Analytical Electron Microscopy:

A multiple-tool technique for combined analysis

Stefano Gialanella
Outline:

• Analytical Electron Microscopy

• Electron Diffraction
  Selected area electron diffraction (SAED)
  Convergent beam electron diffraction (CBED)
  Kikuchi lines

• Imaging
  Diffraction contrast
  Applications
  Bright Field – Dark Field

• Spectroscopies
  Energy Dispersive X-Ray Spectroscopy (EDXS)
  Electron Energy Loss Spectroscopy (EELS)
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Analytical Electron Microscopy

- Incident Beam
- Auger Electrons
- Cathodoluminescence
- Absorbed Electron
- Bragg Diffracted Electrons
- Transmitted Electrons
- Energy Loss Electrons
- Characteristic x-Rays (EDS)
- Specimen
Analytical Electron Microscopy

IMAGING

MICROSTRUCTURE

DIFFRACTION

CRYSTALLINE STRUCTURE

SPECTROSCOPIES

COMPOSITION
Analytical Electron Microscopy

Diagram showing electron path through a microscope with labels for object, lens, back focal plane, image plane, specimen, objective lens, back focal plane, intermediate lens, image plane, and viewing screen.
Analytical Electron Microscopy

Bright Field

Dark Field
Analytical Electron Microscopy

SAED

Bright Field

Dark Field
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Electron Diffraction

Selected Area Electron Diffraction (SAED)

**Basics**

- Incoming beam
- Trace of the SAED aperture
- Diffracted beam
- Transmitted beam
- Specimen
- Plate
Electron Diffraction

The patterns
Electron Diffraction

The patterns

Spot pattern

Ring pattern
Electron Diffraction

The patterns

100 nm
Sample orientation

Plate

$B = \bar{g}_1 \times \bar{g}_2 = \text{Zone axis}$

$-\bar{B} = \text{Beam direction}$
Electron Diffraction

Sample orientation

Zone axis: $[1,1,1]$

Ex.: $\overline{g}_1 = [1\overline{1}0]$ $\overline{g}_2 = [10\overline{1}]$ zone axis = $\begin{bmatrix} 1 & -1 & 0 \\ 1 & 0 & -1 \end{bmatrix} = [111]$
Electron Diffraction

Convergent beam electron diffraction (CBED)
Electron Diffraction
Electron Diffraction

Kikuchi lines
Electron Diffraction

Kikuchi lines
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Diffraction contrast:

Applications

Imaging

Objective Aperture

Bright → Dark → Bright

70 nm
Imaging

Applications

Diffraction contrast

$\varepsilon = 0$

$\varepsilon$ Large
Imaging

Applications

Diffraction contrast

DF image, only a fraction of the particle is clearly visible, that is the distribution within the objective aperture. Consequnetly, two reflections are included in it. This artifact can be regarded as a blur of the electron beam perpendicular to it. The electron beam is clearly visible, that is the distribution within the objective aperture. Consequently, two reflections are included in it. This artifact can be regarded as a blur of the electron beam perpendicular to it.
Imaging

**Bright Field – Dark Field**

Diffraction contrast
Imaging

**Bright Field – Dark Field**

[Diagram of optical paths showing incident beam, reflecting plane, transmitted beam, and diffracted beam.

- Incident beam
- Reflecting plane
- Transmitted beam
- Diffracted beam
- Objective lens
- Specimen
- Back focal plane
- Objective aperture
- Intermediate lens
- Image plane
- Viewing screen]
**Bright Field – Dark Field**

- Tilted Incident Illumination
- Specimen
- Objective Lens
- Objective Aperture
- Back Focal Plane
- Image Plane
- Intermediate Lens
- Viewing Screen
- Optic Axis
- Direction of Tilt of Incident Beam
- $\theta = \text{angle of tilt of incident beam}$
- Diffracted Beam
- Transmitted Beam
Imaging

**Bright Field – Dark Field**

- Incident beam
- Optic axis
- Specimen
- Tilt of incident beam
- Objective aperture
- Transmitted beam
- Diffracted beam
Imaging

