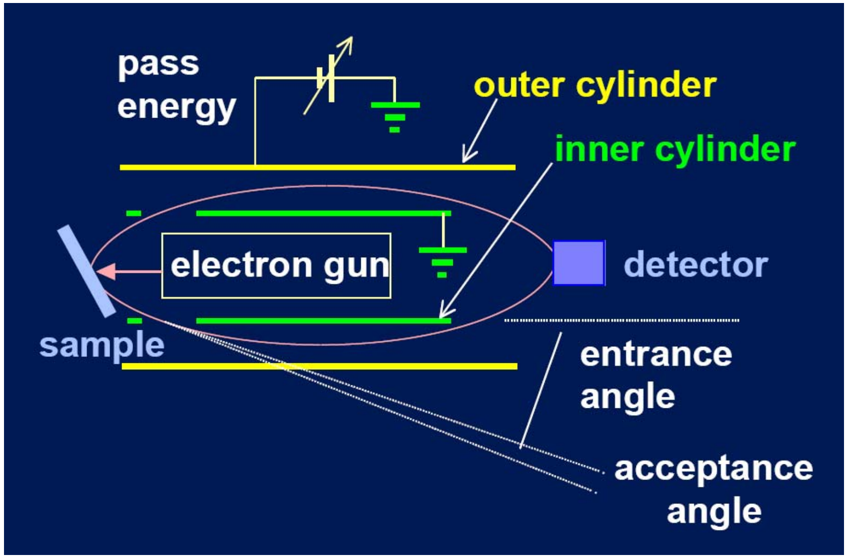


Field emitter tip



Electron Analyzers

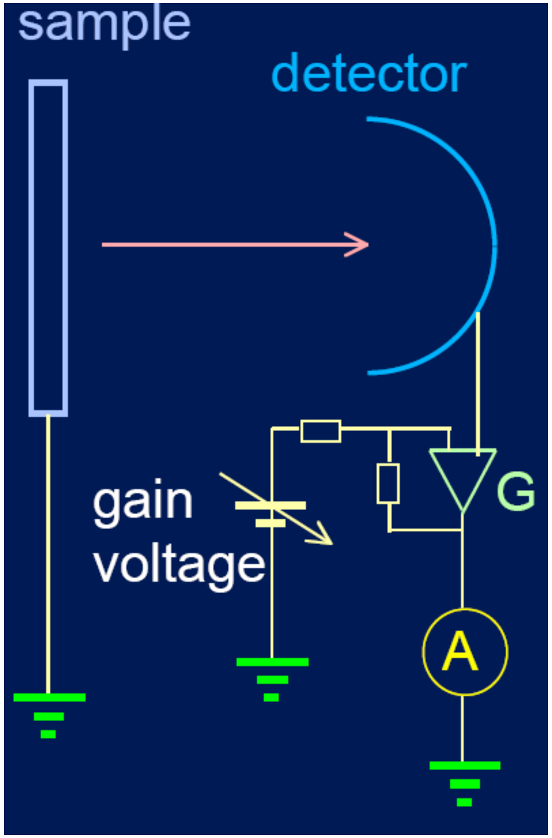
- They use electrostatic or electromagnetic fields to deflect electrons and sort them according their initial kinetic energy.
- Some types are:
  - Cylindrical Mirror Analyzer (CMA)
  - Hemispherical Sector Analyzer (HSA)
  - Retarding Field Analyzer (RFA)
  - Cylindrical Sector Analyzer (CSA)



CMA

Electron Detectors

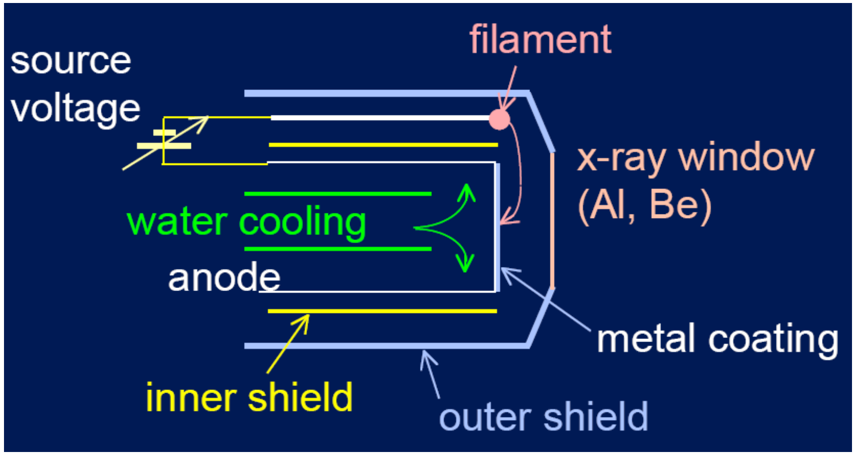
- The detector receives electrons.
- Each electron contributes to a current that is measured.
- An amplification scheme is usually incorporated.
- Some types are:
  - Electron multiplier
  - Channeltron
  - Channel plate



