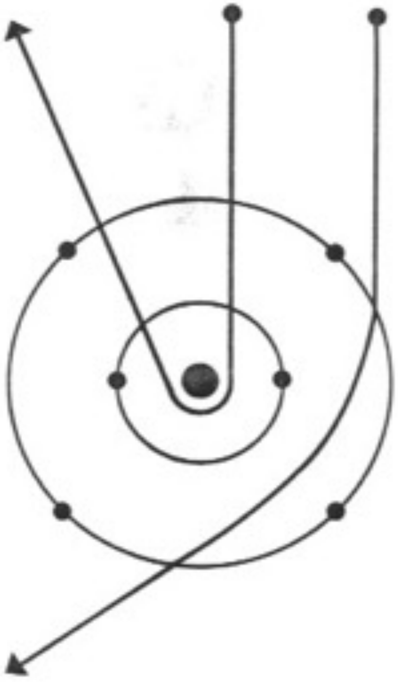
Chapter 9
The introduction of EELS
EELS principle

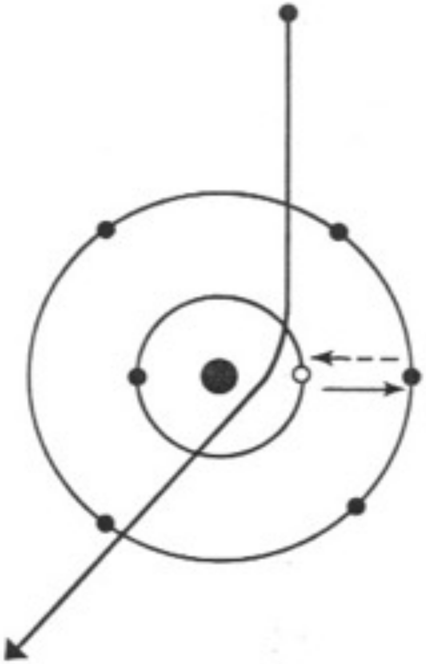
(Chap. 37, 38, 39, 40)

Textbook: R.F. Egerton, Electron Energy-Loss Spectroscopy in the Electron Microscope, 2nd edition

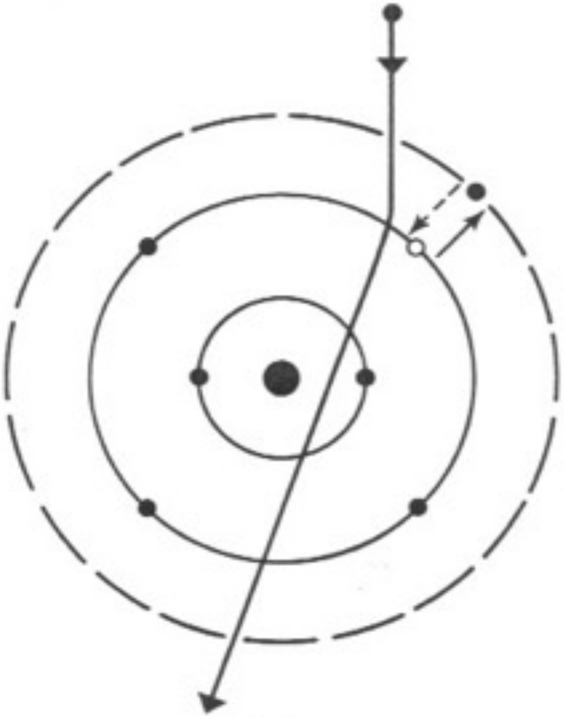
Particle picture of scattering



elastic

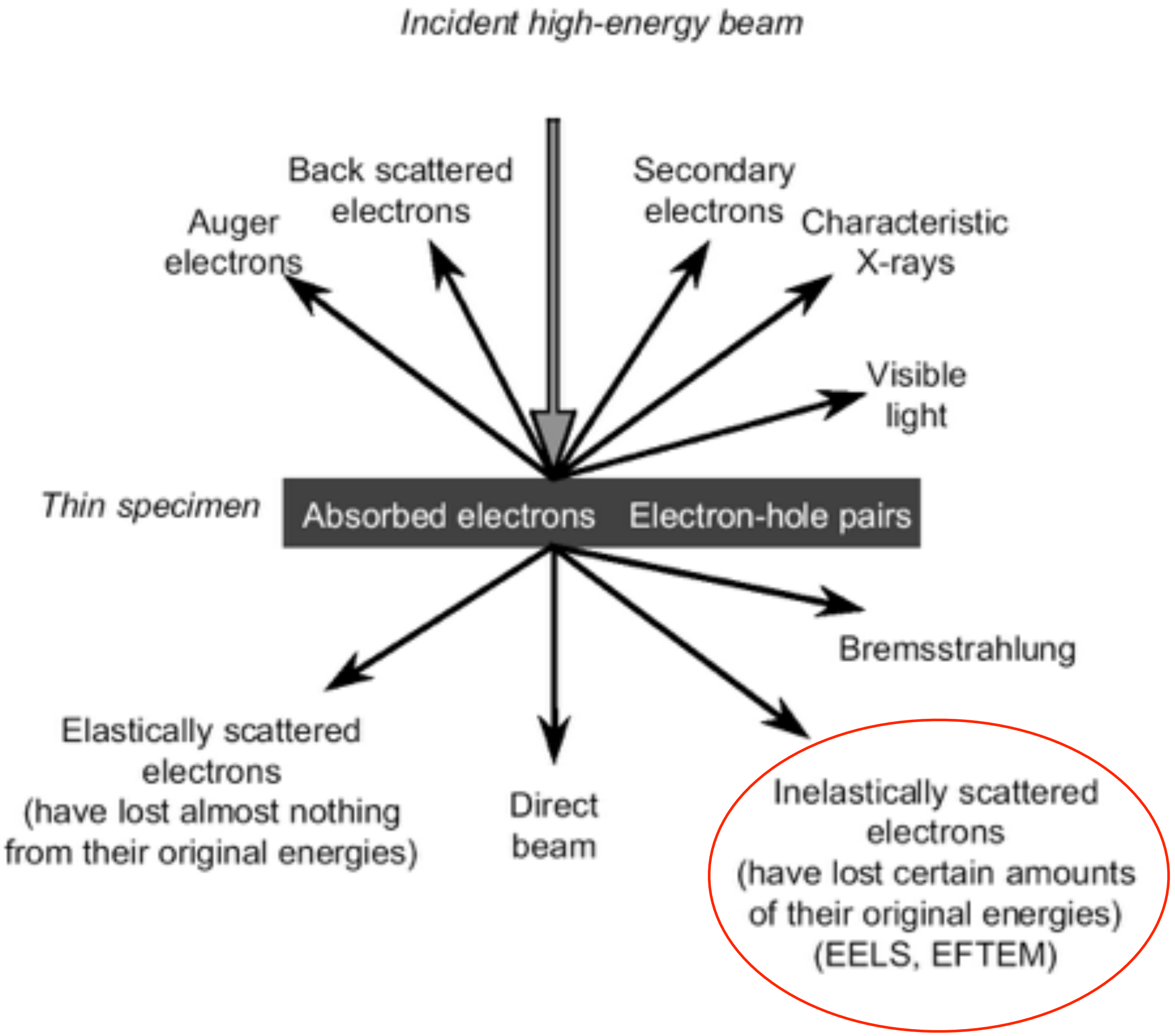


inner-shell
inelastic



outer-shell inelastic

TEM beam-specimen interactions and signals



Incident high-energy beam

Auger electrons

Back scattered electrons

Secondary electrons

Characteristic X-rays

Visible light

Thin specimen

Absorbed electrons

Electron-hole pairs

Bremsstrahlung

Elastically scattered electrons (have lost almost nothing from their original energies)

Direct beam

Inelastically scattered electrons (have lost certain amounts of their original energies) (EELS, EFTEM)

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

$$\Delta E = E - E_{abs}$$

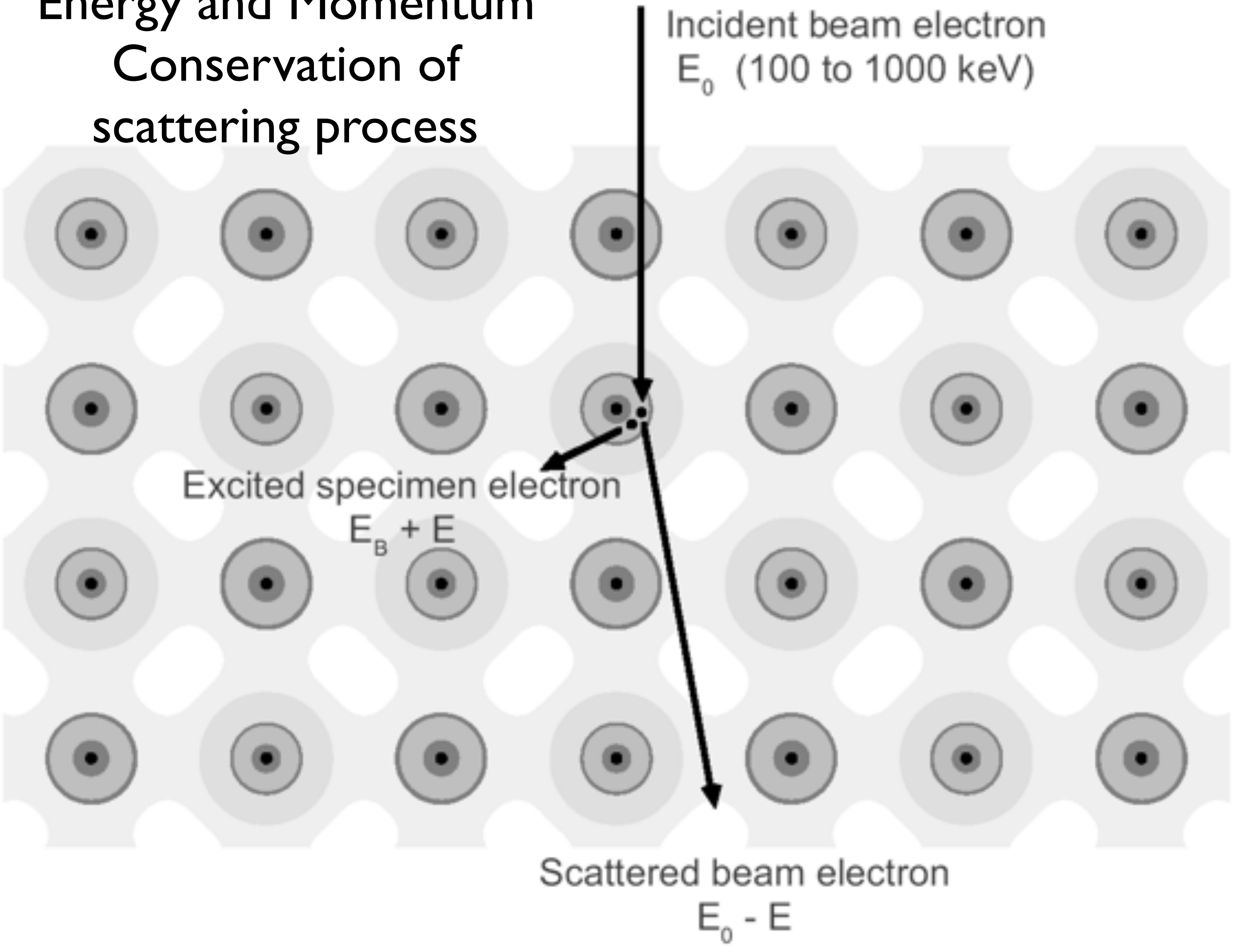
Energy after
inelastic scattering

incident
electron energy

Specimen
absorption energy

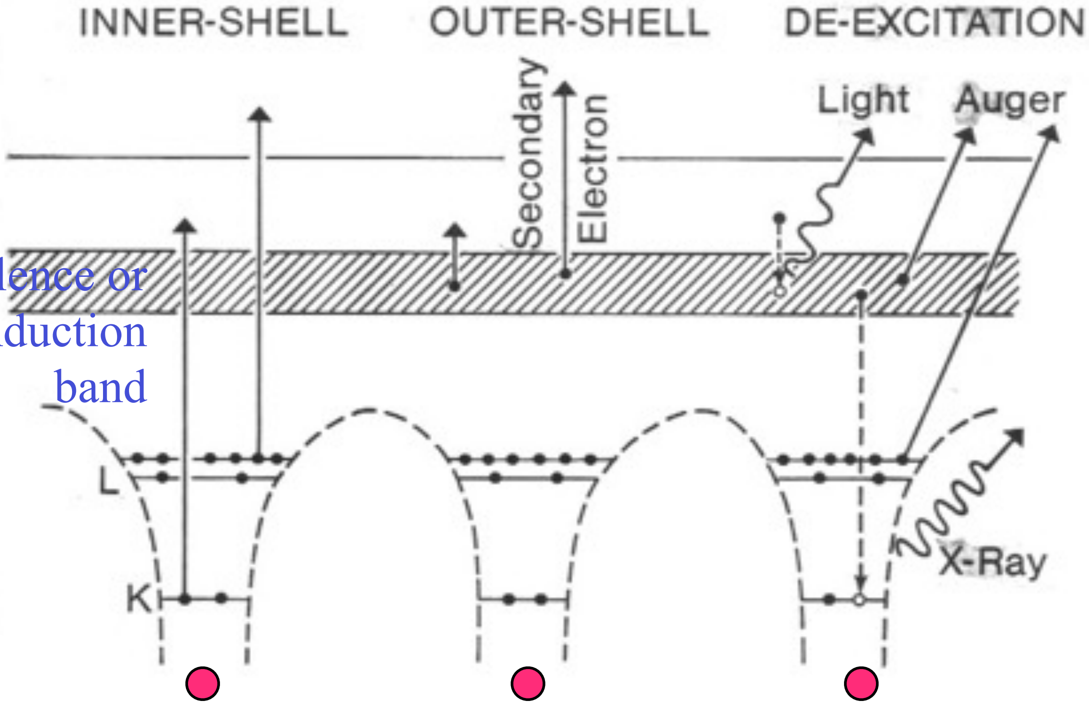
Atomic-scale view of electron energy loss in TEM

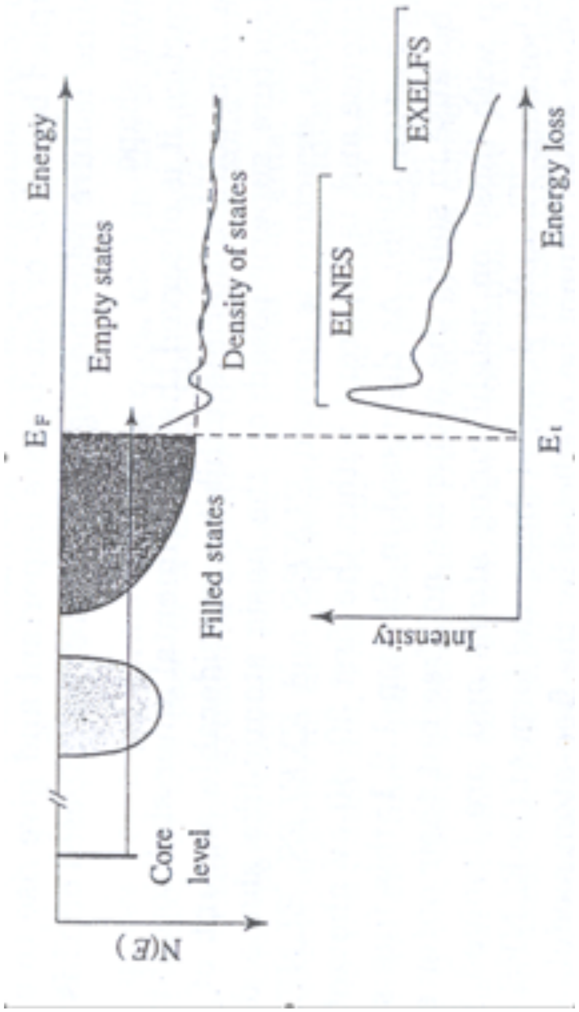
Energy and Momentum
Conservation of
scattering process