**Bright Field – Dark Field**

Diffraction contrast
Bright Field – Dark Field

C- ZnS H- ZnO

Imaging

**Bright Field – Dark Field**
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  Energy Dispersive X-Ray Spectroscopy (EDXS)
  Electron Energy Loss Spectroscopy (EELS)
Energy Dispersive X-ray Spectroscopy (EDXS)

\[ X\text{-ray formation} \]
Spectroscopies

**TEM-EDXS Interface**

Diagram showing the TEM-EDXS Interface with labels for:
- Incident beam
- Upper objective pole piece
- Desired X-ray collection angle $\Omega$
- Specimen
- Lower objective pole piece
- Transmitted electrons
- Collimator
- Window
- Si(Li) detector
TEM-EDXS Interface
Spectroscopies

EDXS Detectors

LN₂ cold finger

Si(Li)

Courtesy N.J. Zaluzec.
Spectroscopies

**EDXS Detectors**

- **Si Drift Detector**
  - Courtesy N.J. Zaluzec.
EDXS Detectors

Comparing SDD vs. Si(Li) @ E0 = 300 keV

Si(Li)

SDD

Dead Time (%) vs. Input Count Rate (Kcps)

Courtesy N.J. Zaluzec.
EDXS Detectors

Si(Li) vs SDD

Relative Efficiency

Energy (eV)

- SDD - 0.35 mm
- SDD - 1.0 mm
- Si(Li) - 3.0 mm

Courtesy N.J. Zaluzec.
**Spectroscopies**

**Spatial resolution & electron interaction volume**

- **Spatial resolution increases with electron energy**
- **Interaction volume extremely limited**
  - Low count rates
  - High resolution

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**TEM**

**SEM**

**EDXS**
Spectroscopies

Qualitative analysis

EDXS

MAUD - Trento
Dipartimento di Ingegneria Industriale
Università di Trento
2015
Spectroscopies

Qualitative analysis

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<th>Element</th>
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<th>$K\alpha_2$</th>
<th>$K\beta_1$</th>
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<td>4 Be</td>
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<td>108.5</td>
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<td>5 B</td>
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</table>
Spectroscopies

Qualitative analysis

![Graph showing qualitative analysis of Ni L, Ni K, O K, Windowless XEDS Detector, Beryllium Window XEDS Detector]
Spectroscopies

Qualitative analysis
Spectroscopies

Qualitative analysis

I e II: BSE
III: SE
Spectroscopies

Qualitative analysis

EDXS
Silicon X-ray escape peaks

Silicon internal fluorescence peak

EDXS
Spectroscopies

**Spurious peaks - Detector**

- Detector

![Graph showing spurious peaks](image)

- Silicon internal fluorescence peak

![Graph showing silicon internal fluorescence peak](image)
Spectroscopies

**Spurious peaks - Detector**

Pile-up peaks

![Graph showing spectral intensities and emission energies](image)
Spectroscopies

**Spurious signals - Microscope**

- Incident beam
- Upper pole piece
- Desired X-rays
- Anti-contaminator
- Back-scattered electrons
- Specimen
- Specimen-generated continuum
- Scattered electrons
- Anti-contaminator
- Continuum fluorescent spurious X-rays
- Back-scattered electrons
- Direct electron beam
- Lower pole piece
Spurious signals - Microscope

The Hole Count

Courtesy N.J. Zaluzec.
Spurious signals - Microscope

Electrons
- X-rays

Fixed First Condenser Aperture
Variable Second Condenser Aperture

Upper Objective Pole Piece
Specimen and Goniometer Stage
Objective Aperture
Lower Objective Pole Piece

Electrons
X-rays

Thick Fixed First Condenser Aperture
Thick Variable Second Condenser Aperture

Upper Objective Pole Piece
Specimen and Goniometer Stage
Objective Aperture
Lower Objective Pole Piece

Com-Sows Defining Collimator

Courtesy N.J. Zaluzec.
Spectroscopies

**Spurious signals - Microscope**

[Diagram showing energy spectra for different samples and settings, labeled with elements Ni, Mo, Fe, and energy values.]
Spectroscopies

Spurious signals – Sample Holder

Cu & Zn lines from sample holder

TiO$_2$ - Au
Instrumental parameters:

Channel width: 10 eV/ch or better

Time constant: generally better low values to maximise count rate

Multichannel energy resolution: to be periodically checked.