Basic design of an electron detector

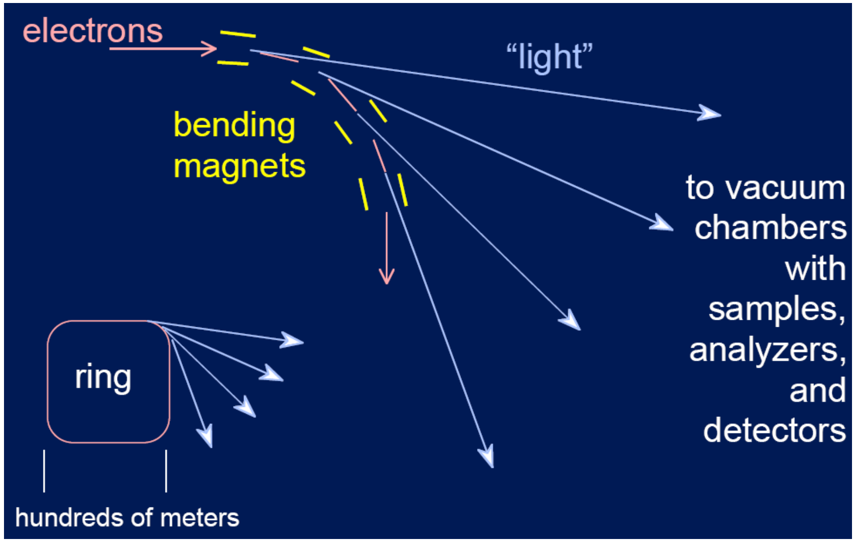
X-Ray Sources

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

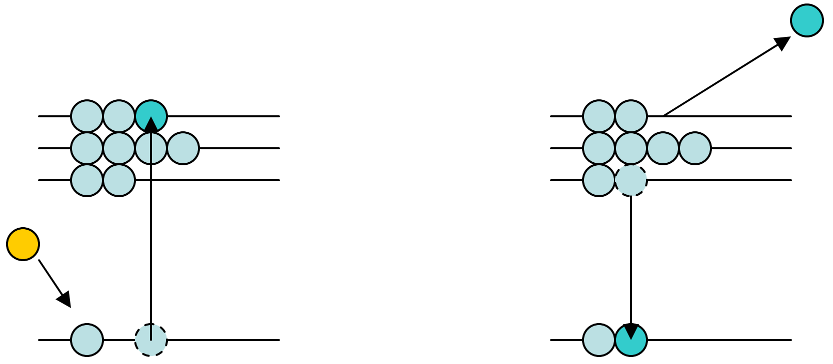
- Wavelength Dispersive
  - Use a crystal and x-ray diffraction just ;like an optical spectrometer.
  - Very sensitive and precise but expensive and slow.
- Energy Dispersive
  - Use absorption in Si or Ge , generate multiple electron-hole pairs and separate them with an applied voltage.
  - Faster and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

