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.
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)
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
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 Å
- Effective probe depth: 15 Å
- 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 Å)
- 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 into 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 Å probe depth) for chemical composition and dopant analysis.
- Very sensitive ($\sim 10^{-4}$ at. %)
- Average lateral resolution ($\sim 1 \mu$m).
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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, $\rho$, 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):
  – \( k \): 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