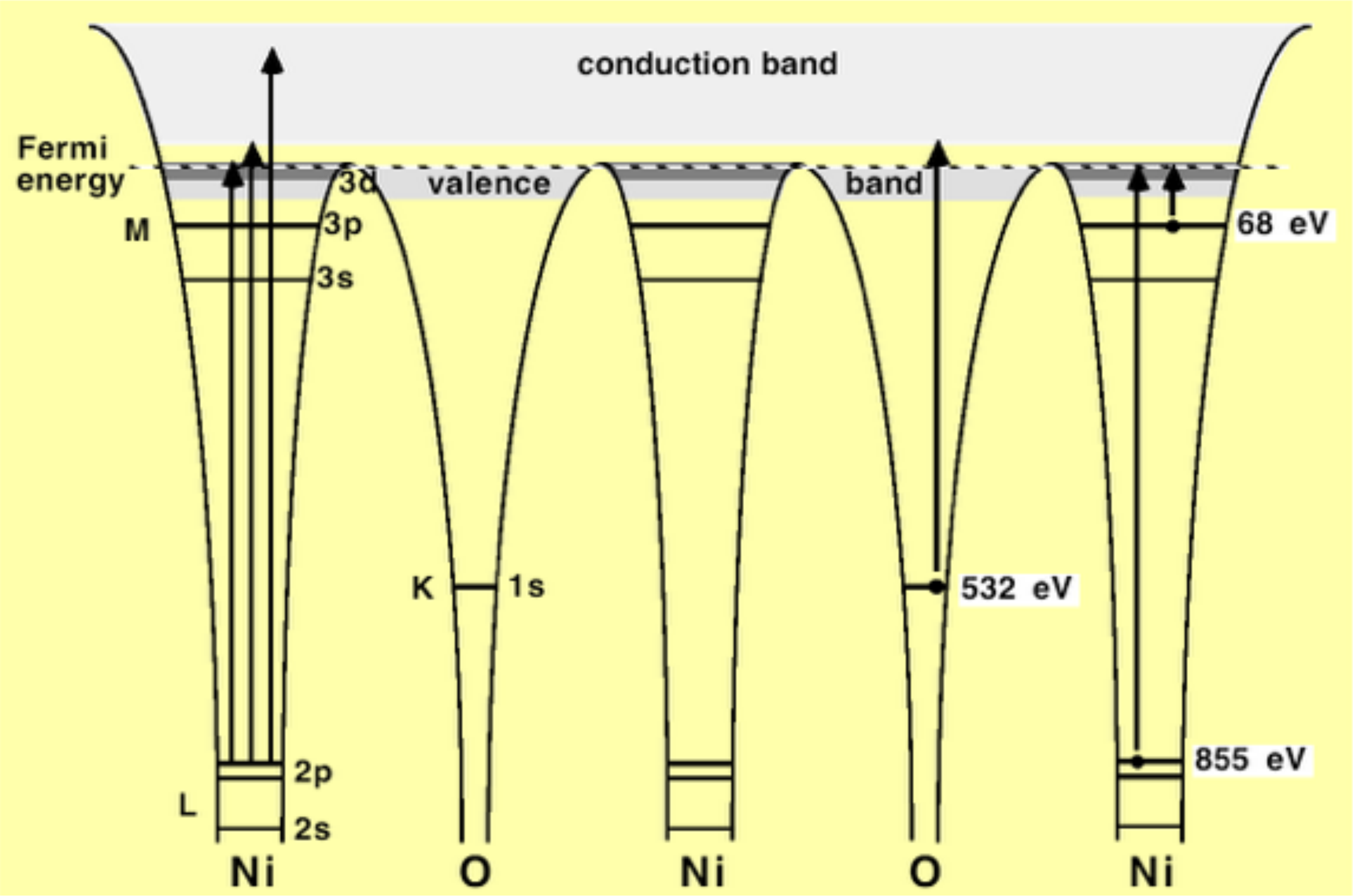
energy-band diagram

valence or conduction band



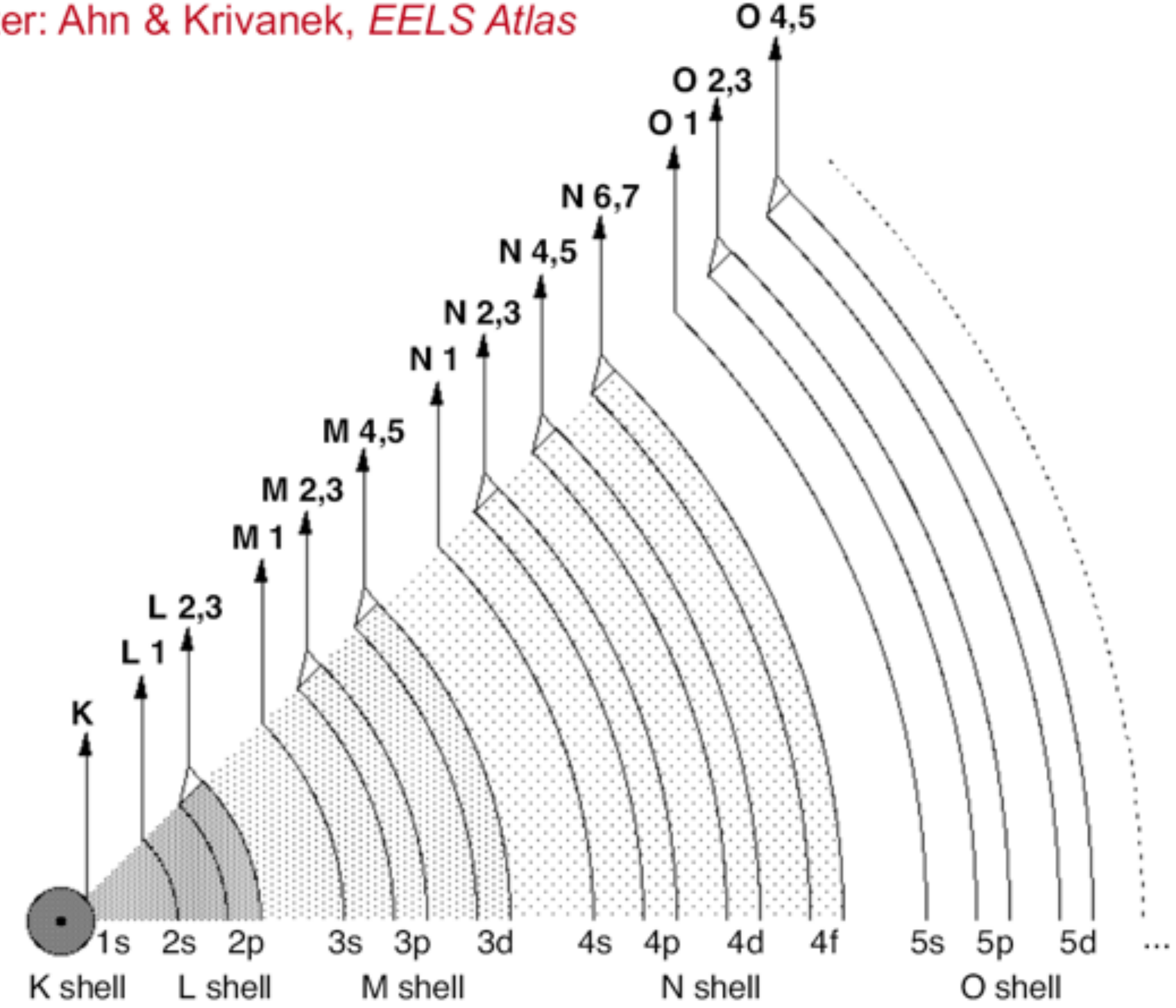


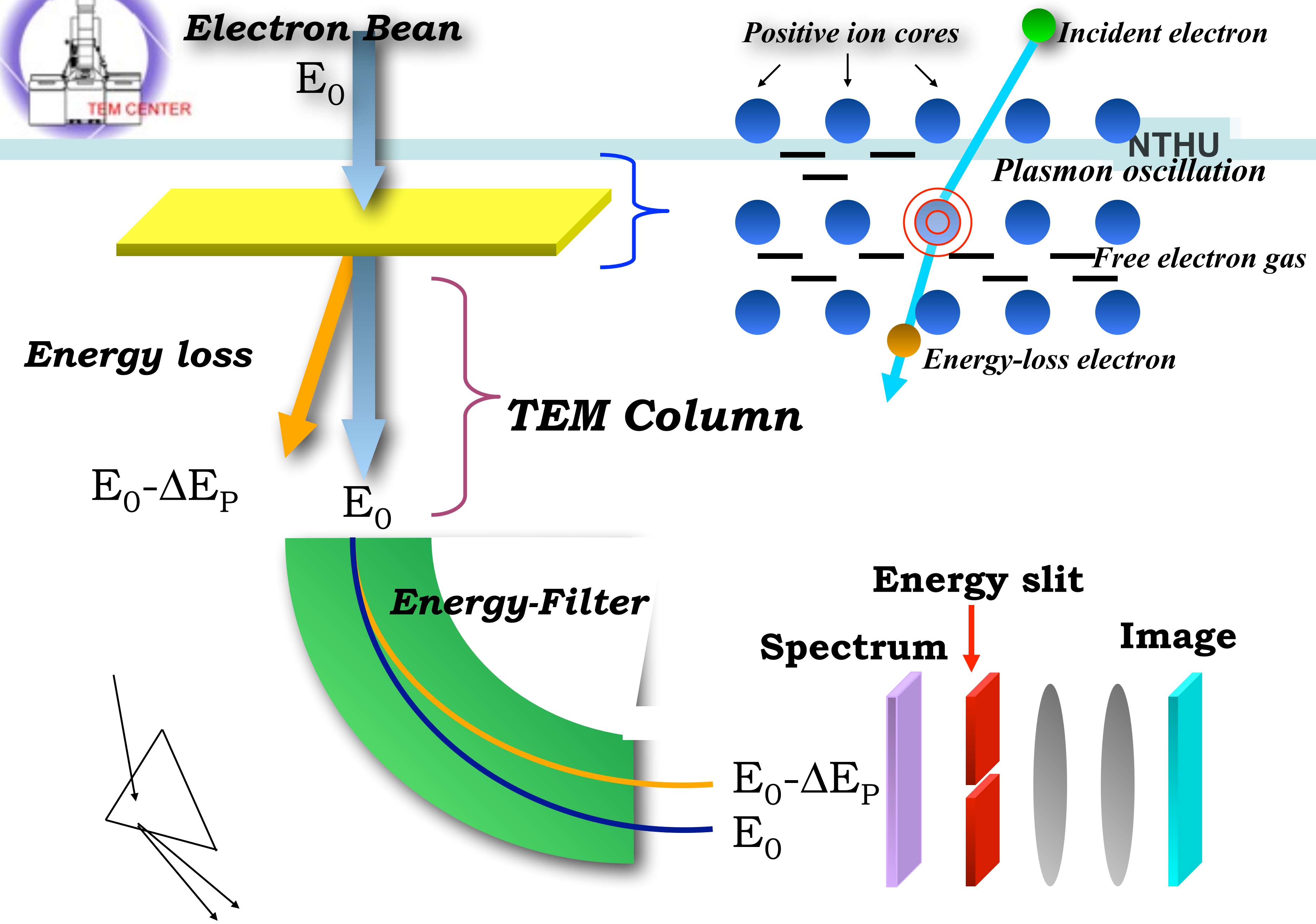
Core ionization edges and the core level diagram



Nomenclature of EELS ionization edges

After: Ahn & Krivanek, *EELS Atlas*





Electron Bean

E_0

Energy loss

E_0-ΔE_P

E_0

TEM Column

Positive ion cores

Incident electron

Plasmon oscillation

Free electron gas

Energy-loss electron

Energy-Filter

E_0-ΔE_P

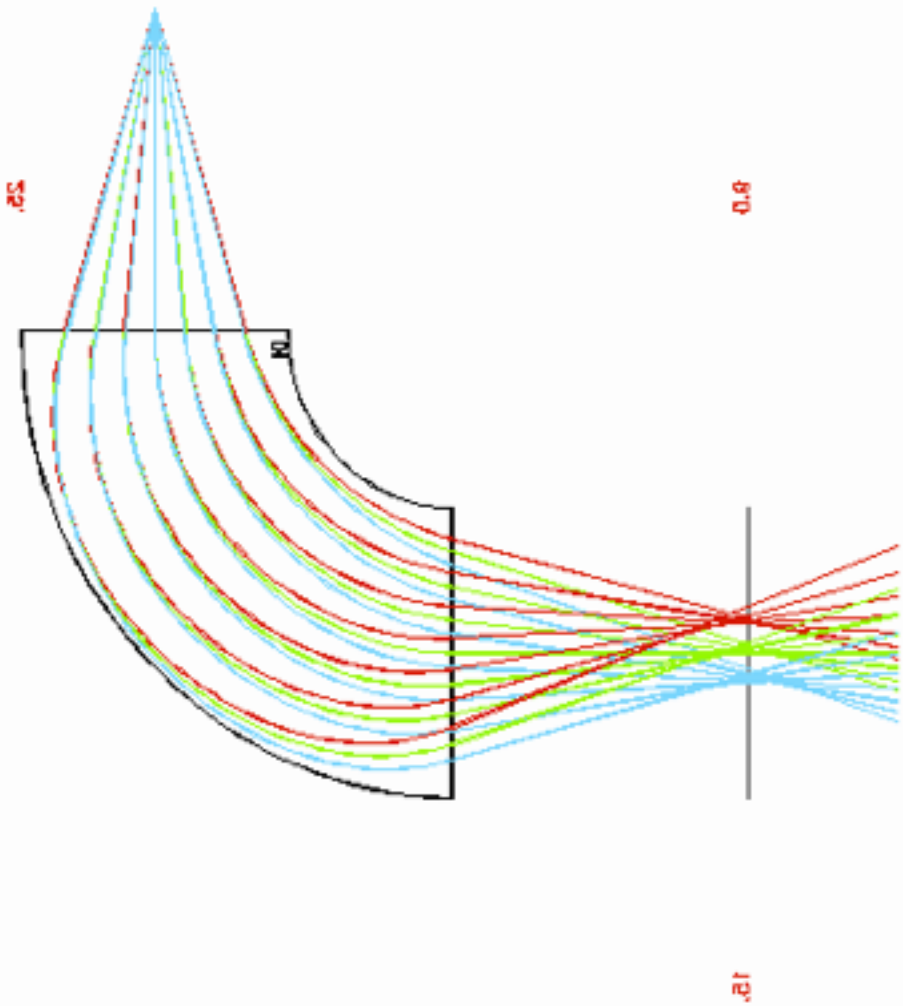
E_0

Energy slit

Spectrum

Image

Ray Tracing for a 90 degree magnetic Sector Spectrometer



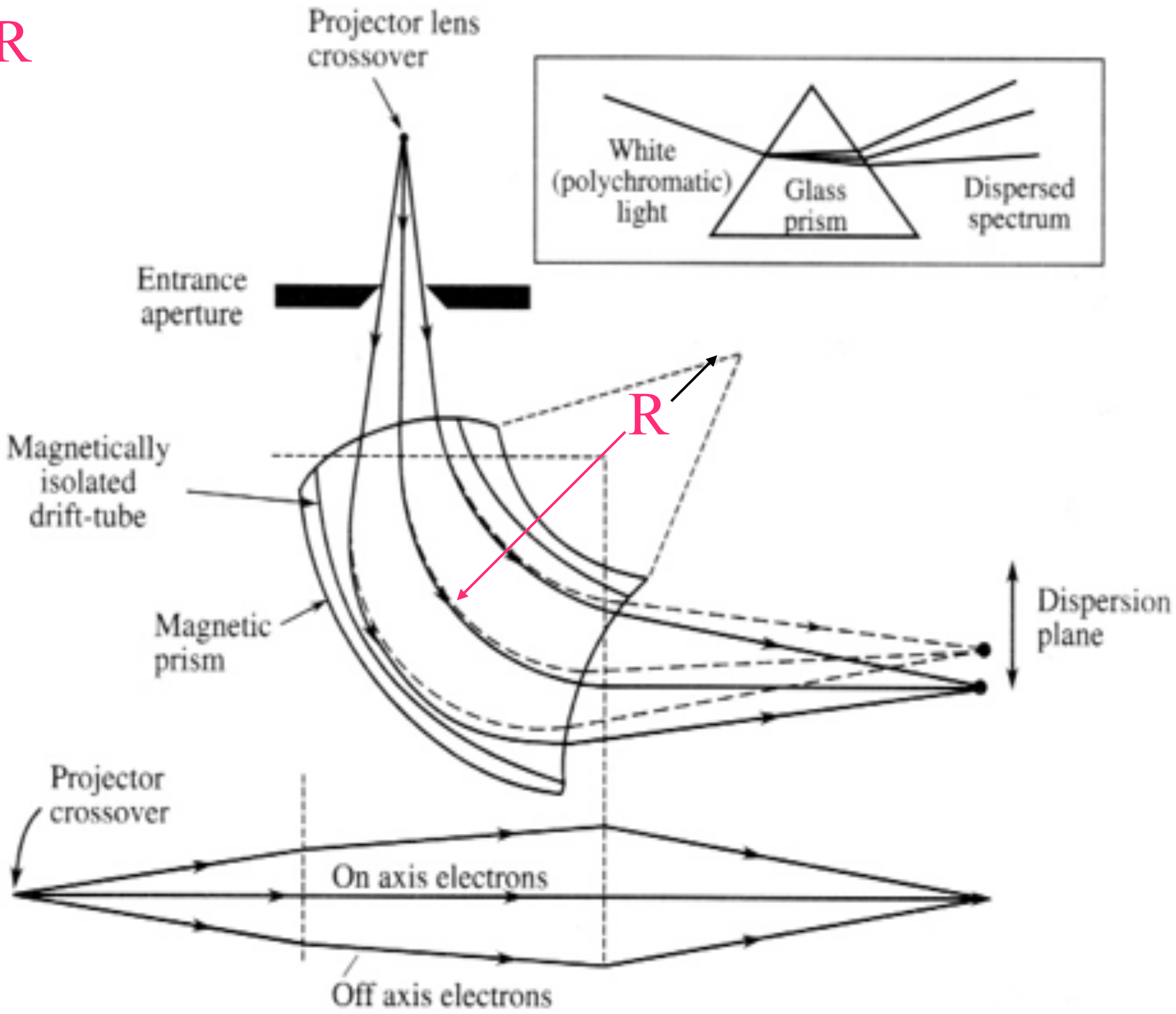
EELS instrumentation spectrum/Imaging

- 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)