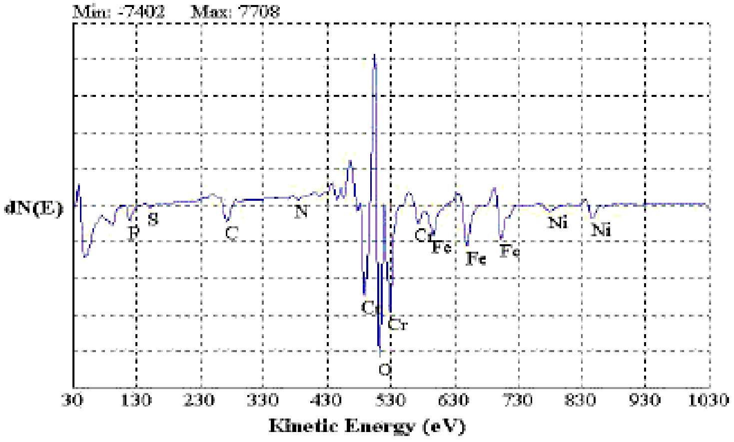
Auger Electron Spectroscopy

- Electrons with moderate energy (~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 technique used for chemical composition and defect analysis.
- Elemental sensitivity: Li – U
- Detection limit: 0.1 – 1 at. %
- Lateral resolution: 500 Ǻ
- Effective probe depth: 15 Ǻ
- Most useful for conductors but will work on most elements in the periodic table.
- Requires UHV.
- May damage the sample.



Auger electron spectrum of stainless steel.

Electron Diffraction Techniques

- Low Energy Electron Diffraction (LEED)
  - Low energy (~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 Ǻ)
- Does not damage samples like AES.
- Not as good lateral resolution (~ 0.1 mm).
- Better chemical sensitivity (chemical bonding information).

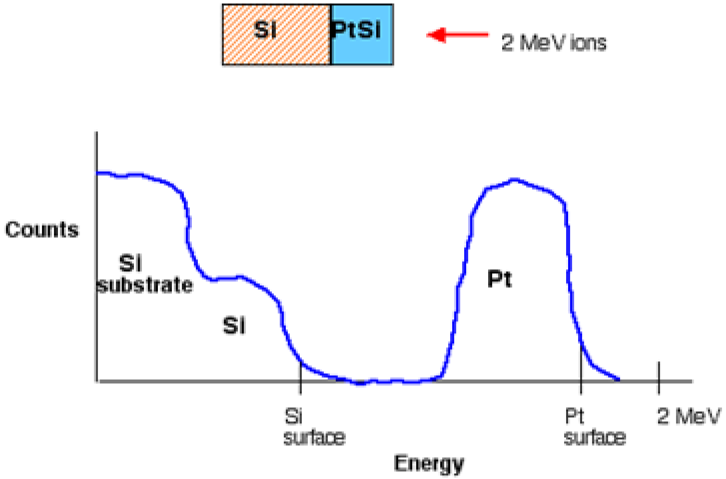
X-Ray Fluorescence Spectroscopy

- 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 (> 200 Å) resolution.
- Detection limit is ~ 1 at. %

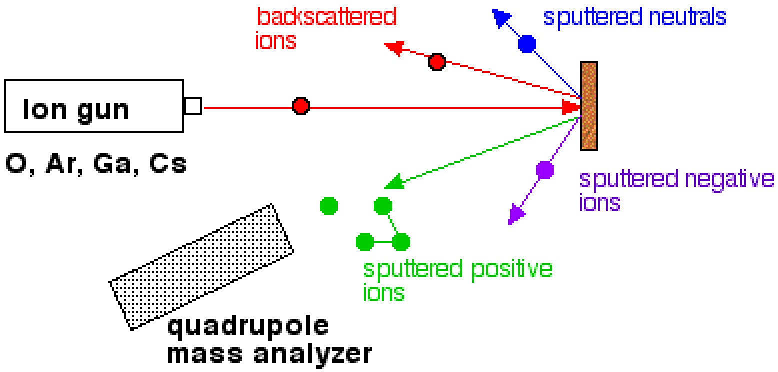
Energy of scattered ions depends on
•element (mass)
•angle
•location in solid

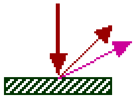
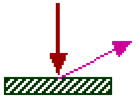
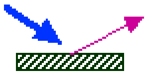
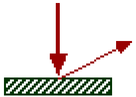
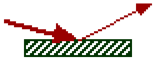
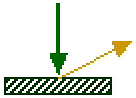


from graph:
•height --> concentration
•width --> layer thickness
•absolute energy value --> element and depth

Secondary Ion Mass Spectroscopy

- Send in ions, detect secondary ions and analyze their mass or charge-mass ratios.
- Surface sensitive technique (15 Ǻ probe depth) for chemical composition and dopant analysis.
- Very sensitive (~ 10^{-4} at. %)
- Average lateral resolution (~ 1 μm).

