Chemical Analysis in SEM/TEM

Marc Willinger
Outline

• SEM:
  – components of the SEM
  – signals and their information content
  – Focused Ion Beam/SEM

• TEM

• Examples
Merely because one says something might be so, it does not follow that it has been proved that it is.

(Newton in conversation with Hooke, concerning Hooke's claim to have discovered the inverse square law of gravitation before him)
Observations in a Microscope can be Unpleasant

Abb. 1. »Thames Water«, Stich von William Heath um 1828.
1897: discovered “corpuscles”, small particles with a charge/mass ratio more than 1000 times greater than that of protons, swarming in a sea of positive charge (“plum pudding model”).

=> Discovery of the ELECTRON

Plum pudding model (1904)
De Broglies doctoral thesis (1924):

Application of the idea of particle – wave dualism (only known for photons up to then) for any kind of matter.

=> Matter Waves

$$\lambda = \frac{h}{p} = \frac{h}{mv}$$

Louis-Victor Pierre Raymond de Broglie
(1892 - 1987)
Nobel prize: 1929
Nachweis: Elektron = Welle


Sir George Paget Thomson  
(1892 – 1975)  
Nobel Prize: 1937  
(shared with C.J. Davison)
Why electrons?

Smallest visible objects...

- with eye: 0.1 mm = 10^{-4} m
  (size of one eye «"stick"»)

- with light microscope ~ 300nm
  (magnification max ~ 2000x)

Can we simply magnify the image of an object to observe every detail?

Rayleigh criterion (1869):

\[
\delta = \frac{0.61 \lambda}{n \sin \beta}
\]

\(\lambda\): wavelength of the radiation,
\(n\): refractive index of the viewing medium
\(\beta\): semi-angle of collection of the magnifying lens.
The interaction of waves with an obstacle:

The boat rides the long wavelength ocean wave, but reflects the small wavelength surface ripple. An observer who wishes to detect the presence of the boat can do so only by observing waves which have wavelengths smaller than, or comparable to, the length of the boat. (From Sherwood, p.19)
Components of the SEM

- Electron Gun
- Microscope column
- Specimen Chamber
- Operator Console
- EDX detector
- SE detector

Diagram of a SEM (Scanning Electron Microscope) showing the various components.
Principle

Electron gun

Detector

256 electrons!
Components of the SEM

Components of the SEM

Deflection Coils

- **a)** $I_1 > I_2$
- **b)** $I_1 < I_2$
- **c)** $I_1 = I_2$

- **Stigmators**
  - Provide means to correct for deficiencies in the magnetic lenses
  - **EM stigmators**:
    - At condenser, objective and diffraction lens (TEM)
    - At condenser, objective (SEM)
    - Close to the lenses
Interaction of high energy (~kV) electrons with (solid) materials—III

- **Auger Electrons (AES)**: 0.5 ~ 5.0 nm
- **Secondary Electrons (SEM)**
- **Backscattered Electrons (SEM)**
- **Characteristic X-rays and Bremsstrahlung**

**Basic electron optics**

- Electrons and ions are charged particles, they can be accelerated in an *E* field.
- The trajectory of an accelerated charged particle can be deflected by *E* and/or *B* field.
- According to de Broglie, the accelerated (high-energy) particles also behave like waves.

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Signals and their Information Content

- SE1 - at point of primary interaction
- SE2 - away from initial interaction point
- SE3 - by BSE outside of sample
- BSE1 - at point of primary interaction
- BSE2 - away from initial interaction point

Electron yield as a function of the energy of the emitted electron

• SE:  less than 50 eV of kinetic energy originate from a very shallow region at the sample surface
  → good for high resolution
  → topographic information

• BSE: back scattered primary electrons (from the beam) due to elastic collision with nuclei of sample atoms
  → high energy
  → larger interaction volume
  → contrast related to average atomic number

• EDX, Cathodoluminescence, EBSD, …
Everhart-Thornley SE detector

- Secondary Electrons
- Photons
- Backscattered Electrons

10kV

Scintillator

Photomultiplier

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Combined SE/BSE Detector

SE: a positive collector voltage (ca. +200 to +400V) attracts SE toward the detector, where a 10kV post acceleration gives them enough energy to create a bunch of photons for each SE.