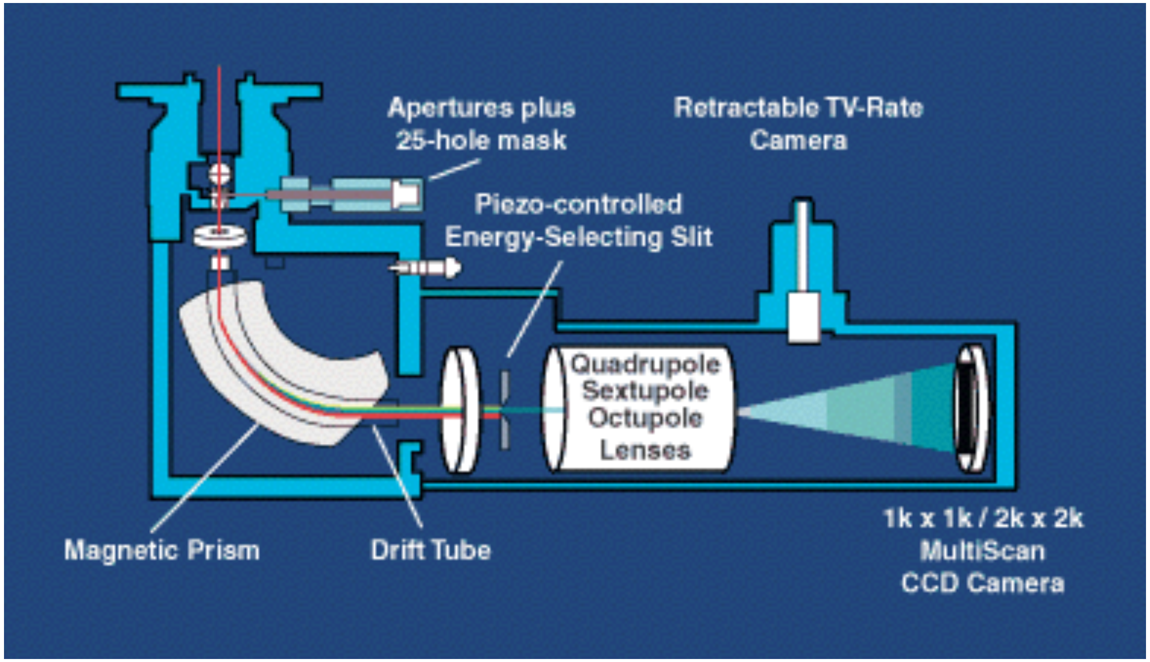
A magnetic prism bends, disperses and focuses an electron beam

$e\ v\ B = F = mv^2/R$

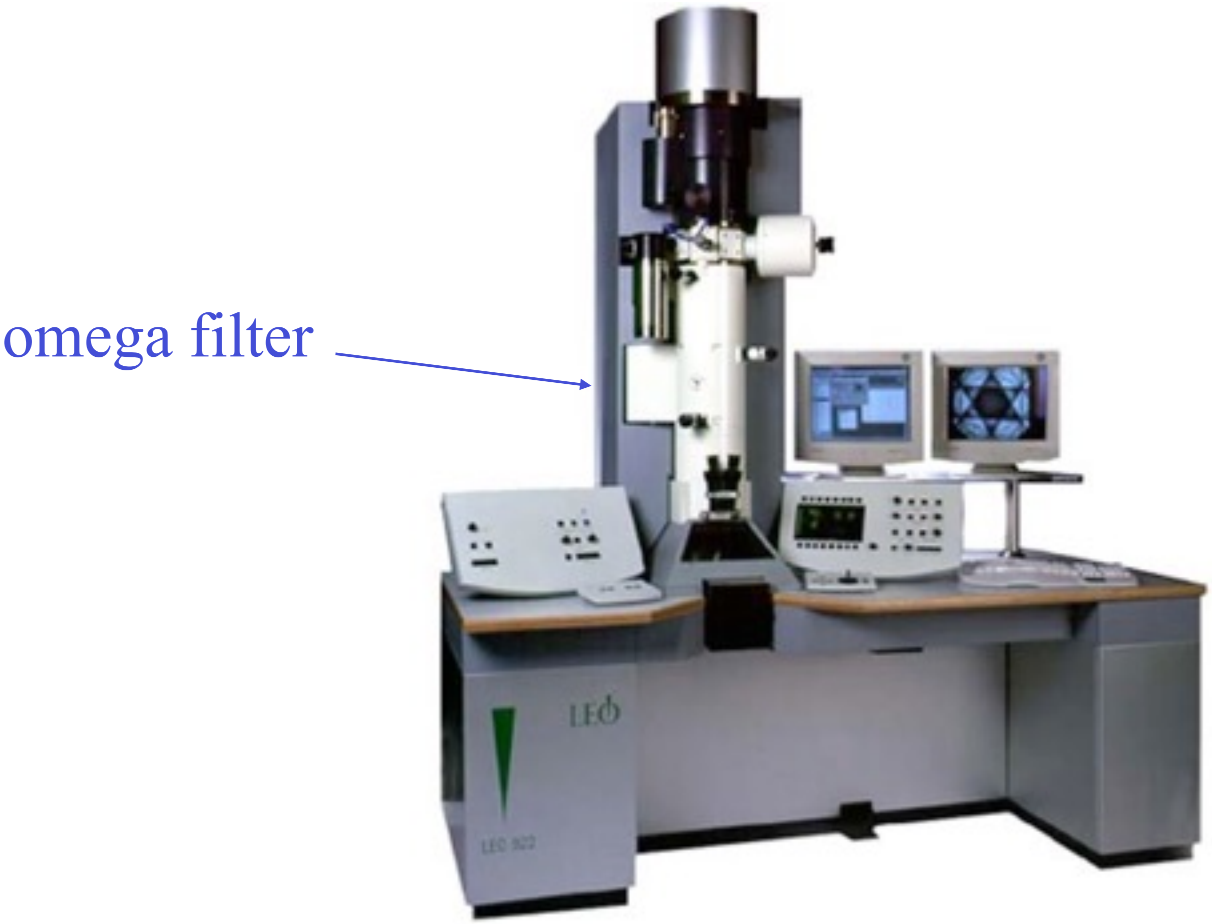
$R = (m/e)(v/B)$



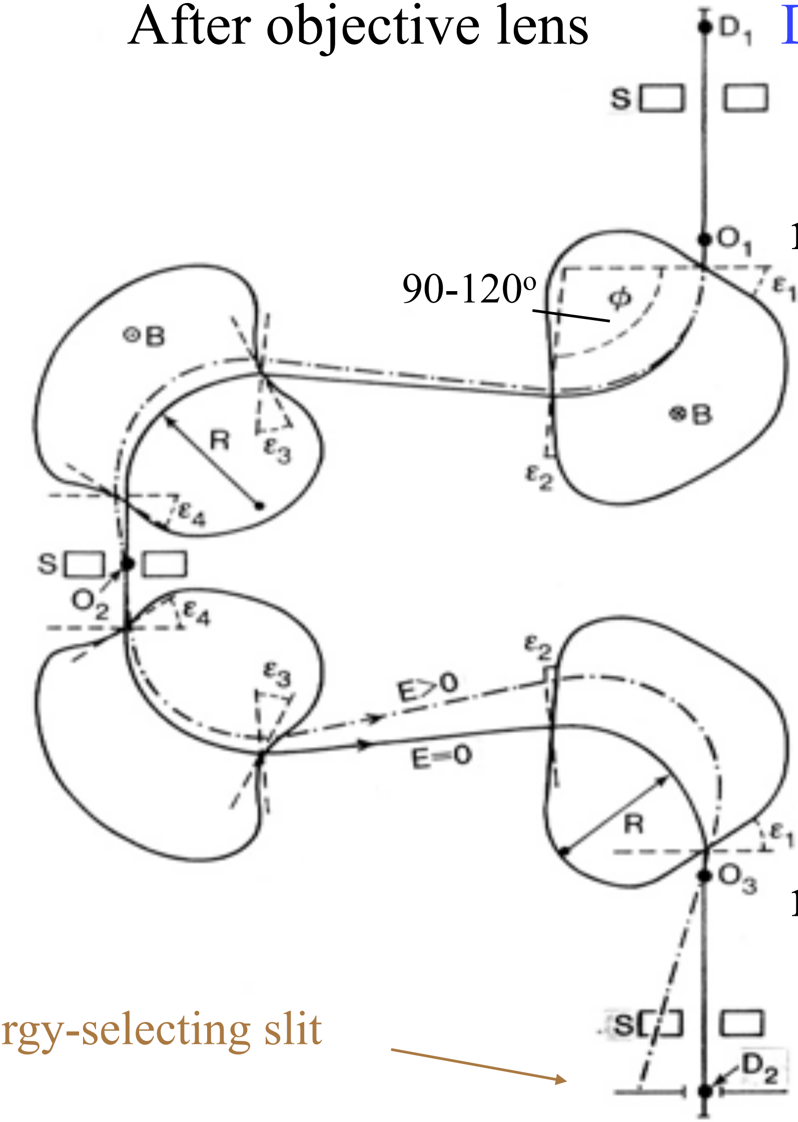
Gatan Image Filter (GIF)



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°

real or virtual image of specimen

energy-selecting slit

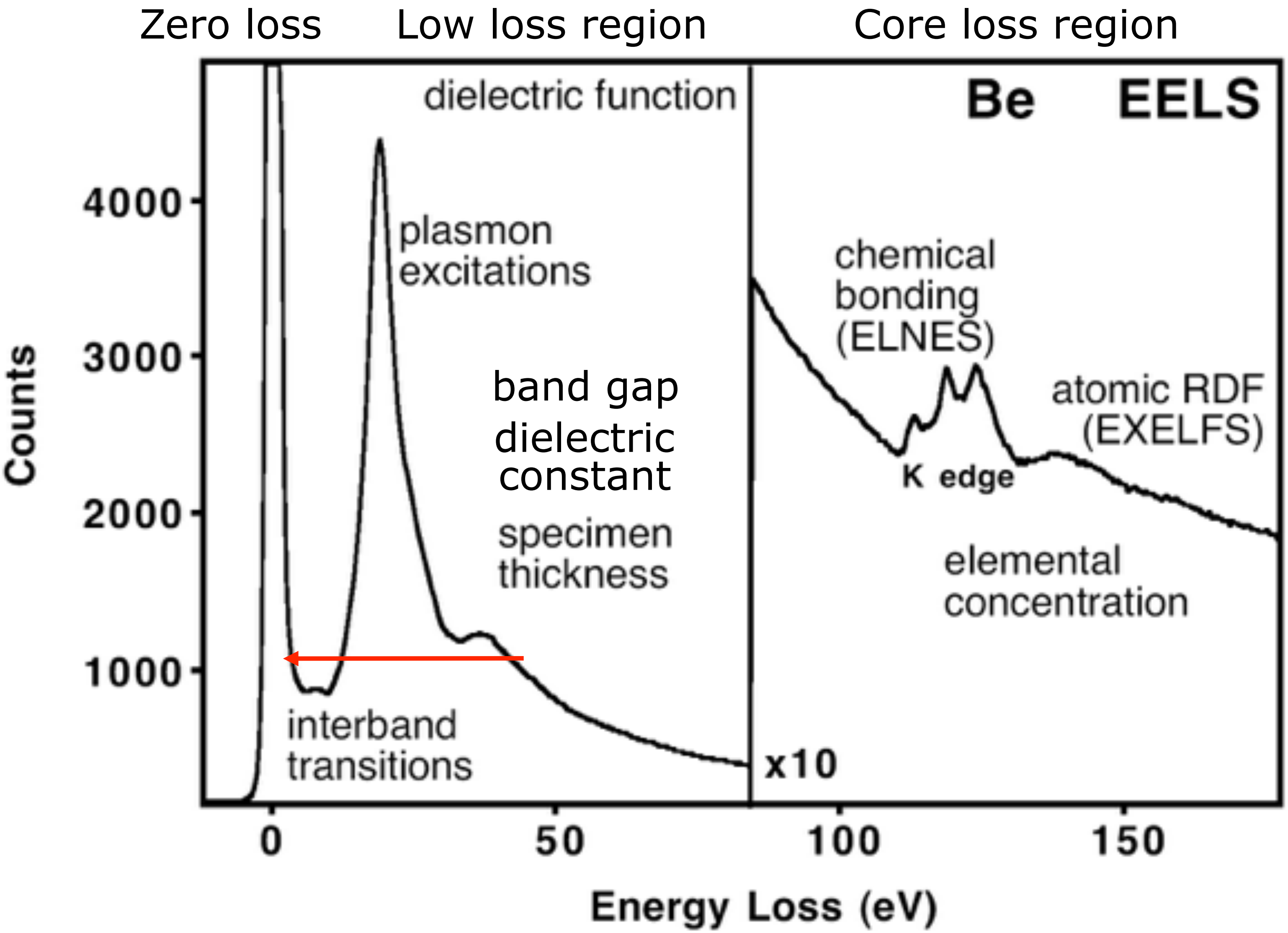
Diffraction pattern

D2 is conjugated with D1

optical axis

Before projector lens

The EELS looks like



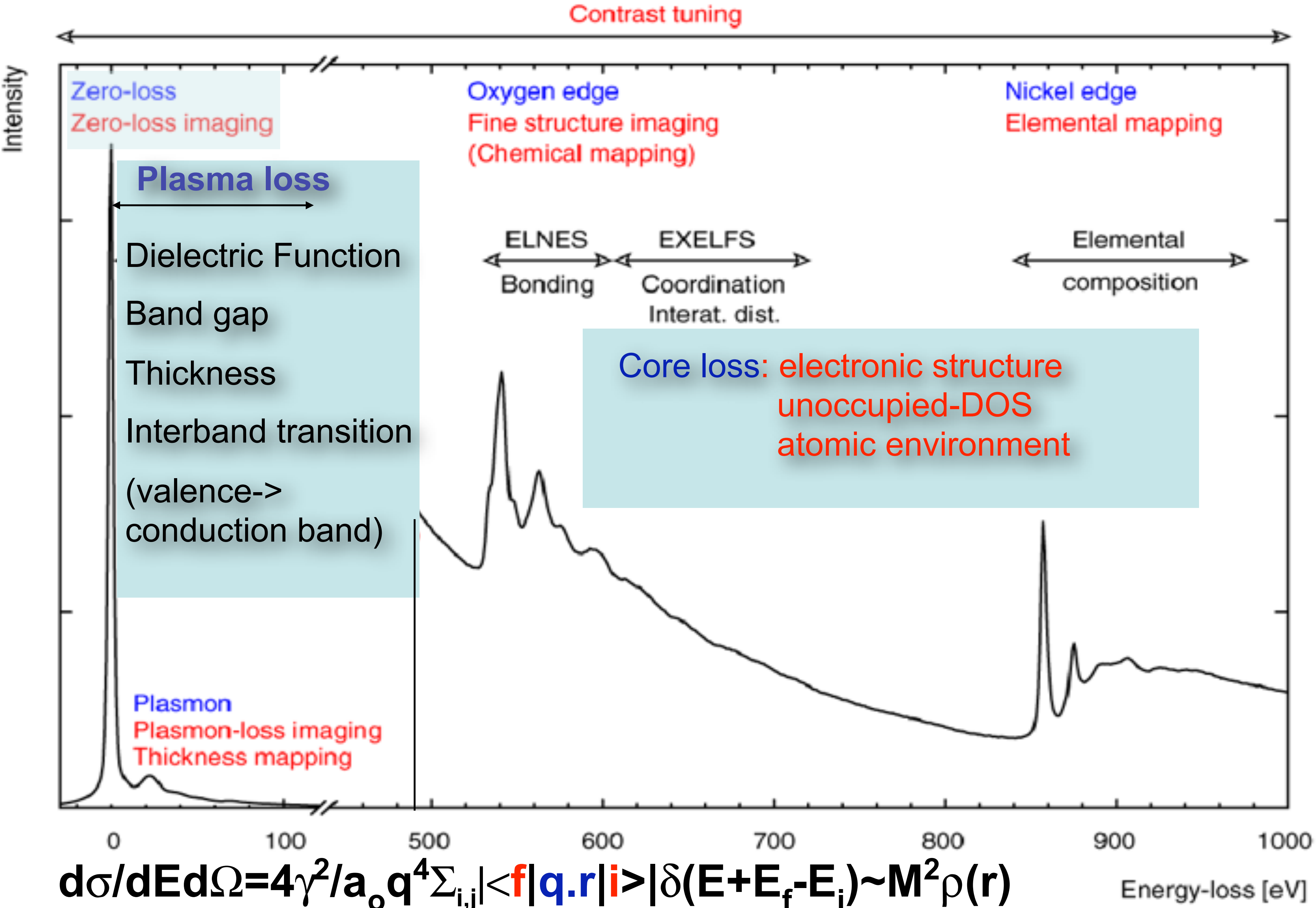
Zero loss

Low loss region

Core loss region

band gap
dielectric
constant

EELS spectral information



Plasma loss

Dielectric Function

Band gap

Thickness

Interband transition

(valence->
conduction band)

Core loss: electronic structure
unoccupied-DOS
atomic environment

$$d\sigma/dEd\Omega=4\gamma^2/a_o q^4\Sigma_{i,j}|<f|q.r|i>|\delta(E+E_f-E_i)\sim M^2\rho(r)$$

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 a 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

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

$$\varepsilon = 1 + \frac{P}{\varepsilon_0 \mathscr{E}}$$

χ is the electronic susceptibility and n is the number of electrons per unit volume

The relative permittivity or dielectric function ε(ω)=1+ χ is then given by

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

ω_p is the plasmon frequency (the frequency ε_1 passes through 0)

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

The energy loss function is defined as

$$\mathrm{Im}[\frac{-1}{\varepsilon(\omega)}] = \frac{\varepsilon_2}{\varepsilon_1^2 + \varepsilon_2^2} = \frac{\omega\Gamma\omega_p^2}{(\omega^2 - \omega_p^2)^2 + (\omega\Gamma)^2}$$

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 : $[Kr]4d^7 5s = 8$ O : $[He]2s^2 2p^4 = 6$