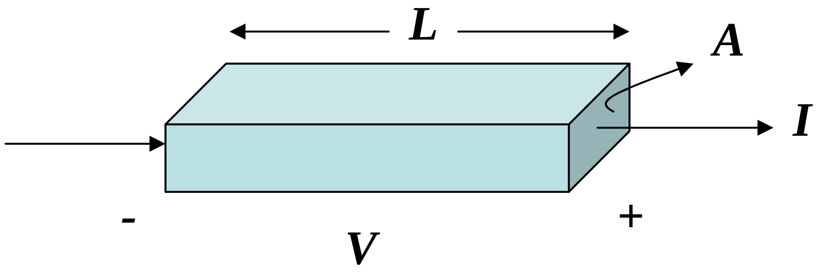


IN		DETECT	Technique
high energy electrons (30 keV)		backscattered and secondary electrons	Scanning Electron Microscopy
moderate energy electrons (5 keV)		secondary electrons	Auger Electron Spectroscopy
light (X-rays - 1 keV)		secondary electrons	X-ray Photoelectron Spectroscopy
low energy electrons (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

Electrical, Magnetic and Mechanical Measurements

Resistance Measurements

- Remember V = IR
- R (resistance) is dependent on the geometry and composition of the thin film.
- For a simple shaped object;



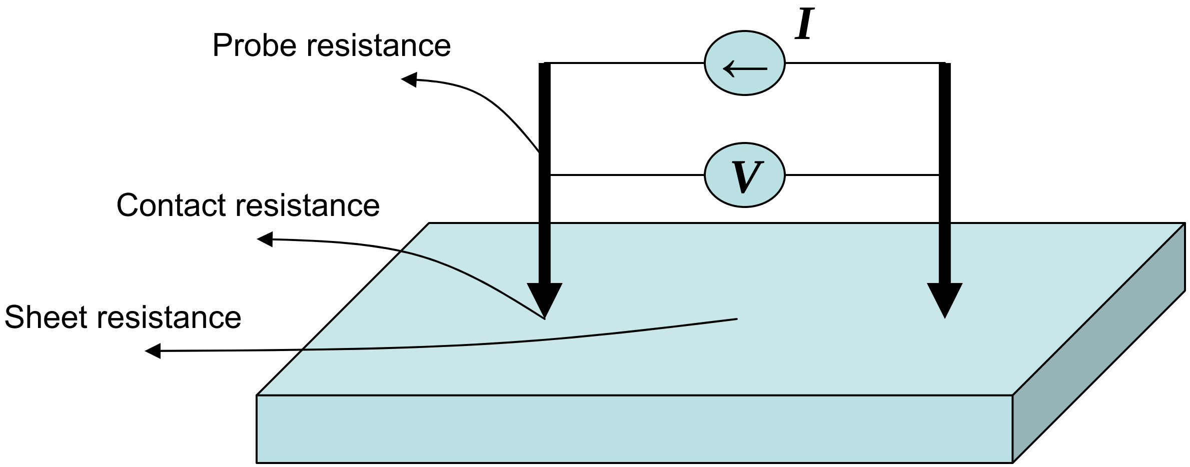
$$R \equiv \frac{V}{I}$$

$$R = \rho \frac{L}{A}$$

- The resistivity, ρ, is a constant of the material (with some dependence on temperature, pressure, etc.) and can be used to gather information on the impurity levels, etc.
- Alternatively, if the material resistivity is known, then the overall resistance can be used to calculate thickness.

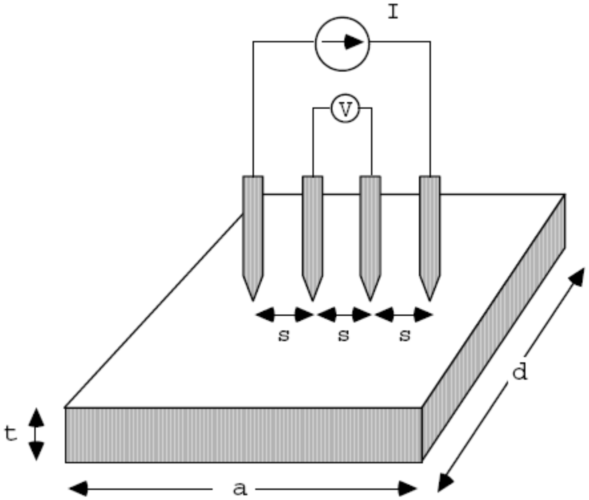
Problems With a Simple Measurement

- Normally, one would apply a current and measure the potential difference between the two ends of the film to calculate the resistance.
- However, such a measurement actually includes several extraneous effects.
- In the setup below, the probe resistance has to be low for current to flow, but this in turn distorts the voltage reading.



