Sample preparation

Conditions for SEM:
- Solid material
- Low vapor pressure (vacuum!)
- Conductive surface / material

In addition, for EMP analyses:
- Flat surface, well polished (1 μm or better)

Electron Microprobe Samples

Petrographic thin sections
...or polished sections

Use mounting epoxy with low vapor pressure*
- Buehler Epoxide, Epo-thin
- Petroxy 154
- Struers EpoFix

Important to polish surface flat (minimum relief)
- Flatness generally achieved with diamond polishing on low-nap cloths

Eliminate visible scratches and pits if possible
- High polish: 0.3-0.05 μm
- Generally finish with alumina – low nap
- Can use colloidal silica polishing (chemical-mechanical)
  ➔ Essential for EBSD or any other nano-surface analysis

* Should not release too much vapor/gas under vacuum ≠ volatile
Electron Microprobe Samples

Thick specimens
Generally encapsulated in low vapor pressure, hard-curing epoxy
- Buehler Epo-Thin
- Struers EpoFix, SpeciFix
- Can use conductive fillers (e.g., Cu, C, Ag, or Ni; micron-size particles)
- Cut & polished as above
- Porous materials can be vacuum-impregnated with low-viscosity epoxy

DO NOT use stained thin section in EMP/SEM:
If scanning at high current on stained epoxy, stain will volatilize and coat parts of the EMP/SEM notably crystals, mirrors...

⇒ EXPENSIVE repair!

Grain mounts
Potting - Casting ceramics
Micro-drill, press fit, and Ni-epoxy

BSE images
SE image
Cleaning:
After polishing and before coating, all samples should be as clean and dry as possible

1) 2-stage ultrasonic cleaning in clean water followed by isopropyl alcohol preferable

2) Quick acetone rinse (acetone may dissolve epoxy!!!)

3) Final rinse in methanol, be sure there is no residue (use lint-free cloth, such as "Kimwipes")

4) Dry in oven, on hot plate, or in vacuum

Most geologic materials are INSULATORS

- Valence band full or nearly full
- Wide band gap with empty conduction band
- Essentially no available energy states to which electron energies can be increased

Electron beam will "pile-up" electrons at surface of insulator, building potential

Dielectric breakdown at high potential
Charging

- Deflects electron beam
- Can lead to extreme emission of secondary electrons and “bursts” of electrons
- Can be reduced at lower accelerating voltage

Charging can cause (strong) image distortion!
Charging can cause (strong) image distortion! (cont’d)

Mystery grain, possibly amphibole (courtesy C. Condit)
**Special case:** charging an insulator to create… an "electron mirror"

**Explanation: electron mirror effect…**

"Normal" case: secondary electrons produced from the surface of the sample

Electron mirror effect: an insulator (sample) is charged; incoming primary electrons are reflected, and the **specimen chamber** is actually scanned.
**Sample voltage calculation…**

**Current balance:**  
\[ i_{\text{beam}} = i_{\text{backscattered electron}} + i_{\text{secondary electron}} + i_{\text{sample current}} = i_{\text{BSE}} + i_{\text{SE}} + i_{\text{SC}} \]

**Resistance:**  
\[ R = \frac{\rho}{A} \]

**Sample voltage:**  
\[ V_{\text{sample}} = i_{\text{SC}} = \frac{\rho}{i_{\text{SC}}} \]

\[ \rho = \text{resistivity in ohm}\cdot\text{cm} \]

\[ l = \text{sample length (cm)} \]

\[ A = \text{cross section (cm}^2) \]

For 1 cm long sample with 1 cm\(^2\) cross section, with beam current 1 nA (= 10\(^{-9}\) A), and assuming sample current is \(~60\%\) of total beam current (\(i_{\text{SC}} \approx 0.6 \times i_{\text{B}}\)):

- **Conductor (metal)**  
  \[ \rho \approx 10^{-6} \text{ ohm}\cdot\text{cm} \]  
  \[ V_{\text{sample}} \approx 10^{-15} \text{ V} \]

- **Semi-conductor (e.g. Si, Ge)**  
  \[ \rho \approx 10^{6} \text{ ohm}\cdot\text{cm} \]  
  \[ V_{\text{sample}} \approx 1 \text{ mV (10^{-3} V)} \]

- **Insulator (e.g. oxide)**  
  \[ \rho \approx 10^{12} \text{ ohm}\cdot\text{cm} \]  
  \[ V_{\text{sample}} \approx 1000 \text{ V or more!} \]

Although not fully understood, charging effect vary over time with sudden discharge and recharge period…

Because of this dynamic behavior, a fast sample scanning might be less affected by charging effect compared to a slow scan…

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**Charging and the Duane-Hunt limit**

The Duane-Hunt limit describes the maximum X-ray energy (or frequency) = maximum voltage of the primary electron.

- When sample is positively charged (electron are accelerated), this limit will be higher.
- When sample is negatively charged (electron are decelerated), this limit is lowered.
- When negative charging occurs X-ray peaks intensity will be diminished.

The difference between the Duane-Hunt limit of grounded vs. charged sample is equal to the potential on the charged sample (here \(~350 \text{ V}\)).
How to avoid charging?