BSE: a negative collector polarisation (ca. -100V) repels SE and the only (fast) BSE emitted in the narrow cone to the scintillator are detected.
BSE Detector

Secondary electron detector: (Everhart-Thornley)

Backscattered electron detector: (Solid-State Detector)
Interaction volume / Information Depth

- Kanaya-Okayama Depth Penetration

\[
R = \frac{0.89}{(Z U^2)} 0.0276 A E
\]

Where:
- \( R \) = Depth Penetration
- \( A \) = Atomic Weight (g/mole)
- \( E \) = Beam Energy (KV)
- \( Z \) = Atomic number
- \( U \) = density (g/cm\(^2\))

The effect of accelerating voltage on depth penetration:

- 30KV
- 15KV
- 5KV
- 1KV
- 0.5KV

Depth Penetration in Iron:
- 3.1 \( \mu \)m (30KV)
- 0.99 \( \mu \)m (15KV)
- 0.16 \( \mu \)m (5KV)
- 0.01 \( \mu \)m (1KV)
- 35 A (0.5KV)

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Simulate the electron trajectories in a solid constituted of 25 nm thick Ti film on a GaAlAs substrate

- 200 electron trajectories are displayed
- Incident energy varies from 5 to 30 keV
- Red trajectories represent electrons that are backscattered
- Blue trajectories represent electrons that are absorbed

The generation of secondary electrons is not taken into account!

http://www.gel.usherbrooke.ca/casino/download2.html
CASINO : "monte CArlo SImulation of electroN trajectory in sOlids"
Change in SE contrast with the voltage

(from L. Reimer, Image formation in the low-voltage SEM)
SE versus BSE

SEM analysis of a catalyst for the partial oxidation of methane on Pt
To consider in a SEM session:

• Which signals can I use for my sample?
  – characteristic X-rays,
  – backscattered electrons,
  – secondary electrons,
  – cathodoluminescence,…

• Which acceleration voltage should I use?
  – information depth

• Which working distance is best?
  – resolution
The picture element is the size of the area on the specimen from which the signal is collected. The table below gives the linear dimension of these pixels at various magnifications.

For a given choice of magnification, images are considered to be in sharpest focus if the signal that is measured when the beam is addressed to a given picture element comes only from that picture element. The probe diameter can be one of the contributing factors in determining the dimensions of the area on the specimen from which the signal is generated. As magnification increases and pixel dimensions decrease, overlap of adjacent pixels will eventually occur. What is surprising is that the overlap starts occurring at very low magnifications in the 5-30 kV range. For example, a 10 keV beam with a spot size of 50 nm focused on a flat surface of Aluminum will show overlap at 100 x magnification! Gold under the same circumstances will show overlap at 1000 x magnification! We will address the consequences of this later.

<table>
<thead>
<tr>
<th>Magnification</th>
<th>Area on Sample</th>
<th>Edge Dimension of Picture Element</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1 cm²</td>
<td>10 µm</td>
</tr>
<tr>
<td>100</td>
<td>1 mm²</td>
<td>1 µm</td>
</tr>
<tr>
<td>1,000</td>
<td>100 µm²</td>
<td>100 nm</td>
</tr>
<tr>
<td>10,000</td>
<td>10 µm²</td>
<td>10 nm</td>
</tr>
<tr>
<td>100,000</td>
<td>1 µm²</td>
<td>1 nm</td>
</tr>
</tbody>
</table>

Objective aperture size:
The objective apertures on all four FEGS EMS have a range of sizes that can be selected. Decreasing the diameter of the aperture will:
- Decrease lens aberrations and thus increase resolution.
- Decrease the probe current.
- Decrease the convergence angle of the beam and thus increase depth of focus.

The drawing below shows the larger aperture setup above with a greatly increased working distance. The result is an increased depth of focus but reduced resolving capabilities.

We mentioned earlier that manufacturers utilize apertures of a diameter that are a compromise of reducing spherical aberration and diffraction effects. Thus for the most part as an operator you will not be altering the size of the column apertures (there will be exceptions). But there is another way to increase depth of focus….working distance.

Working distance:
The working distance is adjustable on all four FEGSEMs (the Hitachi S-900 has a very small range given its in-lens design). Increasing the working distance will:
- Increase depth of focus.
- Increase probe size and thus decrease resolution.
- Increase the effects of stray magnetic fields and thus decrease resolution.
- Increase aberrations due to the need for a weaker lens to focus.