Critical parameters:

Spectrometer resolution

Calibration of the energy range

Maximum output count rate
Quantitative analysis

\[
\frac{C_i}{C_{i,STD}} = K \frac{I_i}{I_{i,STD}}
\]
$K$, for **bulk/thick** samples depends on:

- $Z$ - Atomic number
- $A$ - X-ray absorption
- $F$ - X-ray secondary fluorescence

**Thin sample (foil) criterion:**
- "Matrix effect" is not so important, as interaction volume is very small.
- Absorption and fluorescence can be disregarded.
CLIFF-LORIMER equation:

\[
\frac{C_A}{C_B} = K_{AB} \frac{I_A}{I_B}
\]

EDXS quantitative analysis is usually quite straightforward in a TEM (\textit{thin-film approximation})
How to decide if the above approximation is valid!?
When the bremsstralung X-rays are not absorbed in the specimen.
Step by step quantitative analysis – Standard approach

1. Verify thin sample approximation

2. Acquire standard sample spectrum/a

3. Measure $I_A$, $I_B$, $I_C$, …

4. Evaluate $K_{AB}$, $K_{BC}$, …

5. Acquire sample spectrum/a

6. Measure $I_A$, $I_B$, $I_C$, …

7. Evaluate $C_A$, $C_B$, $C_C$, …
Quantitative analysis

\[
\frac{C_A}{C_B} = K_{AB} \frac{I_A}{I_B}
\]

\[
\frac{C_A}{C_C} = K_{AC} \frac{I_A}{I_C}
\]

\[
\frac{C_B}{C_C} = K_{BC} \frac{I_B}{I_C}
\]

\[
I_A + I_B + I_C = 100
\]

\[
K_{AB} = \frac{K_{AC}}{K_{BC}}
\]
Spectroscopies

1) Experimental determination, using standard samples
   
   Time spending
   
   More accurate results

2) First principles calculation
   
   Quick
   
   Less reliable results

\( \text{Determination of } K_{AB} \)
**Spectroscopies**

**Electron Energy-Loss Spectroscopy (EELS)**

**EELS – vs - EDXS**

- **Inelastic interaction “products”**
  - Interband transitions (few eV)
  - Plasmons (10 eV)
  - Phonons (10^{-2} eV)
  - **Core electron excitation**
    - Characteristic X-rays (E>10^2 eV up to E>10^4 eV)
    - Energy loss electrons (10^2 eV (range) < E < 10^4 eV (range))
Spectroscopies

**EELS – vs - EDXS**

![Spectroscopy Diagram](image)
Spectroscopies

Instrumentation

- spectrometer entrance aperture
- $\beta$, entrance semi-angle

- Energy Loss [eV]
- Intensity [counts x10$^3$]

- Plasmon
- Zero loss
- Gain change
Spectroscopies

Instrumentation

(A) Ray paths through the $\Omega$ filter system inserted in the imaging lens system of the LEO TEM. (B) The Gatan Imaging Filter attached to the TEM column after the imaging lenses, in the same position as a PEELS.
Spectroscopies

- Zero-loss peak
- Plasmon peak(s)

Absorption edges

State Notation

Absorption Edges
Spectroscopies

Quantification

\[ \frac{N_A}{N_B} = \frac{I_K^A(\beta \Delta) \sigma_K^B(\beta \Delta)}{I_K^B(\beta \Delta) \sigma_K^A(\beta \Delta)} \]

Intensity

Energy-Loss (eV)

Photodiode Counts (x10^3)

Energy Loss (eV)

\[ S_B(\delta, \beta) = 3.67 \times 10^6 \]
\[ S_N(\delta, \beta) = 6.83 \times 10^5 \]

\[ \delta = 50 \text{ eV} \]
\[ \beta = 20 \text{ mrad} \]
Spectroscopies

Fine structure

EELS
Plate-like precipitate in a Al-Cu-Ag-Mg alloy
Spectroscopies

Imaging & mapping
Essential Bibliography