1) Coating sample with conductive material
Deposition of a thin conductive film (1-20 nm). Among various materials, Carbon and gold are the most commonly used. Two main deposition methods:
- Evaporation (heat material up to vaporization temperature under high vacuum)
- Sputtering (bombard negatively charged material with ions under low vacuum)

Each coating medium has a specific granularity. Pictures width ~1μm

<table>
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<th>Material</th>
<th>Symbol</th>
<th>Thermal conductivity at 300 K (W/cm.K)</th>
<th>Melting point (K)</th>
<th>Boiling point (K)</th>
<th>Vaporization temperature at 1.3 Pa (K)</th>
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<td>* Aluminum</td>
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</table>

* Common coating
Readily oxidizes

** "new" coating material for ultrahigh resolution FE-SEM or -EMP

Finest granularity = high \( T_{\text{melting}} \) metals
How to avoid charging?

2) Use a low vacuum SEM (= Environmental SEM or variable pressure SEM)
In presence of some pressure (conductive “air”) and without coating, charging
can be dissipated. However this option will also (strongly) reduce signals such
as X-rays, which will be absorbed by particles in the low vacuum environment.

WARNING! Pressure should still remain low (~10-20 Pa = 0.1-0.2 mbar) to avoid
beam deflection (e.g., skirt effect) that would cause imaging and analytical
problem… More on this with lecture about variable pressure SEM / EBSD.

Effect of coating on absorbed current

Ideally, sample current (or absorbed current) should remain constant, indicating
of the absence of charging or beam damage. Monitoring the sample current
gives indication about the coating. Changing the beam diameter will affect the
value, as energy is dissipated over a larger area (volume).
Goals of coating: Improve conductivity and emissivity (for SEM)

Conductors:
• Conduction bands and valence bands overlap → no coating required
• Easy to energize electrons to the continuum = secondary electrons

Other:
• For biological specimens, can load metals into surface
• For most samples, especially geological material (insulator), coating is required
• For quantitative analyses, coating on sample AND standard should be the same (more on this later...), even if standard is a conductor...

Coating techniques:
Thermal evaporation*
Many metals and some inorganic insulators evaporate to monatomic state when heated in a vacuum.
Requires high vacuum (10^{-3} to 10^{-5} Pa), although in some case lower vacuum can be acceptable (e.g., carbon at ~1 Pa). Chamber usually flushed with inert gas (N_{2}, Ar).

How to heat:
• Resistive heating: current used to heat support or unsupported C rods
• Electric arc method: Arc between two conductors, conductor surface evaporates
• Electron beam evaporation: Evaporant is anode target, heated by 2-3 keV cathode

* Also possible, sputtering method, not review here
High vacuum evaporation
(10⁻³ to 10⁻⁷ torr = 10⁻³ to 10⁻⁵ Pa)

1) Atoms arrives on substrate
2) Migrate, Re-evaporate, collide
3) Form islands
4) Islands grow and coalesce

Choice of evaporant: some considerations...

Most SEM/EMP work: want coat as thin as possible, small emission range, faithful reproduction of surface features, and good conductivity (5-10nm or smaller for FE-SEM): \( \text{Au, Au-Pd, Pt, Pt-C} \)

“Wetting” Pre-coat can help nucleation density

\( \text{Au}_{60}\text{Pd}_{40} \) Less granularity

Pt-C Good wetting but not great conductivity

C Best for X-ray analysis (5-50nm thickness)
- Low absorption
- Does not emit X-rays in energy range of general interest
- Added to another coating reduces risk of recrystallization or minimize oxidation (e.g. C-coating on Al-coating)

Heat Evaporant requiring high-T can damage sample (biological material!)

X-ray Avoid X-ray interferences from evaporant, minimize absorption, and evaporant should not be an element to be analyzed

Price Some coating material can be VERY expensive (Au, Pt, Os, Ir…)

Rotation Rotating (and tilting) can ensure homogeneous coating
Bad coating, beam damage or contamination?

Too thin: surface charging
- Background distortion
- Bright raster lines
- Bright banding on surface
- Bright areas (surface, cavities)
- Dark areas on surface
- Dark halo around bright sample
- Whole image distorted / shifted
- Image movement
- Decrease in Duane-Hunt limit

Too thin: beam damage
- Growing bubbles on surface
- Cracks on surface
- Small holes on surface
- Growing holes on surface
- Surface shriveling
- Surface movement

Surface charging OR beam damage
- Gradual decrease in a selected X-ray spectrum

Surface charging OR surface contamination
- Raster square remains of surface
- Dark and bright raster squares

Contaminated coater
- Speckled surface

Too much coating
- Particles on sample surface
- Increased particle dimensions
- Obscured surface detail
- Large surface cracks

Incorrect coating
- Surface crazing (fine network of cracks), etching

Thermal damage during coating
- Surface melting
- Chemical alteration of surface (diffusion)

Measuring thickness

During coating:
1) Mass sensing device to determine weight of deposit (change in oscillating frequency of quartz crystal – actively cooled)
2) Measure light absorption
   - Transmittance
   - Reflectance
   - Color change on polished brass
3) Measure resistance across glass slide
4) Carbon coating: appearance of fingerprint on piece of paper (~15-20 nm)

After coating:
1) Optical techniques
2) Gravimetric measurements
3) X-ray absorption and emission
4) Multiple beam interferometry (very precise)
Measuring thickness

Fingerprint on paper

Use a clean white paper and leaves your fingerprint on its edge. Carbon will stick on the paper, but not on the oily mark left by your finger.

Carbon coating is reaching ~15-20 nm when your fingerprint appears on the paper.

!!! Use powder-free glove when handling samples !!!