Chapter 9
The introduction of EELS

EELS principle

(Chap. 37, 38, 39, 40)

Particle picture of scattering

- elastic
- inner-shell inelastic
- outer-shell inelastic
TEM beam-specimen interactions and signals

**Incident high-energy beam**

- Back scattered electrons
- Auger electrons
- Secondary electrons
- Characteristic X-rays
- Visible light
- Bremsstrahlung
- Inelastically scattered electrons (have lost certain amounts of their original energies) (EELS, EFTEM)

**Thin specimen**

- Absorbed electrons
- Electron-hole pairs
- Elastically scattered electrons (have lost almost nothing from their original energies)
- Direct beam

**Signals used for EELS and EFTEM**
What is EELS

- *Electron Energy Loss Spectroscopy*

EEL spectrum is collected series energy loss electrons which generated with the inelastic scattering collision with specimen.

\[ \Delta E = E - E_{abs} \]

- Energy after inelastic scattering
- Incident electron energy
- Specimen absorption energy
Atomic-scale view of electron energy loss in TEM

Energy and Momentum
Conservation of scattering process

Incident beam electron $E_0$ (100 to 1000 keV)

Excited specimen electron $E_B + E$

Scattered beam electron $E_0 - E$
energy-band diagram

valence or conduction band
Core ionization edges and the core level diagram
Nomenclature of EELS ionization edges

After: Ahn & Krivanek, *EELS Atlas*
Ray Tracing for a 90 degree magnetic Sector Spectrometer
EELS instrumentation
spectrum/Imaging

- **Below the TEM:**
  - Serial EELS (e.g. Gatan 607)
  - Parallel EELS (e.g. Gatan 666)
  - Gatan Enfina
  - Gatan Imaging Filter
- **In-column:**
  - Prism-mirror (Leo)
  - Omega Filter (Leo, JEOL)
A magnetic prism bends, disperses and focuses an electron beam.

\[ e v B = F = \frac{m v^2}{R} \]

\[ R = \frac{(m/e)(v/B)}{} \]
Gatan Image Filter (GIF)
Leo-922 energy-filtering TEM

omega filter
Omega-filter in-column spectrometer (Four magnetic prisms)

After objective lens

Diffraction pattern

real or virtual image of specimen

90-120°

energy-selecting slit

real or virtual image of specimen

D2 is conjugated with D1

Before projector lens

optical axis

Diffraction pattern
The EELS looks like

- **Zero loss**
- **Low loss region**
- **Core loss region**

![EELS diagram](image)

- Dielectric function
- Plasmon excitations
- Specimen thickness
- Interband transitions
- Band gap
- Dielectric constant
- Chemical bonding (ELNES)
- Atomic RDF (EXELFS)
- Elemental concentration

Energy Loss (eV)

Counts

Be EELS
EELS spectral information

- Zero-loss
- Zero-loss imaging
- Oxygen edge
- Fine structure imaging
- Nickel edge
- Elemental mapping
- Bonding
- Coordination
- Interat. dist.
- ELNES
- EXELFS
- Elemental composition
- Plasma loss
- Dielectric Function
- Band gap
- Thickness
- Interband transition
- (valence-> conduction band)

Core loss: electronic structure unoccupied-DOS atomic environment

\[ \frac{d\sigma}{dE d\Omega} = 4\gamma^2/a_0 q^4 \sum_{i,j} |\langle f| q.r|i \rangle|^2 \delta(E + E_f - E_i) \sim M^2 \rho(r) \]
Jellium Model

The resonant motion of electron gas would be self-sustaining if there were no damping from the atomic lattice.

The displacement $x$ of a “quasi-free” electron (effective mass $m$) due to a local electric field $E$ must satisfy the equation of motion.

$$m\ddot{x} + m\Gamma \dot{x} = -eE$$

for an oscillatory field

$$E = E \exp(-i\omega t)$$

The displacement has a solution given by

$$x = (eE/m)(\omega^2 + i\Gamma \omega)^{-1}$$
The displacement $x$ give rise to a polarization $P$

$$P = -enx = \varepsilon_o \chi E$$

$\chi$ is the electronic susceptibility and $n$ is the number of electrons per unit volume.

