Lecture 22
Ion Beam Techniques
Schroder: Chapter 11.3

Announcements

Homework 6/6:
• Will be online on later today.
• Due Wednesday June 6th at 10:00am.
• I will return it at the final exam (14th June).
• I will make the solutions available on June 6th.

Office Hours
• Next week office hours will be Monday June 4th 13:00-14:00.
Announcements

Final Exam

- The final is scheduled for Thursday June 14\textsuperscript{th} at 14:00.
- Strand Agriculture Hall 113.
- The exam will be 90 minutes long.
- More information will be provided next week.
- The next lecture with content will be Monday June 4\textsuperscript{th}.
- Wednesday June 4\textsuperscript{th} will be a review lecture.
  - I will go through some examples.
  - There will be no lecture on Friday June 6\textsuperscript{th}.
  - It will be treated as an opportunity to prepare for the exam.

Lecture 22

- Ion Spectroscopy.
- Secondary Ion Mass Spectrometry.
- Rutherford Backscattering Spectrometry.
Ion Spectroscopy

- Last time we talked about electron spectroscopy.
- The idea here is similar → we accelerate ions towards our sample.
- However ions are $>10^4 \times$ heavier than electrons.
- Hence for similar velocities, momentum will be much larger.
- These high momentum particles can remove (sputter) material from surfaces.
Ion Spectroscopy

- Consider what happens when an ion beam impinges upon a substrate:
  - Reflection
  - Absorption
  - Transmission
  - Particle-induced x-ray emission
  - Sputtering
  - SIMS
  - RBS
  - PIXE
  - Electron emission (FIB imaging)
  - SCANIIR
  - Ion implantation
  - Surface Composition Analysis by Neutral and Ion Impact Radiation

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de Broglie Wavelength

- If a particle is subjected to an accelerating voltage, the wavelength is given by the de Broglie Equation:

\[ \lambda = \frac{h}{\sqrt{2meV}} \]

- Where:
  - \( \lambda \) = Electron wavelength.
  - \( h \) = Planck Constant.
  - \( e \) = Charge on electron.
  - \( V \) = Accelerating voltage.
  - \( m \) = Rest mass of particle.
Example Wavelengths

- Some example wavelengths for some particles are given below:

<table>
<thead>
<tr>
<th>V</th>
<th>Electron</th>
<th>He Ion</th>
<th>Ga Ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 kV</td>
<td>~4 pm</td>
<td>~ 0.05</td>
<td>~ 0.01 pm</td>
</tr>
<tr>
<td>10 kV</td>
<td>~ 10 pm</td>
<td>~ 0.1 pm</td>
<td>~ 0.03 pm</td>
</tr>
</tbody>
</table>

- The heavier the particle → shorter wavelength.

Sputtering

- Sputtering occurs when ions impinge upon a sample surface and transfer enough momentum into the lattice to dislodge atoms, molecules, or ions from the near-surface region.
- Our aim is to detect these particles → say something about the surface.
- Most of the dislodged species are neutral (~99%).
- Detecting neutral species is pretty tricky, since most techniques rely on charged particles.
- Several techniques have been developed to ionize and detect neutrals species.
Sputtering

- Secondary neutral mass spectrometry (SNMS) uses a laser to ionize neutral species.
- Laser microprobe mass analysis (LAMMA) uses a laser for ablation, instead of an ion beam & analyzed via time-of-flight measurements.
- Laser microprobe mass analysis (LIMS) uses a laser for ablation, instead of an ion beam & analyzed via time-of-flight measurements.
- Sputtered species are emitted from the surface with a range of kinetic energies, with the distribution peaking at ~5-10 eV and tailing out to ~20-100 eV.

Sputtering

- Sputtering is envisaged as a collision cascade, in which primary ion hits the surface, losing momentum and energy via a series of elastic and inelastic scattering events with target atoms.
- In turn, some of the target atoms are dislodged by recoil and then displace other atoms.
Sputtering

- Recoiled atoms can leave the surface if they have sufficient energy, appropriate direction, and are located near enough to the surface.
- Argon is usually employed as the sputtering gas, since it is inert, has a large mass compared to He and Ne, and is cheap compared to Kr and Xe.
- Noble gases have filled electronic shells, and are therefore inert.

Secondary Ion Mass Spectrometry
SIMS

• Secondary ion mass spectrometry (SIMS) involves ion beam sputter removal of material from a surface and mass analysis of the ionized sputtered species.
• It is used to analyze composition of a sample as a function of depth.

SIMS

• These instruments are expensive (~$millions).
• We do not have one at OSU, but University of Oregon does have one (which we can use).
SIMS

- Ion beam energies used for SIMS analysis are usually in the range 1-30 keV.
- Smaller energies produce smaller secondary ion yields (5-15 is typical for a SIMS secondary ion yield), while larger energies result in ion implantation.