The images below reveal the effects of aperture diameter and working distance on resolution and depth of focus. Left [3]: light bulb coil with a 600 µm aperture and 10 mm WD. Middle [3]: 200 µm aperture and 10 mm WD. Right [3]: 200 µm aperture and 38 mm WD.
Atom columns align with the ion trajectory = higher penetration

\[ \Rightarrow \] less SE electrons
Electron Channelling Contrast

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Effects of Morphology

David Muller 2008
Effects of Morphology

Increasing the detector bias will wash out the shadows.
Effects of Morphology

What Is "Reality" in the SEM?

David Muller 2008
Effects of Morphology

Previous image turned upside down.
We need to know where the detector is to tell bumps from pits!

David Muller 2008
Effects of Morphology

Why Edges appear brighter

David Muller 2008
One Primary Electron In Can Create Several SEs Out at Low Accelerating Voltages

Secondary Electron Yield Coefficient

$$\delta = \frac{SE_{out}}{PE_{in}}$$
Electron Yield $\delta = \# \text{SE out} / \# \text{e- in}$

Sample charges +ve (increases landing energy Of incident electrons)

Sample charges –ve (reduces landing energy Of incident electrons)
Contrast reversal in SE mode close to the neutrality point

$\text{SiO}_2$-$\text{Cr}$ mask for TEG-FET transistors production

$\text{SiO}_2$ ($E_2 \sim 3.0\text{keV}$)  $\text{Cr}$ ($E_2 \sim 1.8\text{keV}$)

Cliché Kontron (Kuschek) pour CIME

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Sample - Electron Interactions

- Cathodoluminescence (visible light)
- Bremsstrahlung
- Characteristic x-rays
- Auger electrons
- Secondary electrons
- Backscattered electrons
- Elastically scattered electrons
- Heat
- Transmitted beam to energy-loss spectrometer
- Angle-limiting aperture
Energy Dispersive X-Ray Spectroscopy (EDX)

Fluorescence Yield ($\omega$):
$\omega = \# \text{X-ray photons produced} / \# \text{shell ionizations}$
Outline

• **SEM:**
  – components of the SEM
  – signals and their information content
  – Focused Ion Beam/SEM

• **TEM**

• **Examples**
FIB: Focused Ion Beam

- 
  a complete state of the art (high-performance) SEM equipped with
  a) focused ion column
  b) Gas injector system
  c) micromanipulators

Dual beam ®, crossbeam ®
Preparing for slicing

the end

Automated milling and imaging of 170 slices (10h)
One of the biggest challenge in Life Science

\[ \approx 1'000'000'000 \text{ neurons} \]

\[ \approx 10'000'000'000 \text{ connections} \]
THE STACK

2048 x 1536 x 1600 8 x 6 x 8 um voxel: 5x5x6nm

2 days of fully automated acquisition
Reconstruction...
Preparation of TEM Lamella

https://www.youtube.com/watch?v=MadIrIGMhDw

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM HV:</td>
<td>10.0 kV</td>
</tr>
<tr>
<td>WD:</td>
<td>60.00 mm</td>
</tr>
<tr>
<td>View field:</td>
<td>36.9 mm</td>
</tr>
<tr>
<td>Det:</td>
<td>SE</td>
</tr>
<tr>
<td>LYRA3 TESCAN</td>
<td></td>
</tr>
<tr>
<td>Scale:</td>
<td>10 mm</td>
</tr>
</tbody>
</table>
• Set-up of a TEM
  – Electron Gun, Coherency, Lenses

• Basic Interactions
  – Elastic: imaging
    • Demo: Interference, Lattice Fringes, FFT
  – Inelastic: EDX and EELS

• Chemical Information
Ernst Ruska

Nobel Prize in Physics in 1986
Ernst Ruska, Gerd Binnig, Heinrich Rohrer
Basic set-up of the TEM

The electron gun produces a beam of monochromatic (coherent) electrons!!

a field-emission source: extraordinarily fine W needle
Basic set-up of the TEM

High voltage accelerates the electrons to high kinetic energy.

<table>
<thead>
<tr>
<th>$E$ (kV)</th>
<th>$\gamma$</th>
<th>$\lambda$ (nm)</th>
<th>$\frac{v}{c}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>1.098</td>
<td>5.362</td>
<td>0.412</td>
</tr>
<tr>
<td>100</td>
<td>1.119</td>
<td>3.706</td>
<td>0.548</td>
</tr>
<tr>
<td>200</td>
<td>1.391</td>
<td>2.511</td>
<td>0.695</td>
</tr>
<tr>
<td>500</td>
<td>1.978</td>
<td>1.423</td>
<td>0.862</td>
</tr>
<tr>
<td>1000</td>
<td>2.957</td>
<td>0.873</td>
<td>0.941</td>
</tr>
</tbody>
</table>

$$\delta = \frac{0.61\lambda}{n \sin \beta}$$

Rayleigh criterion!
Basic set-up of the TEM

Electron gun

Acceleration stage

Condenser lens system:

Parallel or converging illumination of the specimen
Basic set-up of the TEM

- Electron gun
- Acceleration stage
- Condenser lens system
- Specimen stage
- Objective lens

... a few words on this one...
Magnetic Lenses

Electron optics was born in 1927, when Hans Busch showed that the elementary lens equation is applicable to short magnetic coils.

\[
\frac{1}{d_{\text{object}}} + \frac{1}{d_{\text{image}}} = \frac{1}{f}
\]

\[
M = \frac{d_{\text{image}}}{d_{\text{object}}}
\]
Electrons are focused by simple round magnetic lenses which properties resemble the optical properties of a wine glass....

Unlike in light optics the wavelength (2pm for 300kV) is not the resolution limiting factor.

Lens aberrations and instabilities of the electronics (lens currents etc.) limit the resolution of even the best and most expensive transmission electron microscopes to about 50pm.
Lens aberrations:

Spherical aberration:

Spherical aberration causes wave fronts to bend more strongly at the outside of the lens than those close to the axis.
A famous $C_s$-afflicted instrument

Hubble telescope:
the sides of its $\varnothing$ 2.5 m primary mirror are 2 $\mu$m too low (negative $C_s$) - the mirror was ground very precisely to the wrong shape. The error was avoidable.

Hubble repair:
a modified camera lens assembly corrected for the too-low phaseshift of marginal rays and resulted in a spectacular improvement of image quality. Primary mirror was not changed.
$C_S$ Corrector:

$C_S$-Corrector (Rose, Haider and Urban)
Aberration corrected electron optics

$C_s$ is adjustable!

- TU Darmstadt (H. Rose)
- EMBL Heidelberg (M. Haider)
- Forschungszentrum Jülich (K. Urban)

Haider, Rose, Urban et al.

Chromatic aberration:

Chromatic aberration results in electrons with a range of energies being focused in different planes.
Electrons passing at different directions away from the optic axis have different focal lengths.
Basic set-up of the TEM

- Electron gun
- Acceleration stage
- Condenser lens system
- Specimen stage:

Now things get interesting!
Electron - Sample Interactions

- Incident electron beam
- Cathodoluminescence (visible light)
- Bremsstrahlung
- Characteristic x-rays
- Auger electrons
- Secondary electrons
- Backscattered electrons
- Elastically scattered electrons
- Heat
- Transmitted beam to energy-loss spectrometer

Sample

Angle-limiting aperture
Strahov Stadium in Prague
Electron - Sample Interactions

I = const.

5 - 50 nm

specimen

I = I(\ x,\ y,\ \theta_x,\ \theta_y,\ \Delta E)\\
\text{conventional EELS TEM}

Electron Spectroscopic Imaging (ESI)
Diffraction (ESD)

Energy Filtering TEM
Electron - Sample Interactions

Questions you can ask an electron:

Q1: where are you going to?  (→ direction)
Q2: how is your relation with the others? (→ phase)
Q3: how fast are you travelling?  (→ energy)
Q4: are you up or down? (→ spin)

Well defined energy

i.e. 200 keV

Transmitted beam

Sample

Angle-limiting aperture

Interactions
Electron - Sample Interactions

Energy Loss Spectrum

Angle-limiting aperture

Sample

i.e. 200 keV

Electron Energy Loss Spectrum

Electron Microscopy
Outline

• Part I: Elastic Interactions
• Part II: Inelastic Interactions
  – the EELS spectrum
  – Spectrometer / Energy Filters
  – What kind of information do I get?
Energy Loss Spectrum

Angle-limiting aperture

Sample

Well defined energy

i.e. 200 keV

Transmitted beam

Interactions

Spectrum

Zero Loss

plasmon peak

low loss distribution

near edge fine structure

extended fine structure

ionization edge

Counts

0 50 100 150

Energy Loss (eV)
I. Mass-thickness contrast

- Incident beam
- Higher mass thickness
- Lower mass thickness
- Objective lens
- Objective aperture
- Image plane
- Intensity profile

[Image: TEM diagram showing mass-thickness contrast with Fe$_3$O$_4$ and C labeling]
Diffraction Contrast

\[ f - \text{focal length of the lens} \]

\[ \psi (k_x, k_y) \propto F \left\{ T(X, Y) \right\} \]

\[ T(X, Y) \propto F^{-1} \left\{ \psi (k_x, k_y) \right\} \]
Coherence & Interference

Nothing new... good old Bragg!
Elastic Interactions

**Elastic scattering:**

Elastic scattering at low angle is mostly due to Coulomb interactions with the negatively charged electron cloud.