Four Point Probe

- By separating the current application and voltage readout the effect of the probe resistance is minimized.
- The 4-point probe has 4 Tungsten probes in a line. The outer pair is for current application and the inner pair is for voltage readout.
- One would still need to do some “modeling” to extract useful information such as the resistivity or thickness.



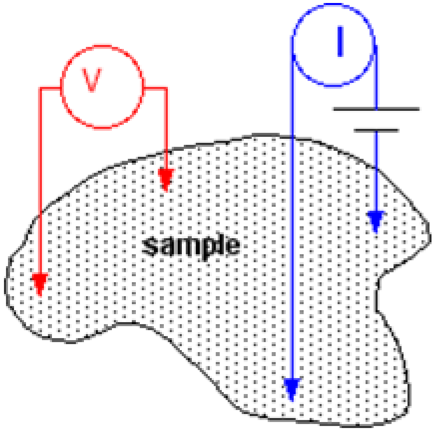
Some Limiting Cases

- For a bulk, thick layer (t > s): $\rho = 2\pi s \frac{V}{I}$
- For a thin layer (t << s): $\rho = kt \frac{V}{I}$
  - ρ: resistivity
  - k: geometric factor (= 4.53 for a semi-infinite sheet)
  - More realistically edge effects require the use of a table of factors:

$$\rho = (CF_d)(CF_t)t \frac{V}{I}$$

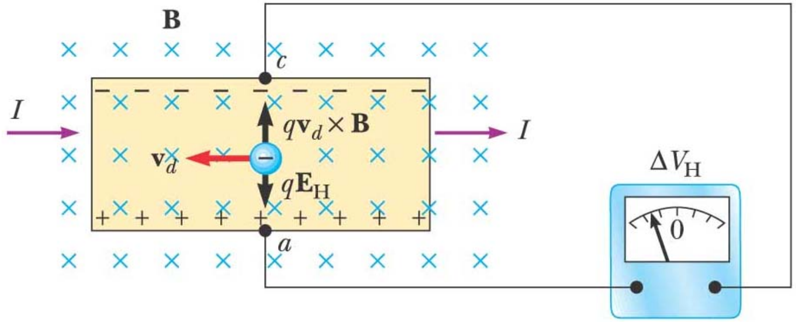
Van Der Pauw Method

- It is an alternative to the inline 4-point probe.
- The voltage and current probes can be placed arbitrarily.
- It requires two measurements (with the contact points alternated) and more post-measurement analysis.



Hall Effect

- A current is applied to the sample under a magnetic field.
- The electrons in motion are deflected by the magnetic field and start accumulating at one side of the film and therefore set up an electric field and a voltage difference.
- Information about the number of carriers, the type of carriers (electrons-holes) can be obtained.



$$V_H = -\frac{IB}{dne} = R_H \frac{IB}{d}$$

Hall voltage for a metal

Magnetic Measurements

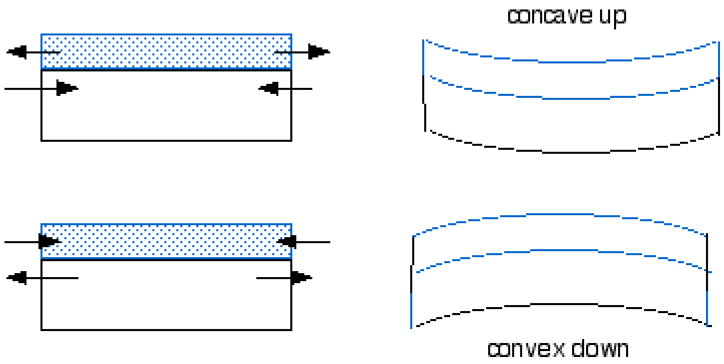
- Direct magnetic measurements using magnetometers
  - Magnetization, de-magnetization
  - SQUID magnetometers
- Magneto-optic Kerr effect
  - An applied magnetic field can cause the polarization of light passing through the film to change.
  - Can be used with ellipsometry.