- Common sputter gases include Cs\(^+\), O\(_2\)\(^+\), O, Ar\(^+\), and Ga\(^+\).
- Cs\(^+\), which is very electropositive, is used to enhance the sputter yield of electronegative elemental constituents (e.g., F, Cl, Br, I, O, S, Se, Te, N, P, As, Sb, Bi, C, Si, Ge, Sn).
- O\(_2\)\(^+\), which is very electronegative, is used to enhance the sputter yield of electropositive elemental constituents (e.g., Li, Na, K, Rb, Cs, Be, Mg, Ca, Ba, B, Al, Ga, In).
SIMS

- SIMS is used extensively in the semiconductor industry because of its high elemental detection sensitivity ($\sim 10^{14}$-$10^{15}$ cm$^{-3}$).
- It is very useful for impurity profiling.
- SIMS requires mass analysis of the sputtered ionized species.
- A quadrupole residual gas analyzer (RGA) is used
  - Basically they are a type of mass spectrometer.

Residual Gas Analyzer (RGA)

- Gas enters residual gas analyzer from chamber.
- Hot filament generated directed electrons.
- Gas molecules are ionized when they enter RGA.
- They are then deflected by a magnetic field.
- Their mass / charge ratio is then detected.
- Relative intensities of each molecule are reported.
Quadrupole Mass Analyzer

- A quadrupole mass analyzer (QMA) is a specific type of RGA.

- A combination of AC and DC signals are applied to the cylinders.

- For a set combination of frequencies and biases, only ions of a particular mass-to-charge ratio are able to pass through a filter, to the detector.

Static SIMS

- Static-SIMS is accomplished when the beam energy and sputter duration is reduced so that only ~1% of the surface is reduced during an analysis.

- This technique is sometimes used for the characterization of sensitive materials (e.g., organics and polymers).
Time-Of-Flight SIMS

- Time-of-flight (TOF) SIMS is another way to measure sensitive materials.
- The idea here is to use pulses of ions and to monitor the time delay of the signal to the detector as a means for estimating the mass-to-charge ratio.

https://www.youtube.com/watch?v=8wxZcsNk_80

Time-Of-Flight SIMS

- We say that the potential energy \( PE \) of a charged particle:

\[
PE = qV
\]

- Where:
  - \( q \) = Charge of particle (not necessarily = \( e \)).
  - \( V \) = Voltage applied across extractor plates.
**Time-Of-Flight SIMS**

- The kinetic energy \((KE)\) is just the standard equation:

\[
KE = \frac{1}{2}mv^2
\]

- Where:
  - \(m\) = mass of charged particle.
  - \(v\) = particle velocity.
  - If the particle has to travel a distance \(L\) in a transit time \(t\), then we could say:

\[
v = \frac{L}{t}
\]

\[
KE = \frac{mL^2}{t^2}
\]

- Equating kinetic and potential energy, we can say:

\[
KE = PE = \frac{1}{2}mv^2 = qV
\]

\[
\frac{m}{q} = \frac{2Vt^2}{L^2}
\]

- Hence, by measuring the transit time for a known applied voltage and length, we can evaluate the mass to charge ratio.
Time-Of-Flight SIMS

- The advantage of TOF SIMS is that it circumvents having to use very narrow slits to the input of the mass detector in order to filter the input mass-to-charge ratio.
- Using larger slits results in much more ion current to the detector.
- Normal SIMS is sometimes designated as dynamic-SIMS to distinguish it from static-SIMS.
- Higher elemental sensitivity requires removal of more material.

ToF SIMS Data

- SIMS experiments produce a lot of data:
  - Number of counts of particular ion.
  - As a function of sputter time.
  - For each ion.
  - Not just atoms but molecules.
ToF SIMS Data

- SIMS experiments produce a lot of data:
  - Number of counts of particular ion.
  - As a function of sputter time.
  - For each ion.
  - Not just atoms but molecules.
  - As a function of position.
  - File sizes can be many GB.

Rutherford Backscattering Spectrometry
RBS

- **Rutherford Backscattering Spectrometry** (RBS) is also sometimes known as high-energy ion back scattering spectrometry (HEIS).

- RBS involves elastic backscattering of high-energy (~1-3 MeV) inert ions [usually He\(^{+2}\) (alpha particles)] from a sample.

- It allows determination of:
  - Mass of elements in a sample.
  - Their depth distribution.
  - Their areal density.
  - Their crystalline structure.

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RBS

- Ions of mass \(m_1\), energy \(E_0\), and velocity \(v_0\) are incident on a solid sample.

- The target sample is comprised of atoms of mass \(m_2\).

- Most of the incident ions are come to rest within the solid, losing their energy through interactions with valence electrons.
• A small fraction (around $10^{-6}$) undergo elastic collisions and are backscattered at various angles.
• After the scattering event, the atom with mass $m_2$ has an energy $E_2$ and a velocity $v_2$.
• The ion is left with energy $E_1$ and velocity $v_1$.