**Diffraction:**

Interference of (coherently) scattered electron waves from periodically arranged atoms in a crystalline solid.

**Diffraction contrast**

Elastic scattered electrons are used for image generation in conventional TEM!

Q1: where are you going to?
1. Elastic Interactions

**Elastic scattering:**

**Elastic scattering** at low angle is mostly due to Coulomb interactions with the negatively charged electron cloud.

**Diffraction:**

Interference of (coherently) scattered electron waves from periodically arranged atoms in a crystalline solid.

*Elastic scattered electrons are used for image generation in conventional TEM!*

Q1: where are you going to?
1. Elastic Interactions

Elastic scattering:

**Elastic scattering** is also the basis for high resolution imaging, where changes in the phase of the electron waves gives rise to contrast variations:

*Phase contrast imaging (HIGH RESOLUTION TEM, HRTEM)*

Coherent, elastic scattering

Elastic scattered electrons are used for image generation in conventional TEM!

Q2: how is your relation with the others?
Contrast transfer function (CTF)

Phase shift $\Delta \phi(r) = \sigma \cdot V_{proj}(r)$

$\sigma_{200kV} = 0.0026 \text{ V}^{-1} \text{Å}^{-1}$
Contrast transfer function (CTF)

\[ \Psi_{\text{inc}}(r) = e^{ikz} \]

\[ \Psi_{\text{exit}}(r) = \Psi_{\text{inc}} \cdot e^{i\pi\lambda V_{\text{proj}}(r)} \]

\[ \Psi_{ab}(r) = \Psi_{\text{exit}} \otimes e^{i\vec{z}(r)} \]

\[ I(r) = |\Psi_{ab}|^2 \]
Transfer function
Transfer function

\[ T(H) < 0 \] implies "positive" contrast: atom columns appear dark (in the print, not the negative!).

\[ T(H) > 0 \] implies "negative" contrast: atom columns appear bright.

- \[ T(H) = 0 \] implies no transfer of the respective spatial frequency at all!

Example: hypothetical crystal with four different sets of planes parallel to the viewing direction

- plane spacing: \( d_1 > d_2 > d_3 > d_4 \)
- corresponding spatial frequencies: \( 1/d_1 < 1/d_2 < 1/d_3 < 1/d_4 \).
- the planes with spacing \( d_1 \) appear with positive contrast
- the planes with spacing \( d_2 \) appear with negative contrast
- the planes with spacing \( d_3 \) do not appear at all
- it is difficult to predict the contrast of the planes with spacing \( d_4 \). We can avoid these problems by introducing an objective aperture.
Interpretation of TEM images
Elastic scattering:

Elastic scattering at higher angles is essentially due to Coulomb interaction with an atomic nucleus.

**Rutherford scattering:**

Incoherent, elastic scattering to high angle

Intensity is related to atomic number and thickness of specimen

High Angle Annular Dark Field
HAADF - STEM Imaging

Elastic scattered electrons are used for image generation in conventional TEM!

Q1: where are you going to?
MoVO:
Channels are filled

M1 phase: \( \text{Mo}_{1.0} V_{0.15} Te_{0.12} Nb_{0.128} O_{3.7} \)
Out-of-center distortion


~ 70pm Resolution + Chemical Information
Outline

- Part I: Elastic Interactions
- Part II: Inelastic Interactions
  - Spectrometer / Energy Filters
  - The EELS spectrum
  - What kind of information do I get?
Our eyes and brain routinely understand reflected light images but are ill-equipped to interpret TEM images and so we must be cautious.

This problem is well illustrated by the picture of the two rhinoceroses side by side such that the head of one appears attached to the rear of the other.

**Figure 1.7.** Photograph of two rhinos taken so that, in projection, they appear as one two-headed beast. Such projection artifacts in reflected-light images are easily discernible to the human eye but similar artifacts in TEM images are easily mistaken for “real” features.
Literature

TRANSMISSION ELECTRON MICROSCOPY
Basics
David B. Williams and C. Barry Carter

Transmission Electron Microscopy
A Textbook for Materials Science
Second Edition
Springer