The relative permittivity or dielectric function $\varepsilon(\omega) = 1 + \chi$ is then given by

$$\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2 = 1 - \frac{\omega_p^2}{\omega^2 + \Gamma^2} + \frac{i\Gamma\omega_p^2}{\omega(\gamma^2 + \Gamma^2)}$$

$\omega_p$ is the plasmon frequency (the frequency $\varepsilon_1$ passes through 0)

$$\omega_p = (ne^2/\varepsilon_o m)^{1/2}$$

The energy loss function is defined as

$$\text{Im}\left[\frac{-1}{\varepsilon(\omega)}\right] = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2} = \frac{\omega\Gamma\omega_p^2}{(\omega^2 - \omega_p^2)^2 + (\omega\Gamma)^2}$$
Drude Model for Volume Plasmon

For RuO$_2$  a=b=0.449 nm, c=0.31 nm (one unit cell has 2Ru and 4O)

Ru : [Kr]$4d^75s^1$ =8    O : [He]$2s^22p^4$=6

# of free electrons = 40=2x(8+2x6)

$$n = \frac{40}{(4.49)^2 \times (3.1) \times 10^{-30} \left[ \frac{\text{#}}{cm^3} \right]} = 6.4 \times 10^{29} [m^{-3}]$$

$$\varepsilon_0 = \frac{10^7}{4\pi c^2} = 8.842 \times 10^{-12}$$

$$\omega_p = \left( \frac{ne^2}{m \varepsilon_0} \right)^{1/2} = \left( \frac{(6.4 \times 10^{29}) \times (1.60219 \times 10^{-19})}{(9.1 \times 10^{-31}) \times (8.842 \times 10^{-12})} \right)^{1/2} = 4.5158 \times 10^{16}$$

$$E_p = \hbar \omega_p = \frac{4.5127 \times 10^{16} \times 1.05459 \times 10^{-34}}{1.60219 \times 10^{-19}} = 29.7271 eV$$

While m=9.10956x10^{-31} kg

e=1.60219x10^{-19} C

$$\varepsilon_0=\frac{10^7}{4\pi c^2}=8.842x10^{-12}$$

1 eV=1.60219x10^{-19} J
Plasmon loss from RuO2 nanowires
Correlating electron energy levels with EELS edges

Unoccupied state

$2p_{3/2} \rightarrow 3d_{5/3}$

$2p_{1/2} \rightarrow 3d_{2/3}$
Energy-loss spectrum (log-intensity) of YBCO
\[ E(k) = \frac{\hbar^2 k^2}{2m} \]

\[ \rho(E) = \frac{\Omega}{\pi^2 \hbar^3} (2m^3 E)^{\frac{1}{2}} \]

(a) Energy dispersion curve and (b) DOS \( \rho(E) \) for an electron in a square potential well with infinite sides.
Simplistically speaking, this means that flat regions in a band structure diagram will correspond to peaks in the DOS and therefore peaks in the ELNES.

$$\rho(E) = \int_{S(E)} \frac{1}{|\nabla E(k)|} \frac{dS}{4\pi^3}$$
Band Structure of Si

a) Band Structure

b) Total DOS

Conduction Band

$E_F$

Valence Band
c) Si L\textsubscript{23} edge

Experimental

Theory

d-DOS

s-DOS

Intensity

states/eV/atom

Energy Loss (eV)

Energy (eV)
What EELS can do

Typically applied to:
* measurement of specimen thickness
* analysis of elemental composition
* phase identification via signature in EELS fine structure

Also applicable to studies of:
* electronic band structure and chemical bonding
* atom-specific near-neighbor distributions (RDF)
* Band gap analysis for optoelectronic material
  * dielectric response, $\varepsilon(\omega, \mathbf{q})$
Measurement of specimen thickness

\[ \frac{t}{\lambda} = \ln \left( \frac{I_t}{I_0} \right) \]