Mechanical Measurements

- Internal - Residual Stress
- Indentation
- Friction and wear
- Adhesion

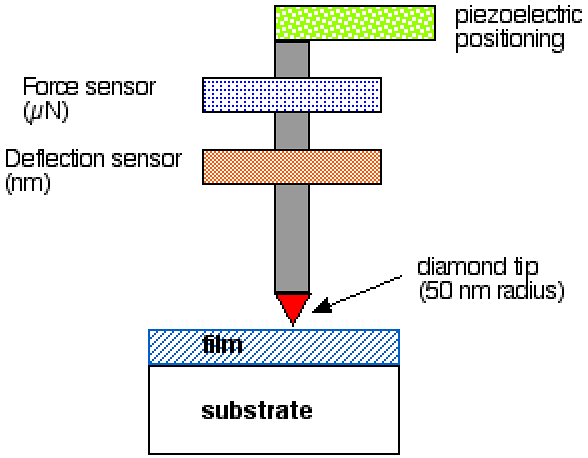
Internal and Residual Stress

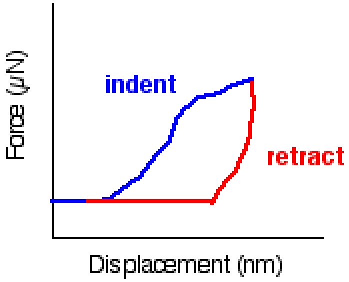
- Film is deposited on a flexible substrate
- Tensile stress (film wants to be smaller)
- Compressive stress (film wants to be larger)
- Measuring the curvature of the sample
  - Height measurements at edge and center using profilometer
  - Interferometry with a flat reference
  - Optical reflection



Micro- and Nano- indentation

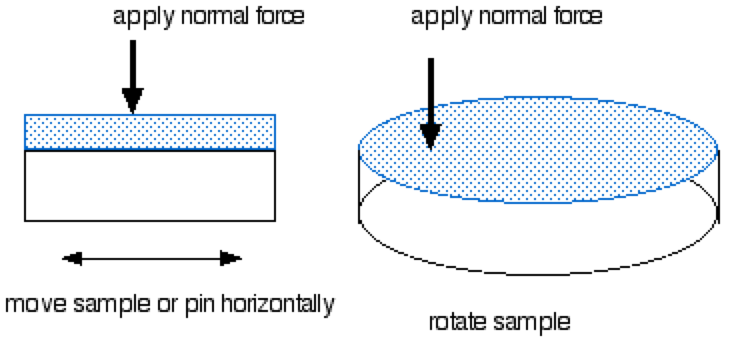
- Generate stress-strain curves
  - Apply a small force (0.3 μN) – measure a displacement on a tip (2 Å)
- Can determine hardness, elastic modulus, stress relaxation.



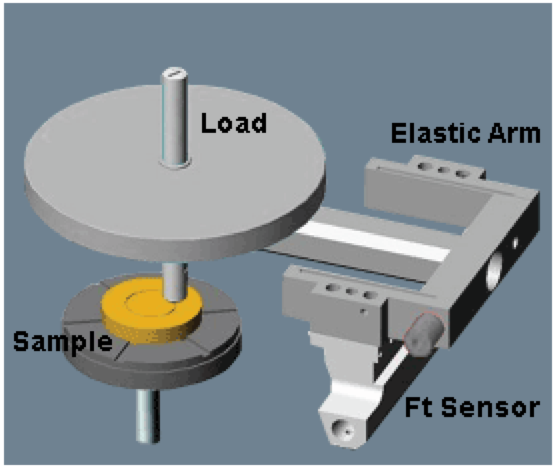


Friction and Wear Testing

$$F_{fr} = \mu F_n$$



- Use strain gauges to measure the forces, calculate the friction coefficient.



Adhesion Tests

- Adhesive tape test
  - simple, cheap, qualitative
- Scratch tests
  - drag stylus of known radius over film find minimum load on stylus needed to remove film completely