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

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

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

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

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

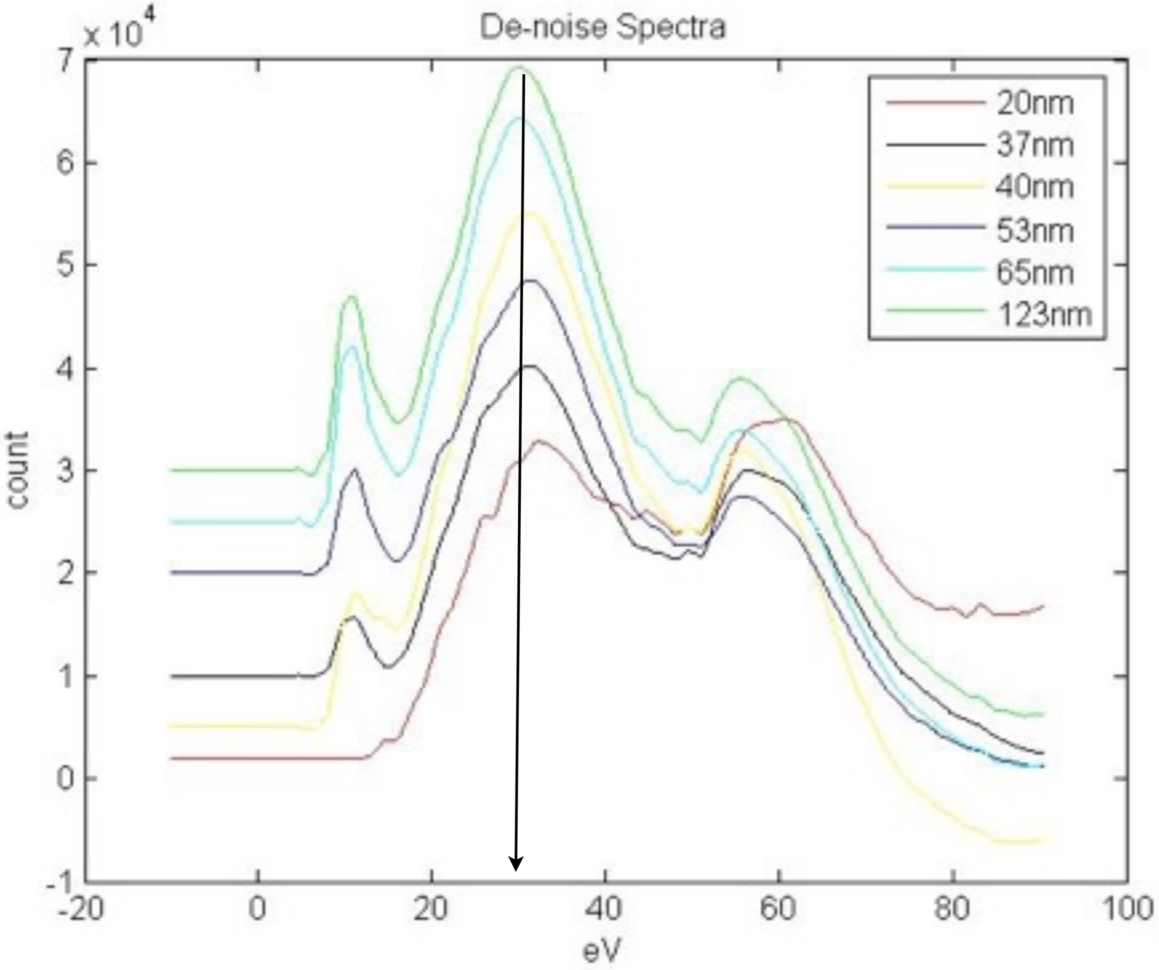
While $m = 9.10956 \times 10^{-31}$ kg

$e = 1.60219 \times 10^{-19}$ C

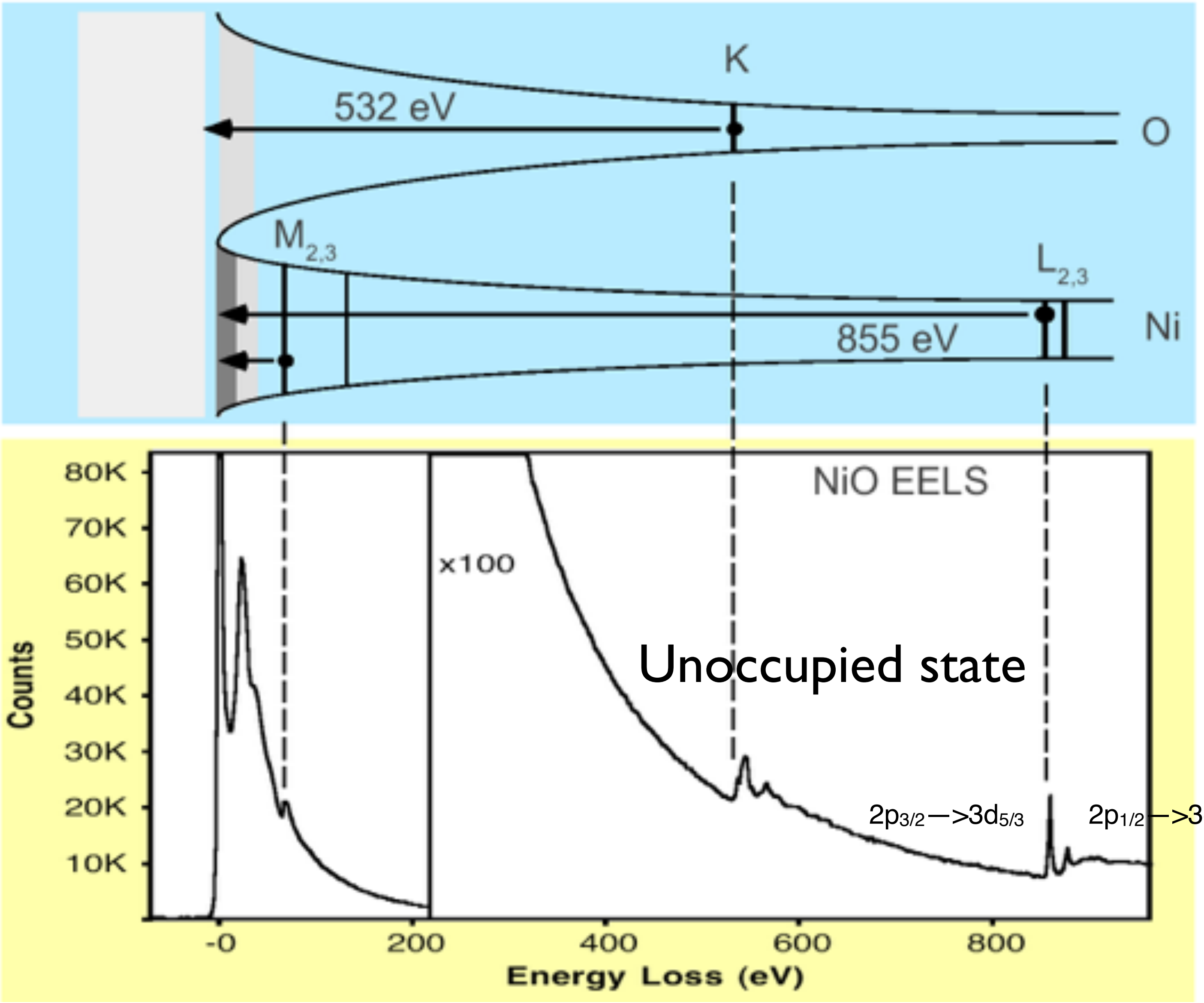
$\varepsilon_0 = 10^7/4\pi c^2 = 8.842 \times 10^{-12}$

1 eV=1.60219×10^{-19} J

Plasmon loss from RuO2 nanowires



Correlating electron energy levels with EELS edges

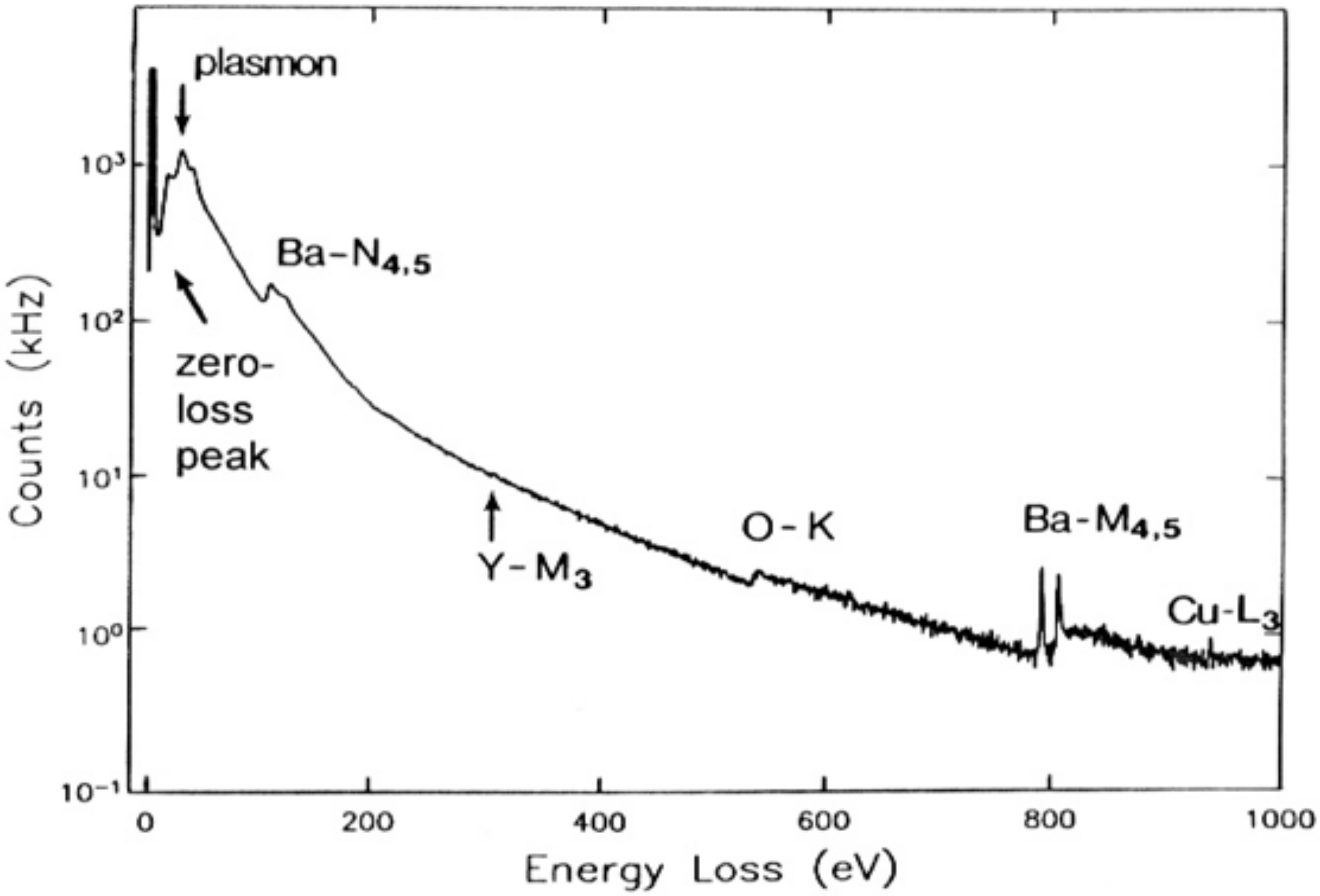


Unoccupied state

$2p_{3/2}$—>$3d_{5/3}$

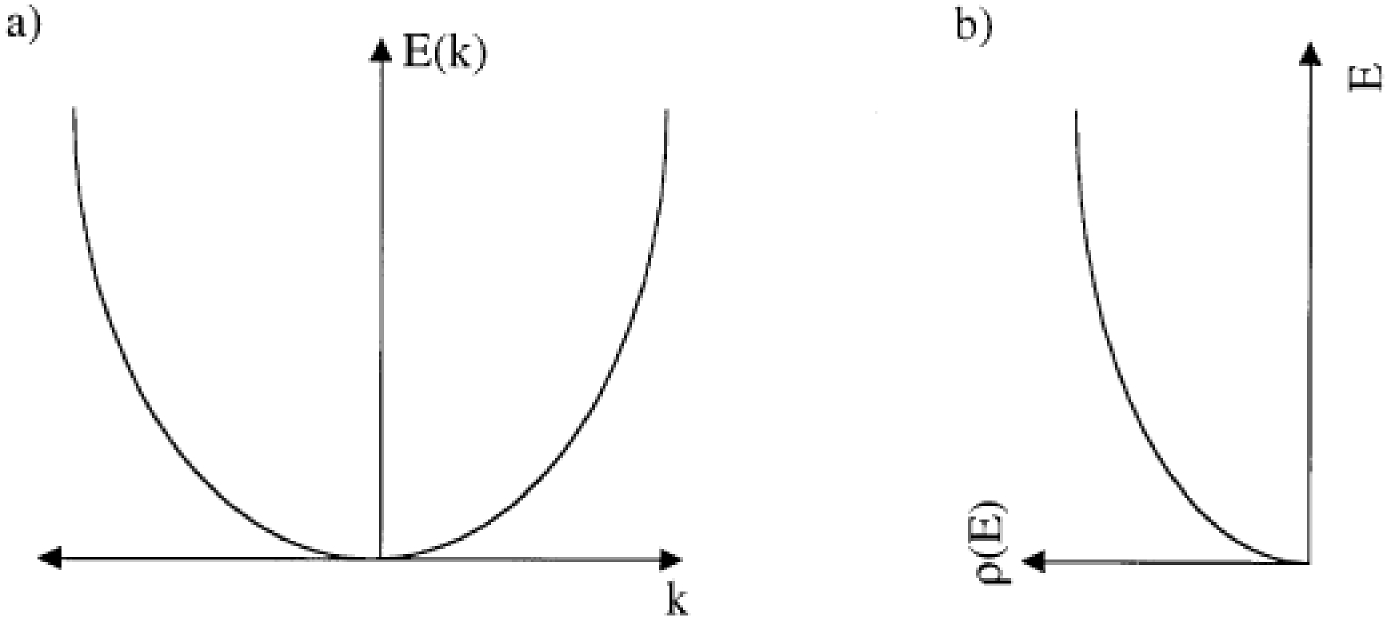
$2p_{1/2}$—>$3d_{2/3}$

Energy-loss spectrum (log-intensity) of YBCO

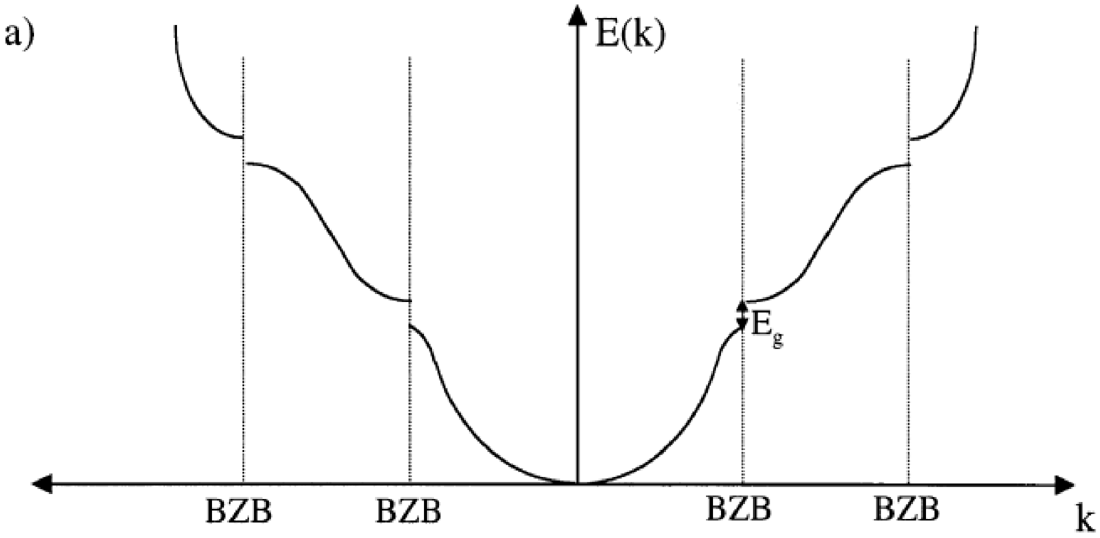


$$E(k) = \hbar^2 k^2 / 2m$$

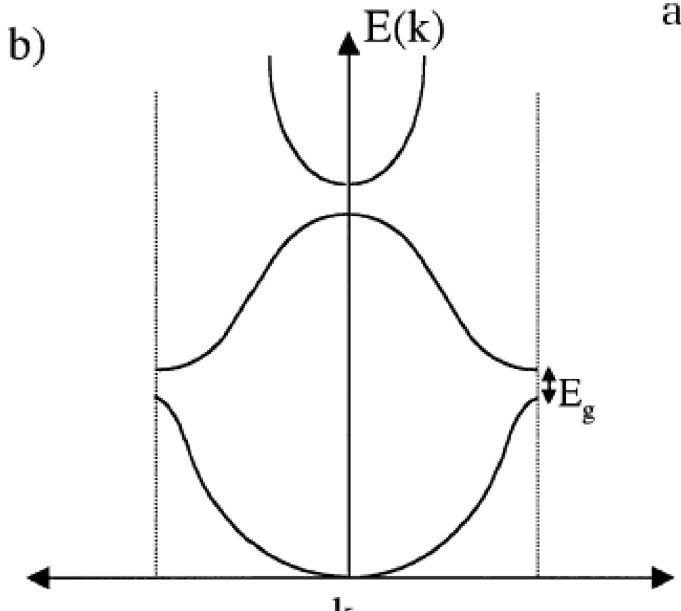
$$\rho(E) = \frac{\Omega}{\pi^2 \hbar^3}(2m^3 E)^{\frac{1}{2}}$$

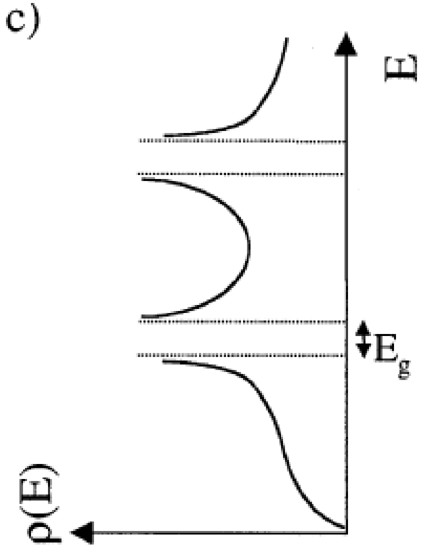


(a) Energy dispersion curve and (b) DOS (ρ(*E*)) for an electron in a square potential well with infinite sides.