\( \lambda \sim 100 \text{ nm but depends on } Z, E_0 \text{ and } \beta \)

Value obtained from calibration specimen or from tables (for common materials) or from parameterized formula
EELS fine structure
(Egerton and Whelan, 1974)
K-edge spectra of diamond and grain from the Allende meteorite

(Blake et al., Nature 332, 1988, 611)
Oxidation state of Cr in a bacterium
(Daulton et al, M&M 7, 479, 2001)
Compare the EELS and EDX technique

• Prior to the 1980, most EDX detector were protected (from the water vapor and hydrocarbon in the microscope column) by a 10µm thickness beryllium window, which strongly absorbs photons of energy less than 1000eV and percludes analysis of elements of atomic number less than 11.

• With development of ultrathin (UTW) or atmospheric-pressure (ATW), elements down to boron can be routinely detected, making EDX competitive with EELS for microanalysis of light elements in a TEM specimen.
EELS and x-Ray Signal Generation
X-ray fluorescence yield (log scale) as a function of atomic number
• The **EELS** is one step signal, while **EDX** is a two step signal (low x-ray fluorescence yield for low Z). In general, the yield rate of the EELS is higher than EDX.

• the signal of EELS concentrates in a small angle range of the transmitted beam, but the EDX signal spans around larger angle range.

(a) These two cause EELS has higher core loss signal (higher Signal to noise ratio, EELS has less recording time)
(b) EDX has better Signal/ background ratio

Background of EELS: arises from the inelastic scattering from the atomic electron whose binding energy less than the edge energy

Background of EDX: arises from bremsstrahlung
The beam broaden effect

EDX bulk beam broaden size for SEM system

EDX thin film (TEM) beam broaden size
(c) x-ray has larger interaction volume than that of electron. The ultimate spatial resolution is higher for EELS than for EDX, but the thin crystal is required for EELS.

Broaden by elastic scattering of x-ray.

Limited by the accept angle.
For example:

Specimen thickness : 100 nm, b is about 10 nm
Nano EDX Beam size (d) : 0.5 nm
The resolution limit: \( R = 5.25 \text{ nm} \)
Follow previous slice, the beta angle for EDX is about 0.82 rad = 820 mrad
For EELS image mode, the beta angle is about 13.06 mrad

For example:
The beam size is about 0.5 nm; specimen thickness is about 100 nm
The EDX beam $R_{\text{max}}$ is 5.256 nm
EELS $R_{\text{max}}$ is about 0.6 nm

de-localization of energy loss electron
• (d) EELS is an absolute, standardless quantitation technique, but quantification error may exist in the case of crystal.
• (e) Structural information is available, but more operator intensive is required.
(f) Comparison of EELS and XEDS sensitivity (depends on strongly on SNR, but not SBR) (Leapman et al.)

EELS is capable of detecting smaller concentrations of elements of low atomic number
(g) EDX resolution is 50 - 100 eV so there is peak overlap below 1000 eV.

EELS resolution is \( \sim 1 \text{ eV} \) so edge overlap can be less.

(stainless steel, Zaluzec 1984)
EELS vs. EDXS

**EDXS**
- X-rays provide elemental information only
- Inefficient signal generation, collection & detection inefficient x-ray mapping
- Slow technique (hours)
- X-ray spectra can contain information from column and other parts of sample
- High detection efficiency for high Z elements
- Energy resolution > 100eV causes frequent overlaps
- Only simple processing required

**EELS**
- Elemental, Chemical, & Dielectric information
- Very efficient in every respect => higher sensitivity to most elements very efficient mapping technique
- Fast technique (seconds to minutes)
- EELS spectra have no such artifacts
  - High detection efficiency for low Z elements
  - Energy resolution 0.3-2eV gives far fewer overlaps
  - More complex processing required => Needs more hardware & software automation
撷取可以定量分析之三維空間EELS訊息 $I(x, y, \Delta E)$。
What is EFTEM

- *Energy Filtering Transmission Electron Microscopy*
The features of EFTEM

- **A contrast-enhancement technique:**
  - it improves contrast in images and diffraction patterns by removing inelastically scattered electrons that produce background “fog”.