If we define the angles $\phi$ and $\theta$ as above, then we can define the kinematic factor ($K$) as the ratio of the energy of the ion after the scattering event to the energy after the scattering event:

$$K = \frac{E_1}{E_0} = \left[ \frac{\sqrt{1 - (R \sin \theta)^2} + R \cos \theta}{1 + R} \right]^2$$

$$R = \frac{m_1}{m_2}$$
RBS

- This equation tells us that if we can measure $K$ (or equivalently $E_1$ for a known accelerating voltage $E_0$) we can determine the mass of the atom in the target.
- RBS spectra are obtained by plotting the number of counts, or the yield, as a function of the backscattering energy.
- Heavier atoms have a higher yield and are located at a larger backscattering energy.
- The width of an RBS feature is related to its thickness.

### RBS Example

**TABLE 11.2** Calculated $R$, $K$, and $E_1$ (For 2.5 MeV He ions, $\theta = 170^\circ$).

<table>
<thead>
<tr>
<th>Target Atom ($M_z$)</th>
<th>Atomic Weight</th>
<th>$R$</th>
<th>$K$</th>
<th>$E_1$ (MeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>14</td>
<td>0.256</td>
<td>0.311</td>
<td>0.78</td>
</tr>
<tr>
<td>O</td>
<td>16</td>
<td>0.25</td>
<td>0.363</td>
<td>0.91</td>
</tr>
<tr>
<td>Si</td>
<td>28.1</td>
<td>0.142</td>
<td>0.566</td>
<td>1.41</td>
</tr>
<tr>
<td>Cu</td>
<td>63.6</td>
<td>0.063</td>
<td>0.779</td>
<td>1.95</td>
</tr>
<tr>
<td>Ag</td>
<td>107.9</td>
<td>0.037</td>
<td>0.863</td>
<td>2.16</td>
</tr>
<tr>
<td>Au</td>
<td>197</td>
<td>0.020</td>
<td>0.923</td>
<td>2.31</td>
</tr>
</tbody>
</table>

![Schroder p662](image-url)
RBS Example

- crystalline Si
- amorphous Si
- 2 MeV He
- random alignment
- aligned with axis
- amorphous
- mass-dependent
- depth-dependent
- heavy substitutional impurity

RBS Real Example

- Si Backscattering Yield (C/s)
- Pt Backscattering Yield (C/s)
- Energy (MeV)
- No Anneal
- 400°C, 10 min
- 450°C, 20 min
- 300°C, 20 min
- Schroeder p664
RBS

- RBS provides atomic composition and depth information and has a detection limit of $\sim 10^{17}$-$10^{20}$ cm$^{-3}$.
- The He$^{2+}$ penetration depth is on the order of microns.
- A 200 nm film has an RBS depth resolution of $\sim 10$-20 nm.
- High-Z elements are more difficult to distinguish from one another than low-Z elements.
- RBS works best for high-Z elements on a low-Z background.

Sample Thickness

- The thickness of a film, $d$, may be estimated from its measured RBS backscattering energy width, $\Delta E$:
  \[
  d = \frac{\Delta E}{[S_0]}
  \]
- $[S_0]$ is the backscattering energy loss factor.
  - It has units of eV/Å and is tabulated for pure elements at certain energies.
  - For example: $[S_0] = 133.6$ eV/Å for gold films with a 2 MeV beam energy.
Sample Thickness

• The RBS backscattering energy width, $\Delta E$ is defined as:

$$\Delta E = \Delta E_{\text{in}} K + \Delta E_{\text{out}}$$

• $\Delta E_{\text{in}}$ is the loss of energy of the ion due to traversing the film before the scattering event.
• $\Delta E_{\text{out}}$ is the loss of energy of the ion due to traversing the film after the scattering event.
• $K = E_1/E_0$ as before.

RBS

• Interpretation of an RBS spectrum is not always straight-forward since the backscattering energy axis is both a depth and a mass scale.
• For example, a low-Z surface atom and a high-Z bulk atom could make similar contributions to an RBS spectrum.
• These sorts of ambiguities may be resolved by changing the beam or detector angles or the incident energy.
SIMS vs RBS

- Both techniques have advantages and disadvantages.

**SIMS**
- **Advantages:**
  - Extremely sensitive.
  - Can detect H.
  - Can give isotope information.
  - Very fast.
- **Disadvantages:**
  - Difficult to quantify.

**RBS**
- **Advantages:**
  - Non-destructive.
  - Can provide absolute quantities.
- **Disadvantages:**
  - Poor depth resolution.
  - Interpretation can be complex.

Next Time...

- X-Ray & UV Techniques.
  - XPS & UPS.

- KE = 0
- \( q \times s \phi_s \) IP
- \( E_C \)
- \( E_F \)
- \( E_V \)
- KE\text{max}