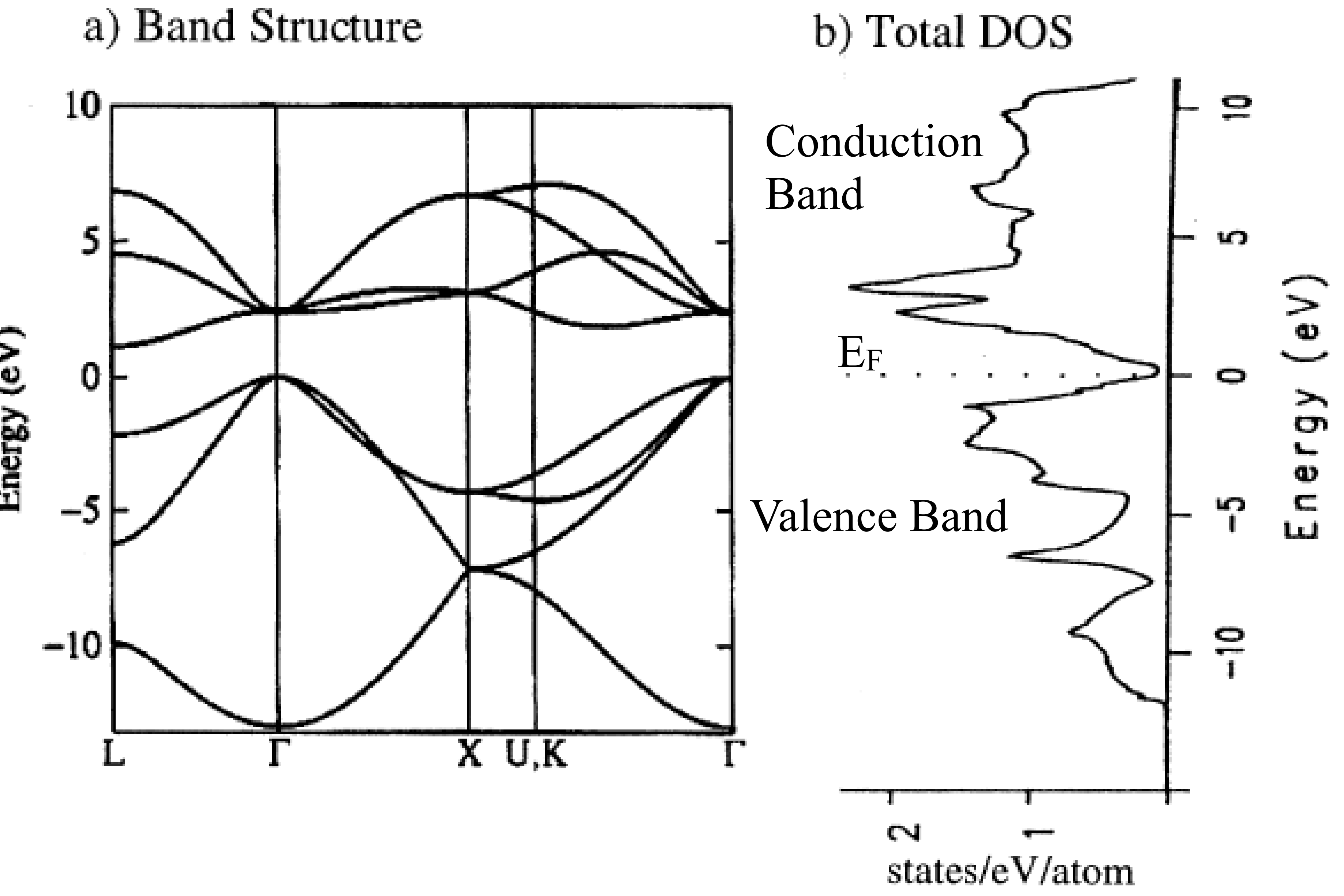
Simplistically speaking, this means that flat regions in a band structure diagram will correspond to peaks in the DOS and therefore peaks in the ELNES.