- **A mapping technique:**
  - it creates elemental maps by forming images with inelastically scattered electrons.

- **An analytical technique:**
  - it records and quantifies electron energy-loss spectra to provide precise chemical analysis of TEM samples.
The standard EFTEM elemental mapping images

Information without EFTEM

Unfiltered bright field image - structural contrast only

Information gain with EELS + EFTEM

Interface Titanium alloy and PVD-grown Gadoliniumboride

EELS spectra

from conventional TEM images via EEL-spectra to energy-filtered images showing elemental distributions

EFTEM - Elemental contrast

Red: Titanium  Green: Boron  Blue: Oxygen
如何在具有圖案結構上之試片決定介電材質之介電常數。

銅製程與低介電常數材料已是半導體元件發展趨勢。0.13μm 乃至於 90nm 的製程技術

Cross-sectional TEM image

Diameter: (8 inches)

Copper Dual-Damascene Structure
傳統之介電常數量測

利用的MOS Capacitor結構
來量測其C-V曲線得到電容值
反推得到介電層之介電常數值

\[ V_{DC} = \frac{t_d C_d}{\varepsilon_0} \quad (\varepsilon_0: 真空介電常數) \]

因此對於有結構圖案之試片無法
使用此方法量測介電層之
介電常數值。
Dielectric Function Imaging

Extract image-spectrum from a 2.82² nm² area

Counts

electron Energy Loss (eV)
Plasmon Peak

Counts vs Position

Black Diamond: 22.1 eV
Si$_3$N$_4$: 20.7 eV
SiO$_2$: 22.4 eV
Si: 16.3 eV

Electron Energy Loss (eV)

A (0 nm)  16.3  34

B (410 nm)
Dielectric Function image

Electron energy Loss (eV)

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\varepsilon_{\text{ref}}$</th>
<th>$\varepsilon_{\text{exp}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>3.8</td>
<td>4.20±0.31</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>3.6</td>
<td>3.72±0.30</td>
</tr>
<tr>
<td>Black Diamond $^{\text{TM}}$</td>
<td>2.5~2.8</td>
<td>2.69±0.27</td>
</tr>
</tbody>
</table>
\[ J^1(E) \propto M^2 \rho(E) = (E - E_g)^a \]

- Bruley and Brown (parabolic band)

\[ M: \text{transition Matrix from Valence band to conduction band} \]
\[ \rho(E): \text{Density of state of conduction band} \]

\[ J^1(E): a = 0.5 \quad \text{(direct band gap)} \]
\[ a = 1.5 \quad \text{(in-direct band gap)} \]
EDX

EELS

EELS spectra

GaN/AlN multi-layers were grown on Si substrate by MBE.

TEM image

Series ESI images

GaN

AI

GaN

AI

GaN

AI

AI

GaN

AI

GaN

AI

Al-L edge

EDX spectra

AI-L edge

Series ESI images

EELS spectra
The map of band energy of AlN/GaN layers is obtained using electron spectroscopy imaging (ESI) technique. The average band-gap energy of AlN and GaN is determined to be about $5.62 \pm 0.35$ eV and $3.47 \pm 0.36$ eV, respectively.
Chemical Bonding $sp^2/sp^3$ Map

Structure of the specimen

<table>
<thead>
<tr>
<th>α-Fe₂O₃</th>
<th>Fe</th>
<th>Cu</th>
<th>Si</th>
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<tbody>
<tr>
<td>Substrate (100)</td>
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Magnification 0300K

0003  -12-13  -12-10

Znoe axis (10-10)
Image to Spectrum

Energy axis From 646eV~742eV

Fe

Fe₂O₃
Valence State Mapping

Cu
Fe
α-Fe$_2$O$_3$