$$\rho(E) = \int_{S(E)} \frac{1}{|\nabla E(k)|} \frac{\mathrm{d}S}{4\pi^3}$$

Band Structure of Si


a) Band Structure

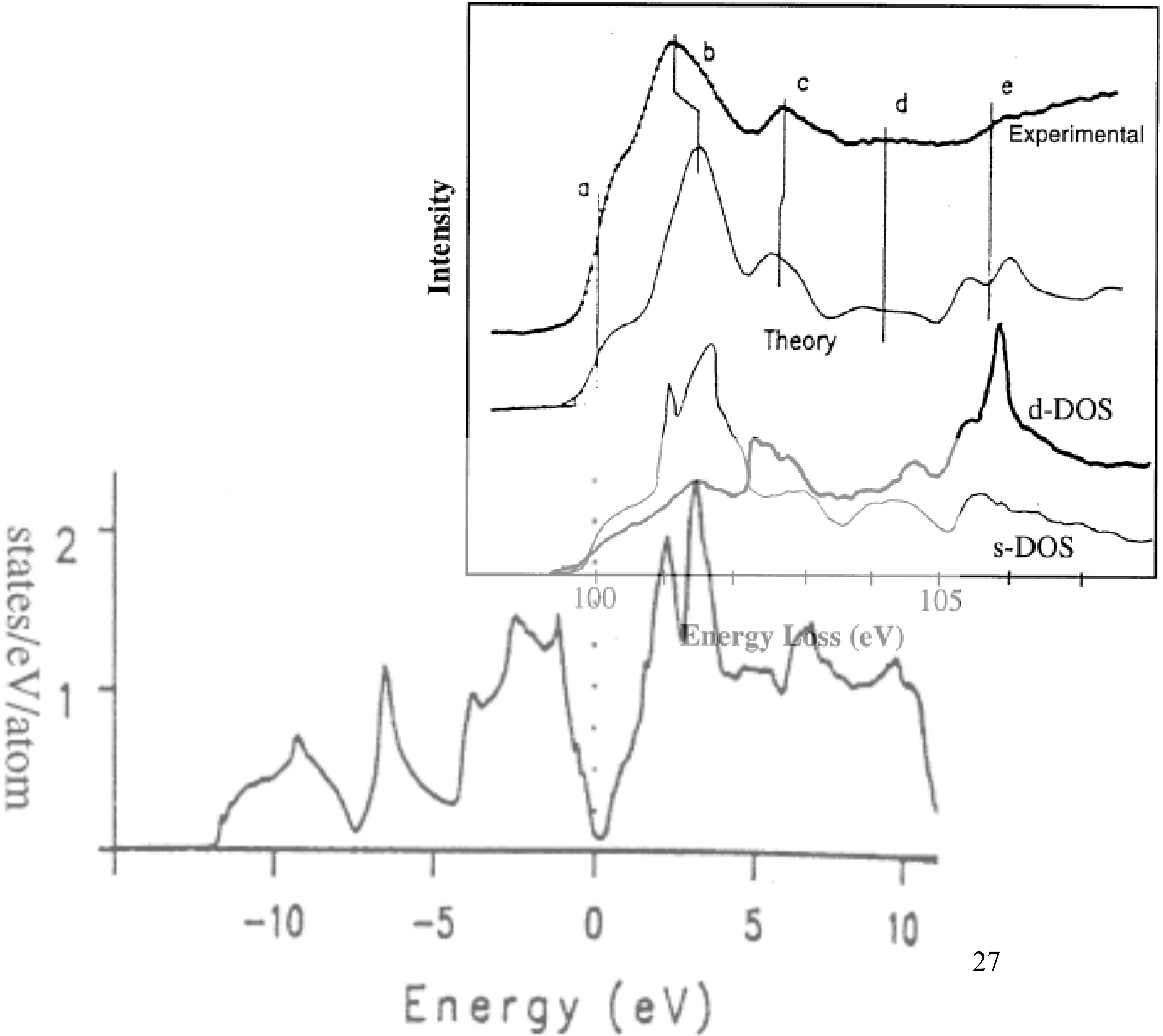
b) Total DOS

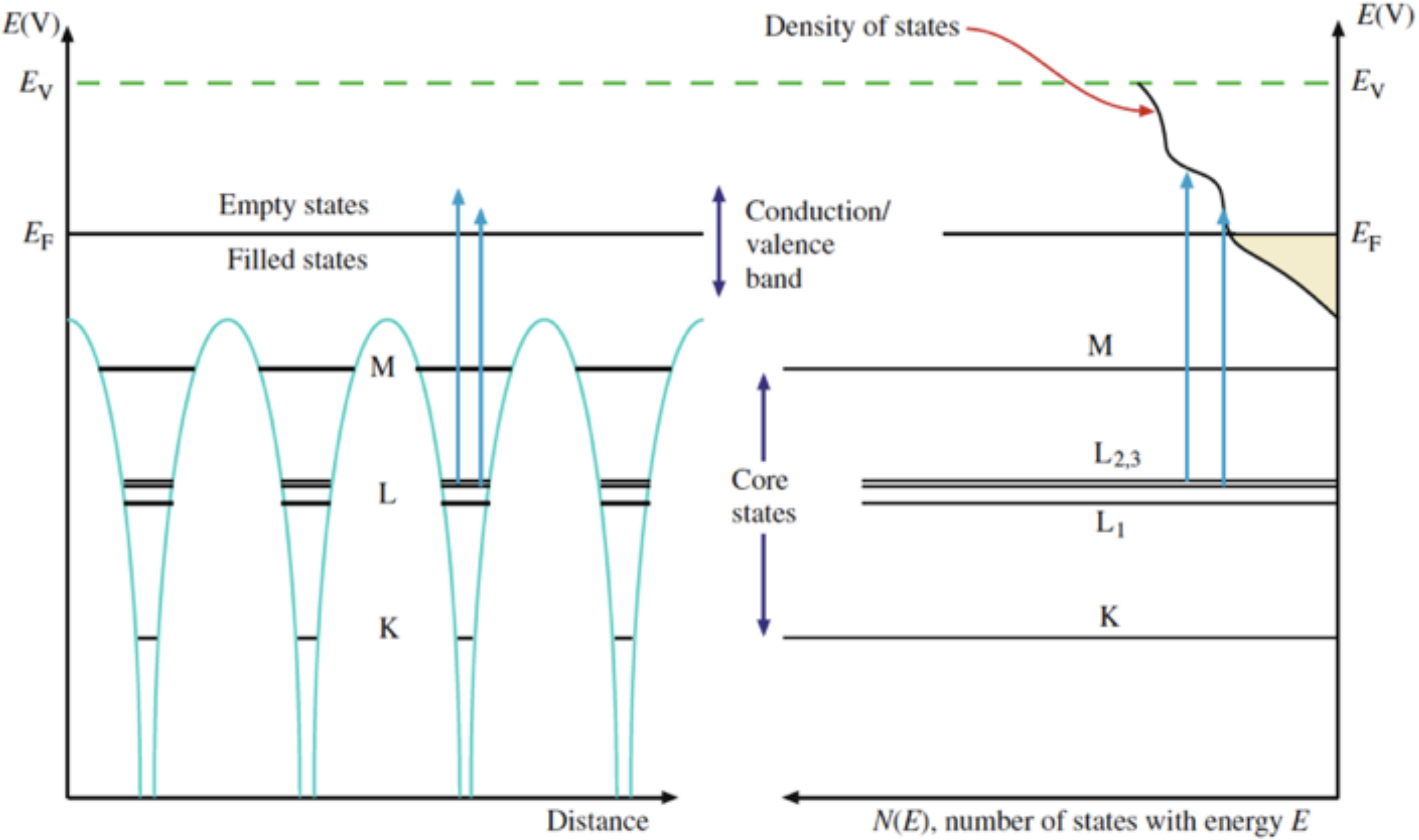
Conduction Band

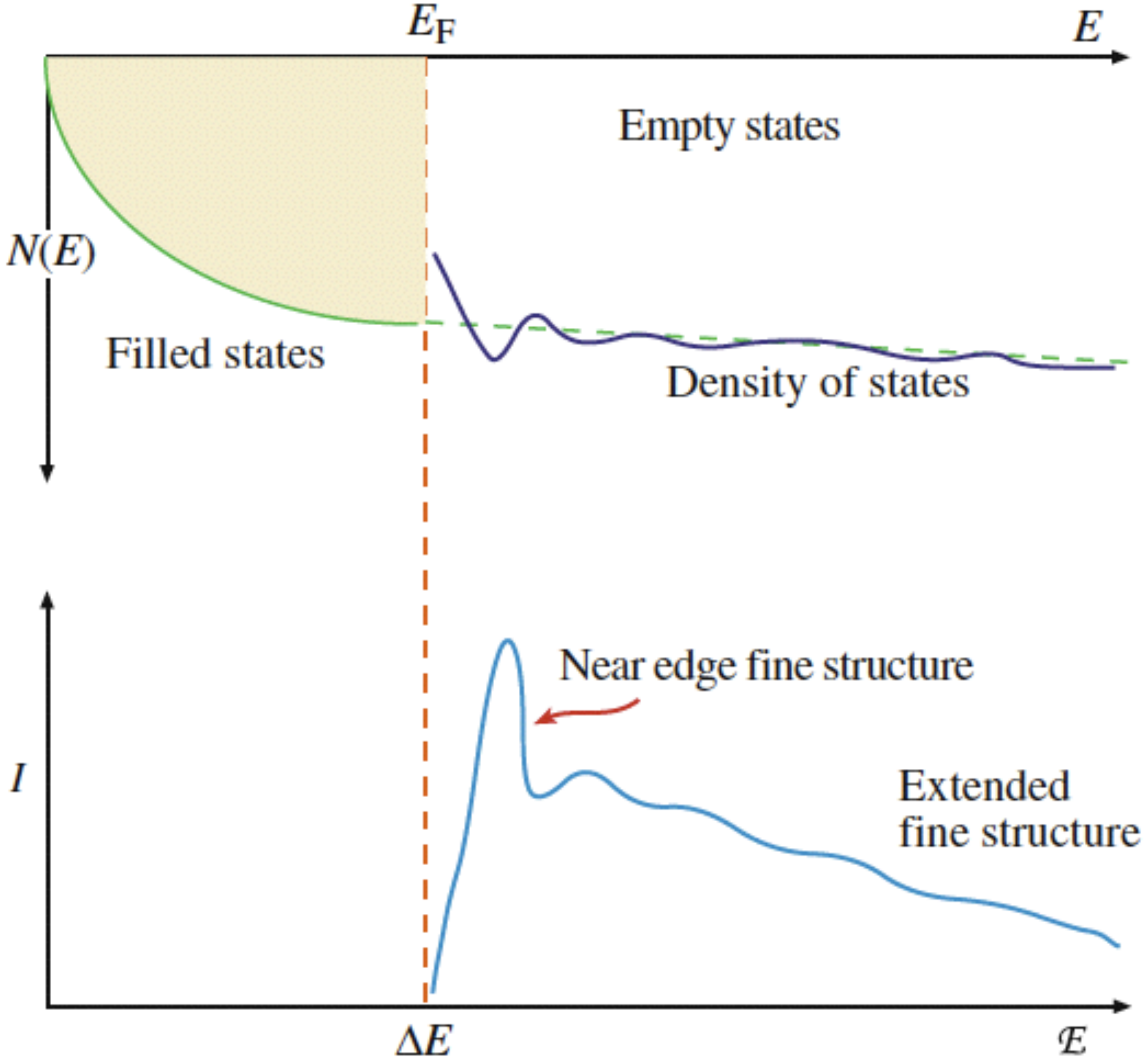
E_F

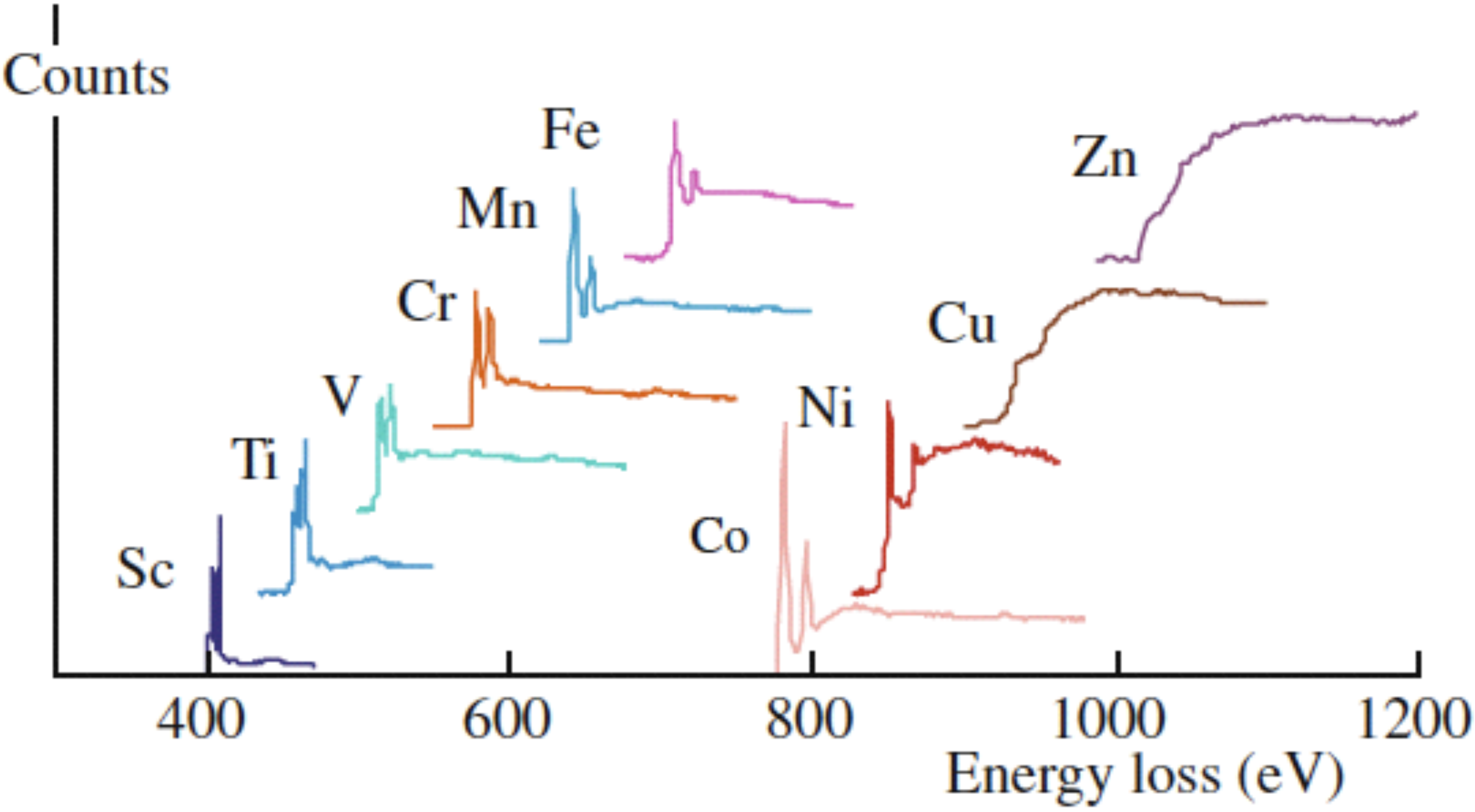
Valence Band

c) Si L_{23} edge


Intensity
a
b
c
d
e
Experimental
Theory
d-DOS
s-DOS
100
105
Energy Loss (eV)
states/eV/atom
2
1
−10
−5
0
5
10
Energy (eV)


E(V)
E_V
E_F
Empty states
Filled states
M
L
K
Distance
Conduction/
valence
band
Core
states
Density of states
E(V)
E_V
E_F
M
L_{2,3}
L_1
K
N(E), number of states with energy E


E_F
E
Empty states
$N(E)$
Filled states
Density of states
I
Near edge fine structure
Extended
fine structure
ΔE
$\mathcal{E}$


Counts
Fe
Mn
Cr
V
Ti
Sc
Zn
Cu
Ni
Co
400
600
800
1000
1200
Energy loss (eV)

What EELS can do

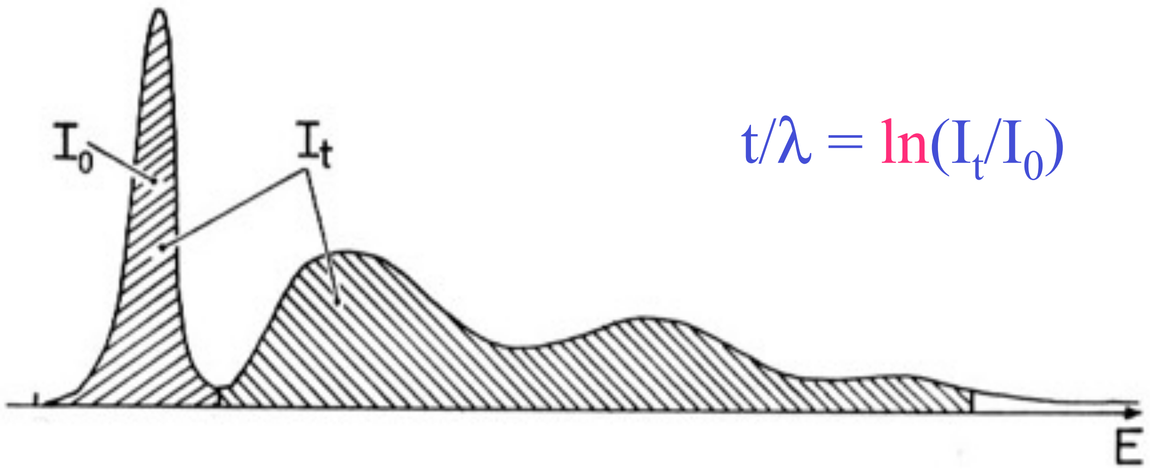
Typically applied to:

* 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



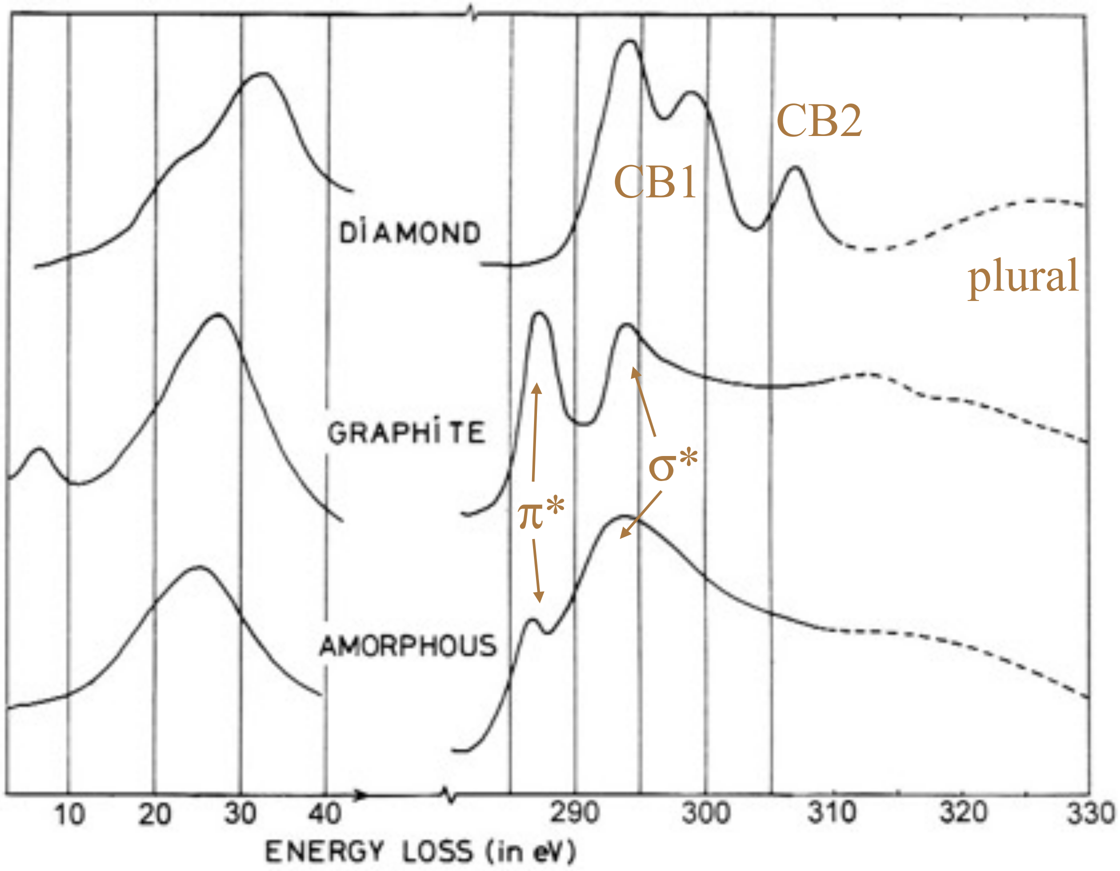
$t/\lambda = \ln(I_t/I_0)$

$\lambda \sim 100$ nm but depends on Z, E_0 and β

Value obtained from calibration specimen
or from tables (for common materials)
or from parameterized formula

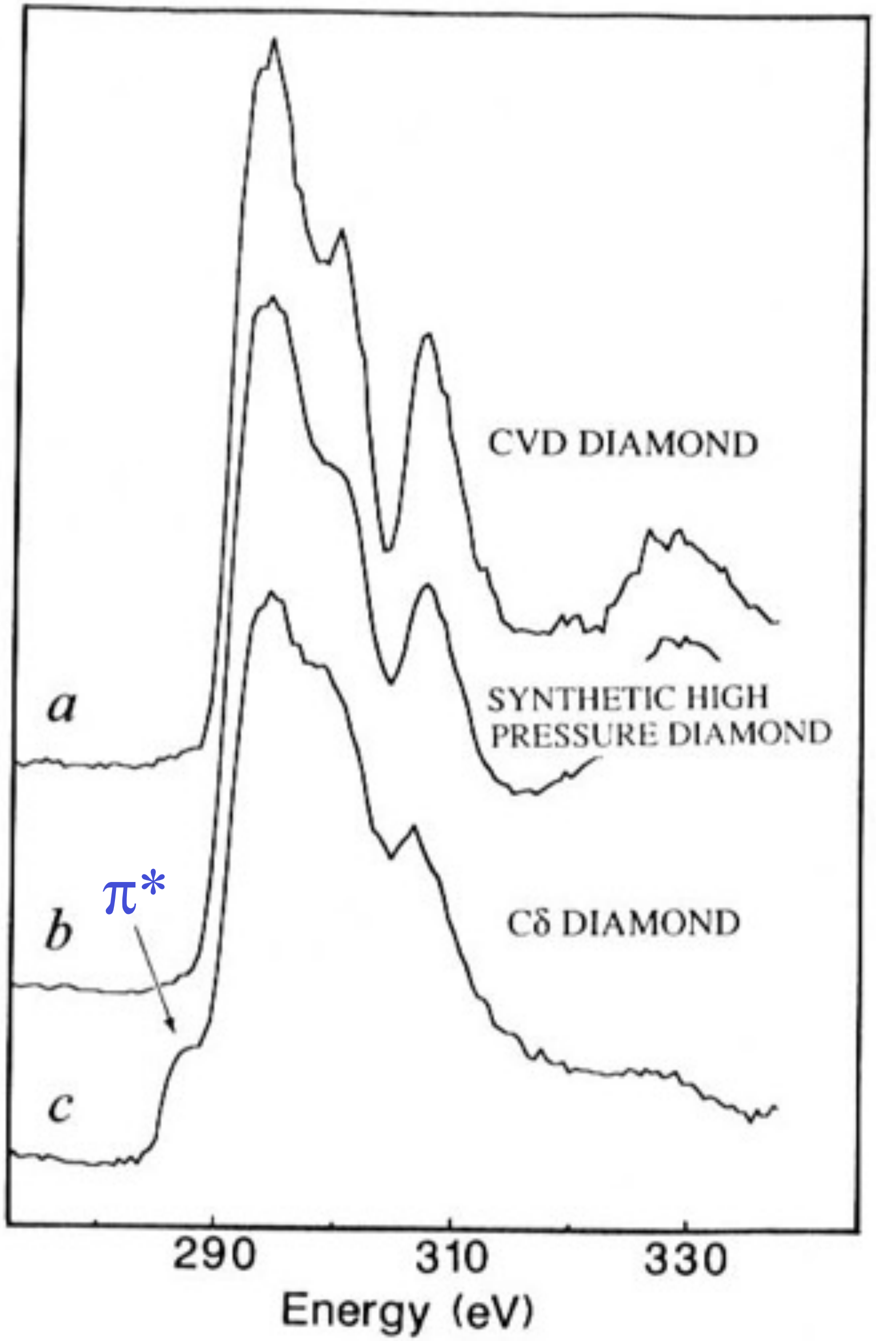
EELS fine structure

(Egerton and Whelan, 1974)



K-edge spectra of diamond and grain from the Allende meteorite

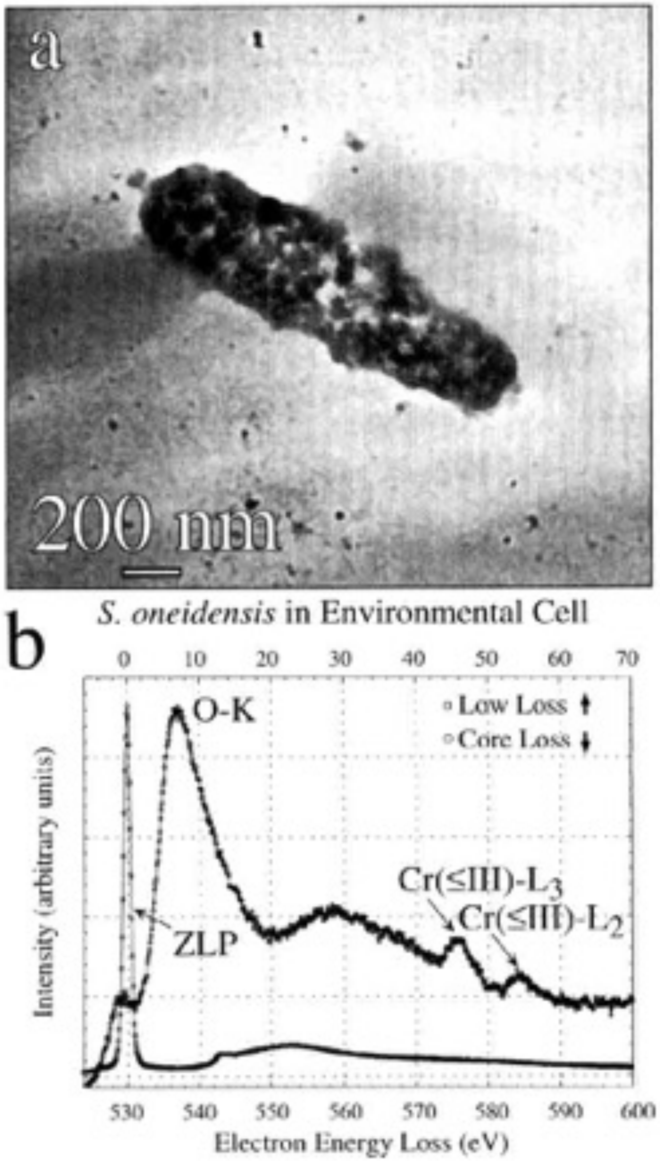
(Blake et al., Nature **332**, 1988, 611)

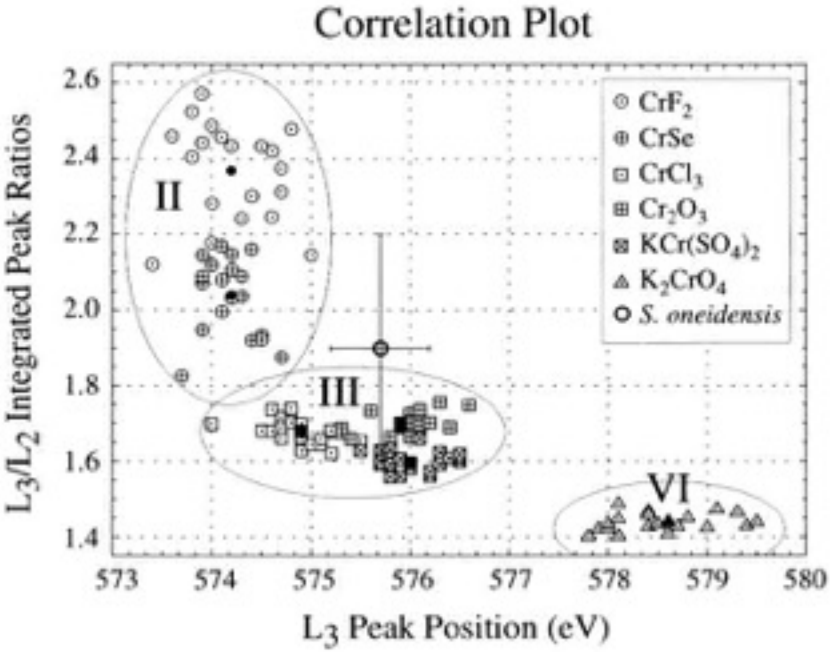


Oxidation state of Cr in a bacterium

(Daulton et al,

M&M **7**, 479, 2001)

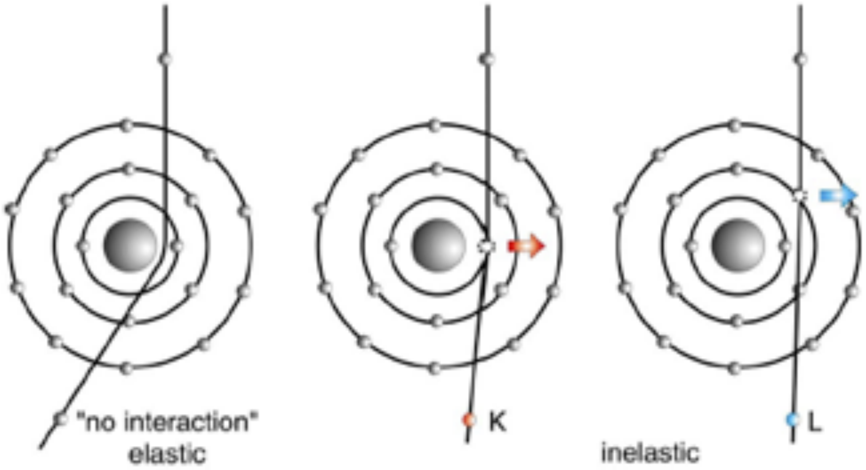


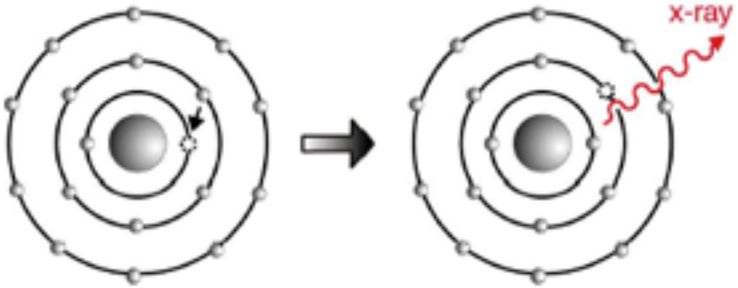


Compare the EELS and EDX technique

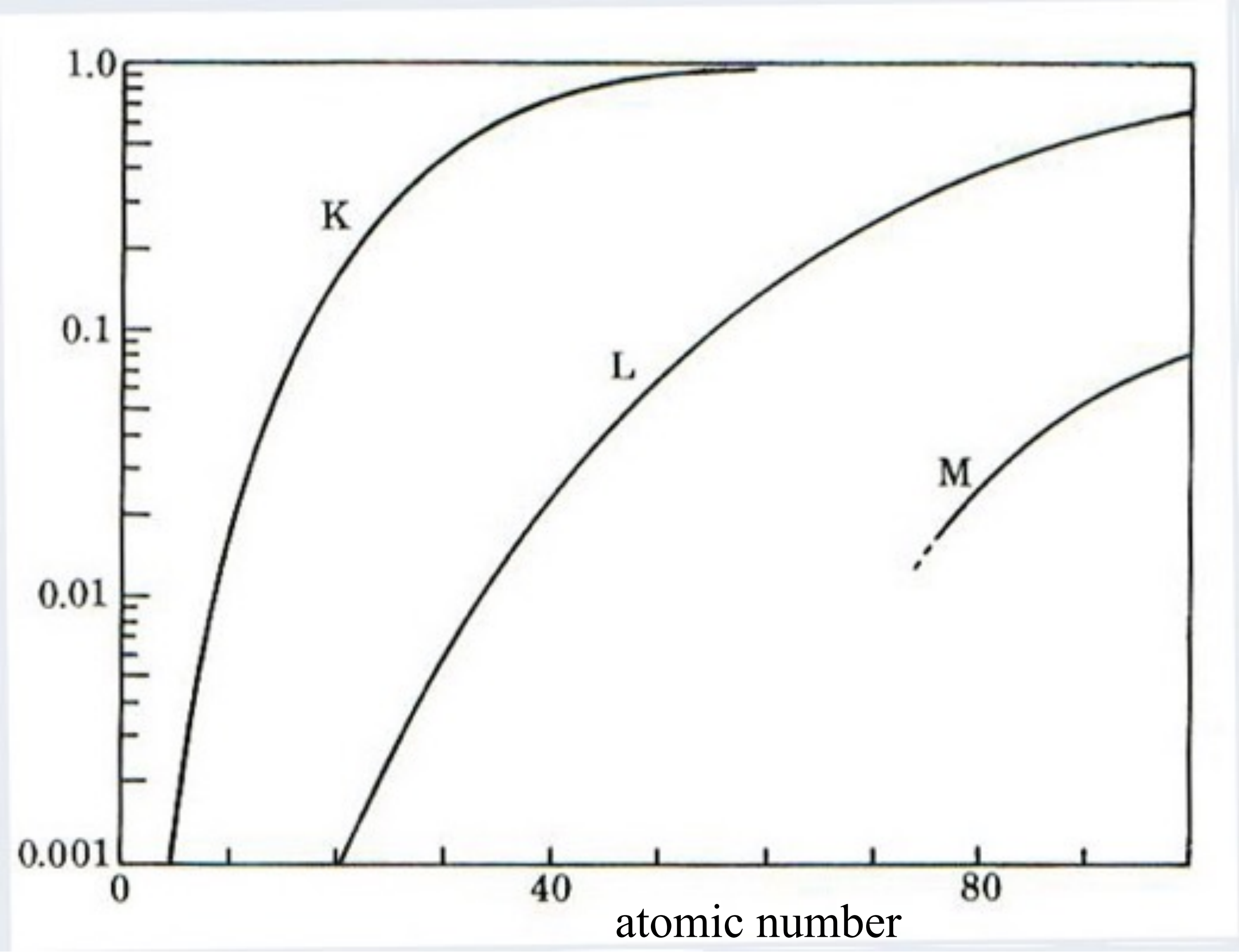
- Prior to the 1980, most EDX detector were protected (from the water vapor and hydrocarbon in the microscope column) by a 10μm thickness beryllium window, which strongly absorbs photons of energy less than 1000eV and percludes analysis of elements of atomic number less than 11.
- With development of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


EELS signal generation


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.

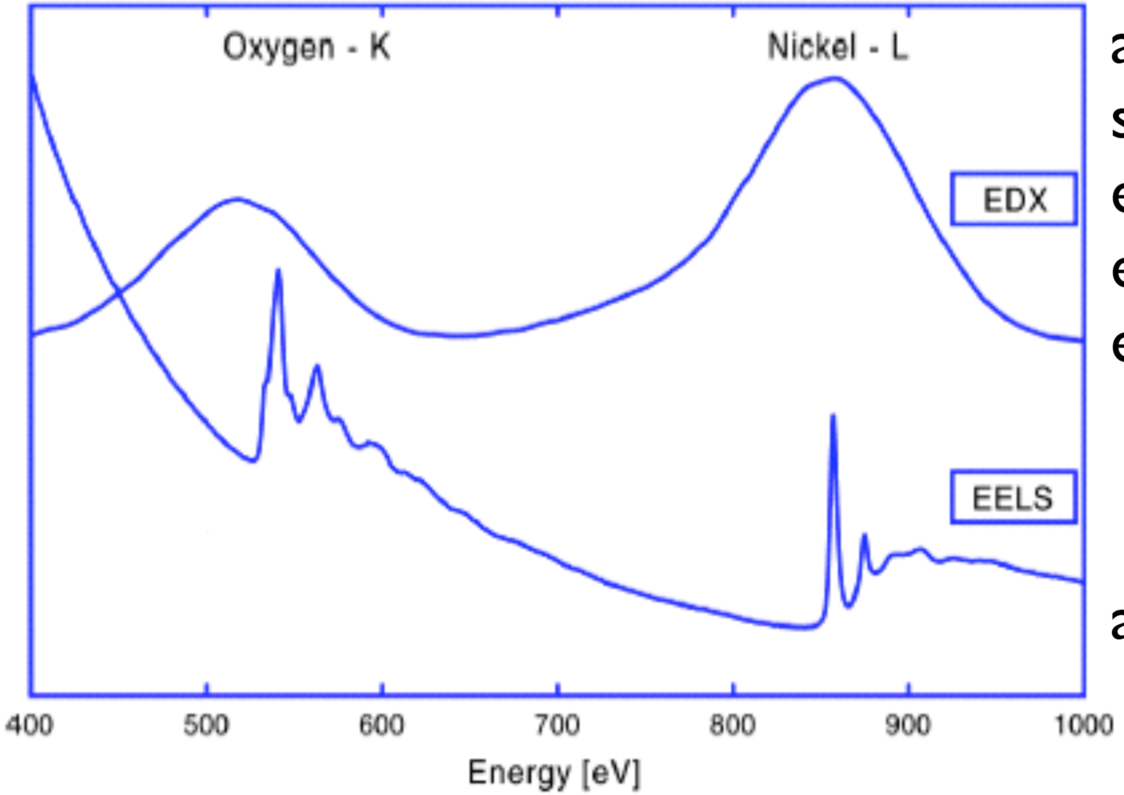
- the signal of EELS concentrates in a small angle range of the transmitted beam, but the EDX signal spans around larger angle range.

(a) These two cause EELS has higher core loss signal

(higher Signal to noise ratio, EELS has less recording time)

X-ray and EELS spectra

(b) EDX has better Signal/ background ratio

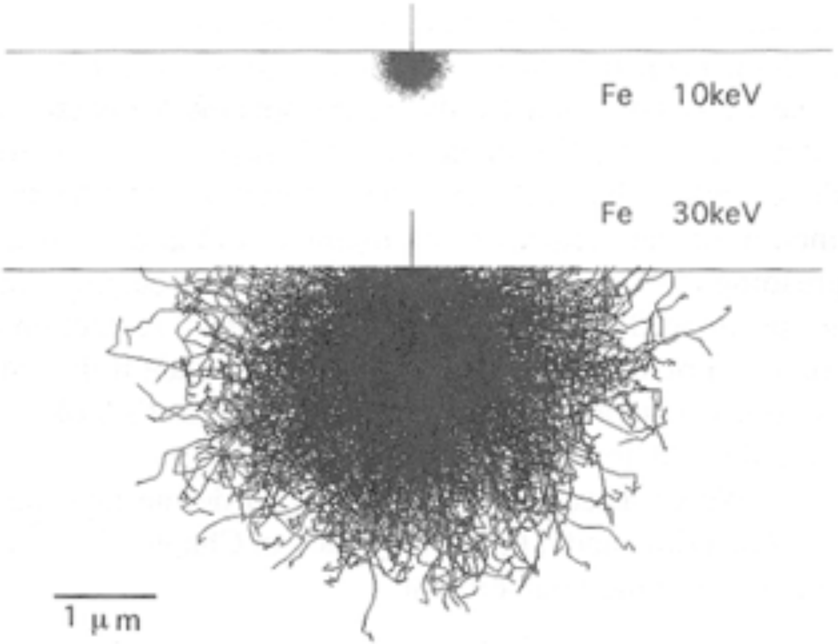


Background of EELS:
arises from the inelastic scattering from the atomic electron whose binding energy less than the edge energy

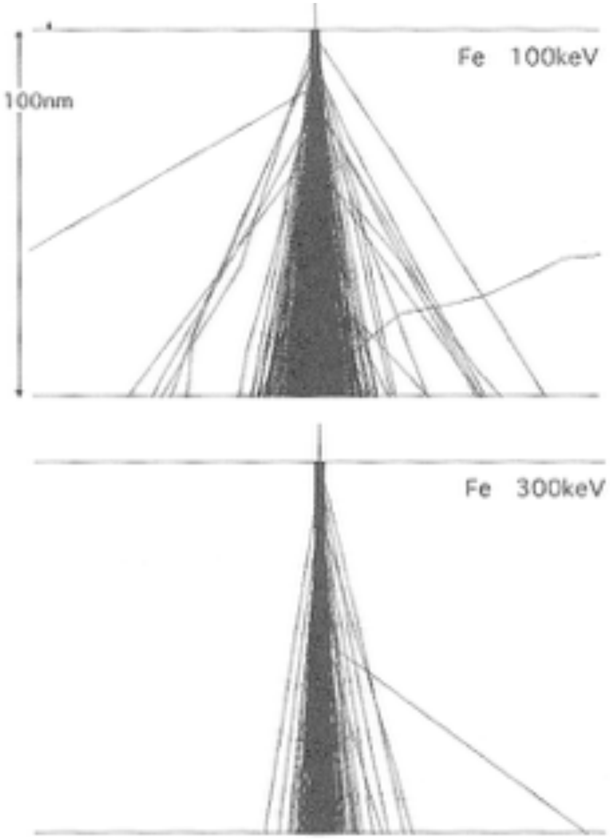
Background of EDX:
arises from bremsstrahlung

The beam broaden effect

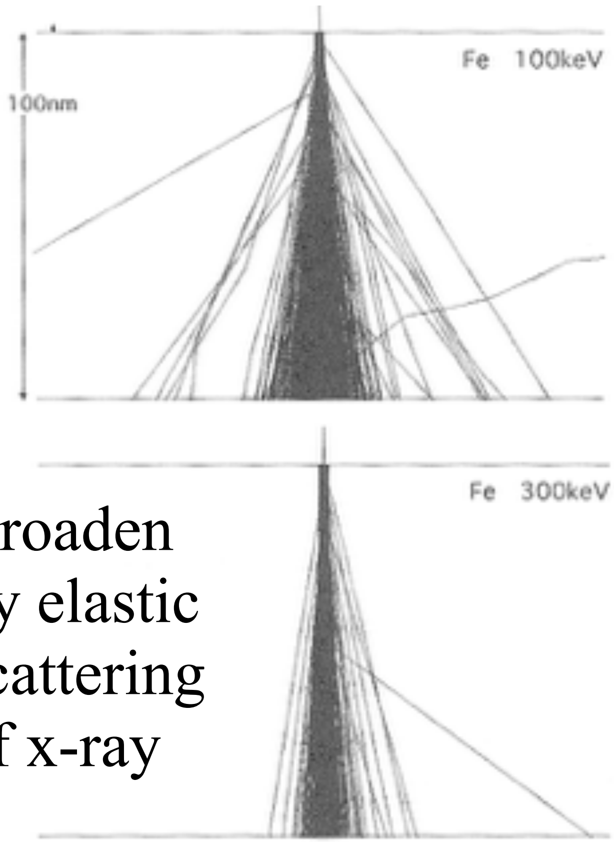
EDX bulk beam broaden size for SEM system



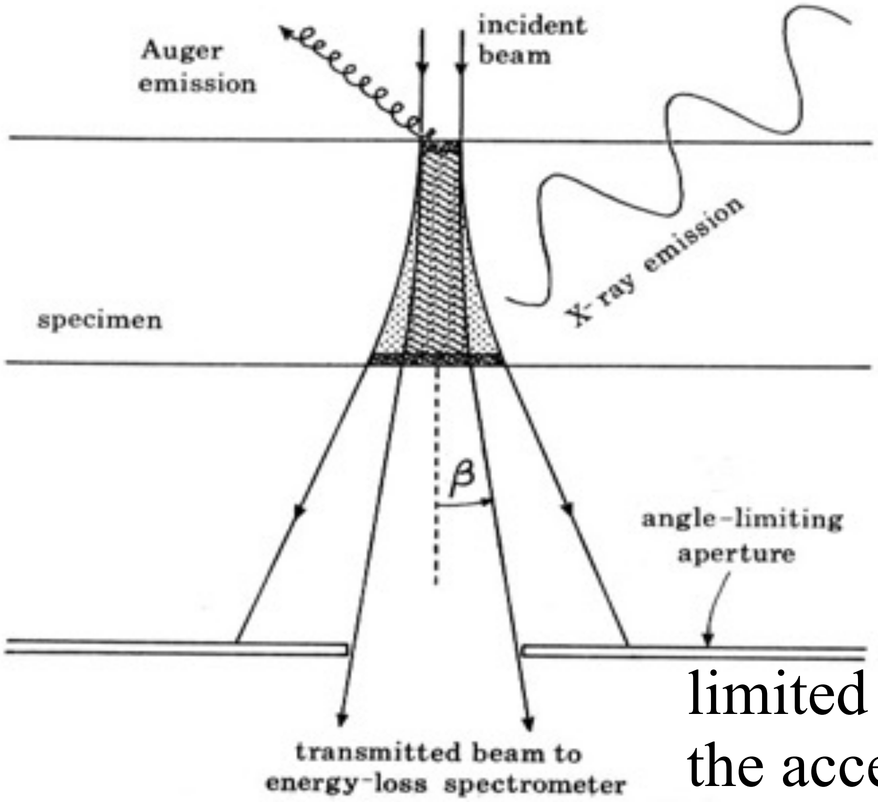
EDX thin film (TEM) beam broaden size



(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

Beam broaden formula:

density

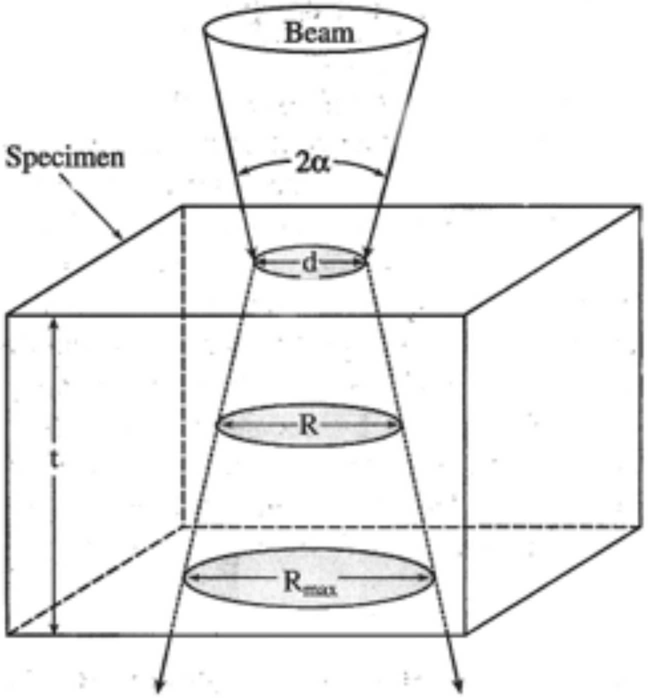
The EDX spatial resolution limit

Energy of Indicate

electron beam

The EDX spatial resolution (R) equation:

$$R = \frac{d + R_{\max}}{2}$$



For example:

Specimen thickness :100nm, b is about 10nm

Nano EDX Beam size (d) :0.5 nm

The resolution limit: *R=5.25 nm*

atomic weight

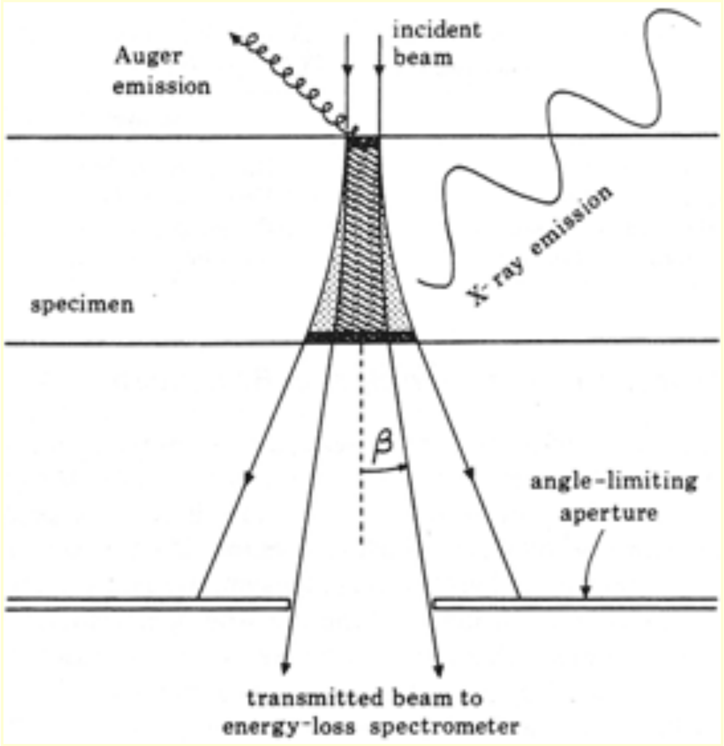
Follow previous slice, the beta angle for EDX is about 0.82 rad=820mrad

For EELS image mode, the beta angle is about 13.06 mrad

For example:

The beam size is about 0.5nm;
specimen thickness is about 100nm
The EDX beam R_{max} is 5.256nm
EELS R_{max} is about 0.6nm

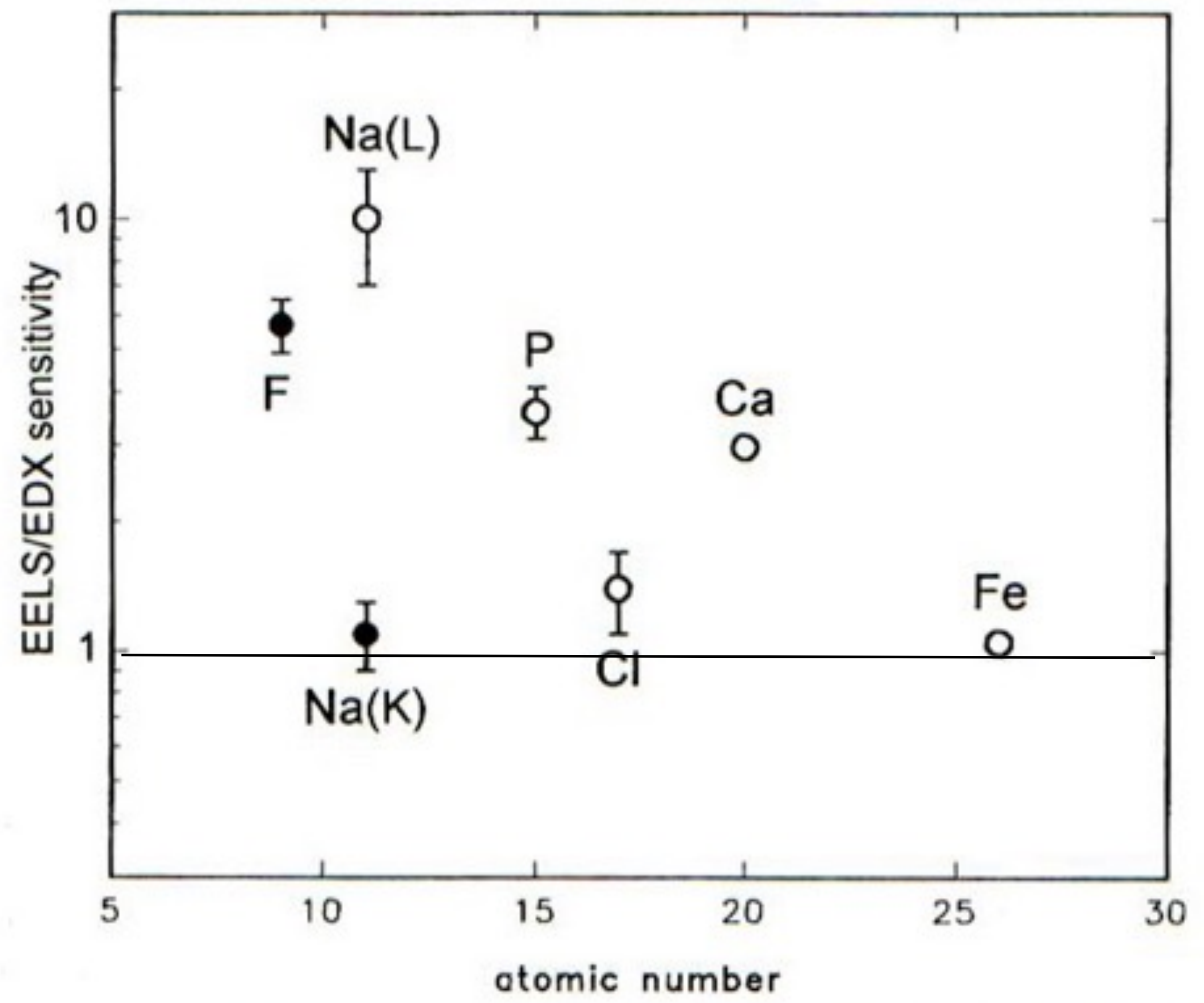
de-localization of energy loss electron



- (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.)

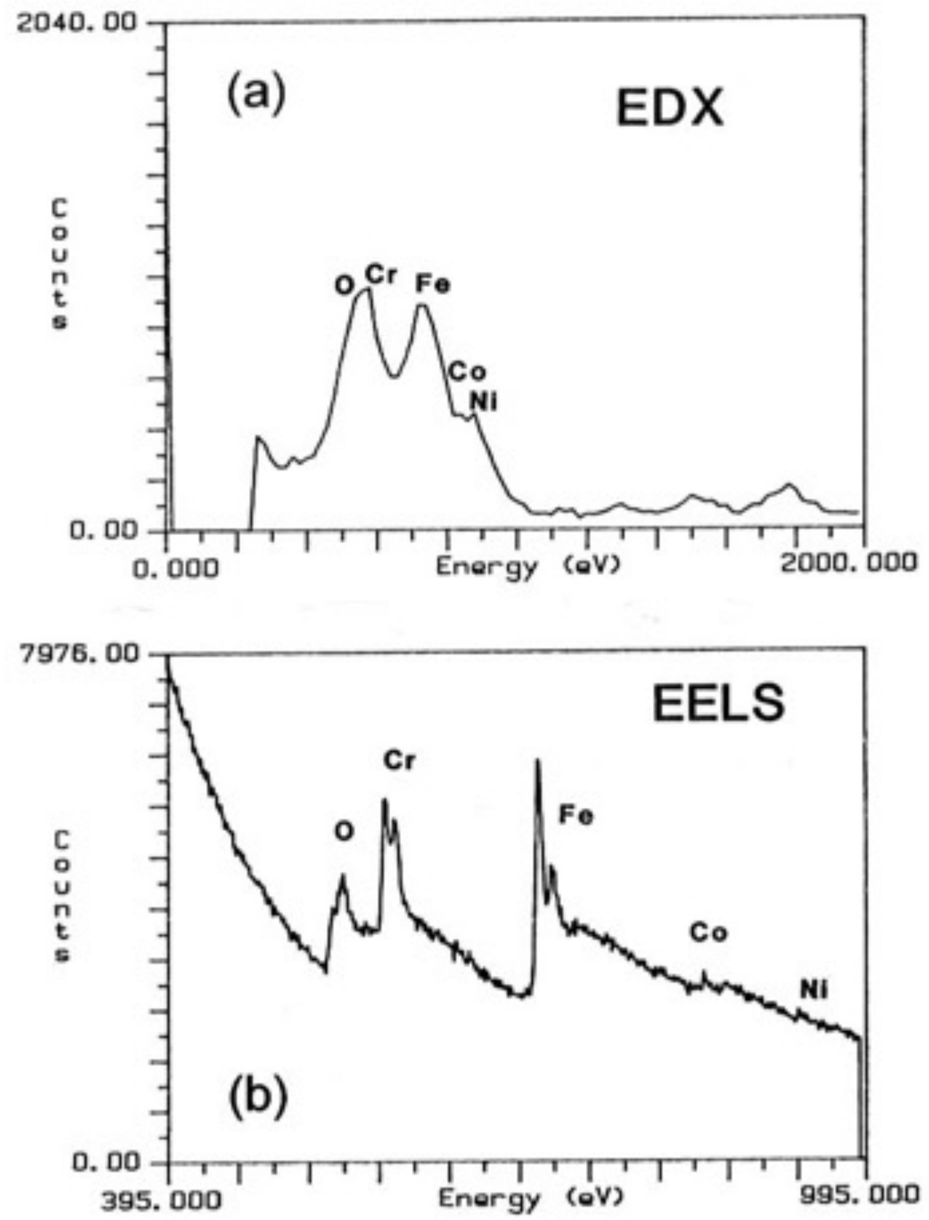
EELS is capable of detecting smaller concentrations of elements of low atomic number



(g) EDX resolution is 50 - 100 eV so there is peak overlap below 1000eV

EELS resolution is ~ 1 eV so edge overlap can be less

(stainless steel, Zaluzec 1984)

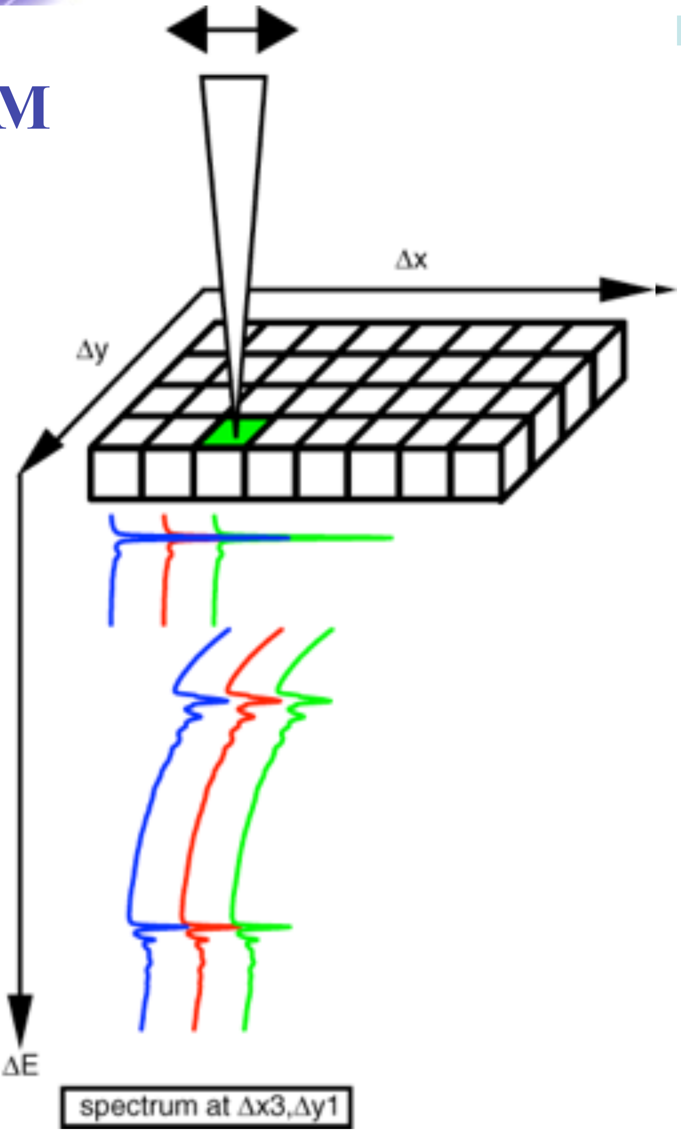


EELS vs. EDXS

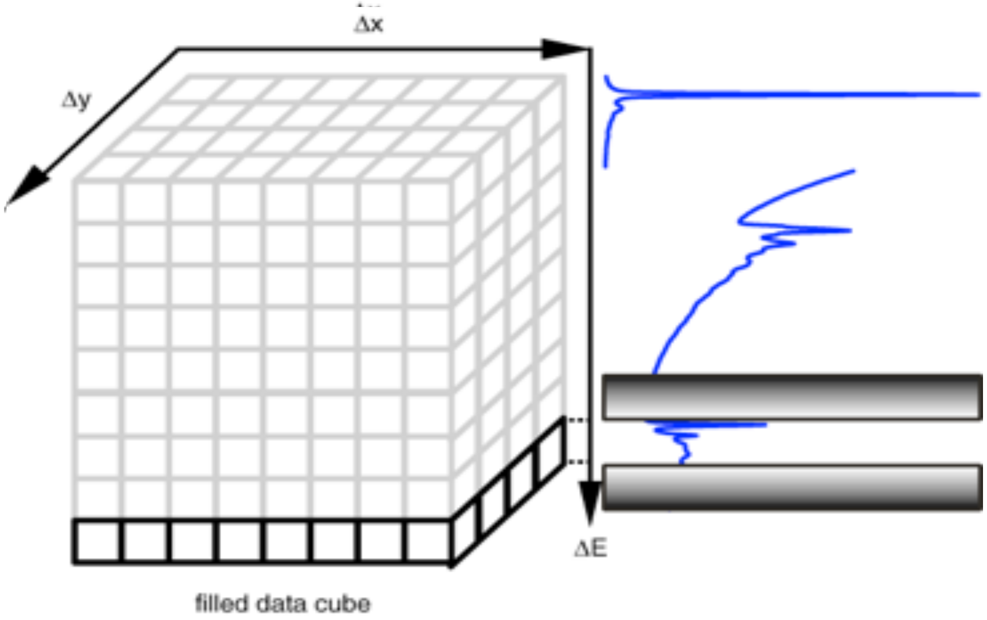
EDXS	EELS
X-rays provide elemental information only	Elemental, Chemical, & Dielectric information
Inefficient signal generation, collection &detection inefficient x-ray mapping	Very efficient in every respect => higher sensitivity to most elements very efficient mapping technique
Slow technique (hours)	Fast technique (seconds to minutes)
X-ray spectra can contain information from column and other parts of sample	EELS spectra have no such artifacts
High detection efficiency for high Z elements	High detection efficiency for low Z elements
Energy resolution > 100eV causes frequent overlaps	Energy resolution 0.3-2eV gives far fewer overlaps
Only simple processing required	More complex processing required => *Needs more hardware & software automation*

擷取可以定量分析之三維空間EELS訊息I(x,y, ΔE)。

- **STEM**

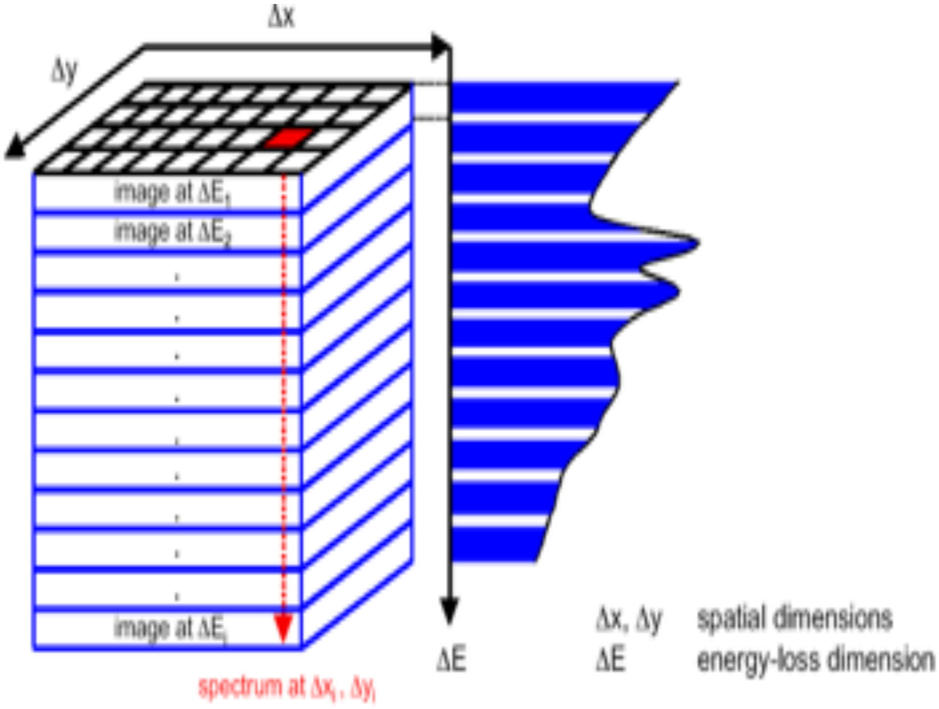


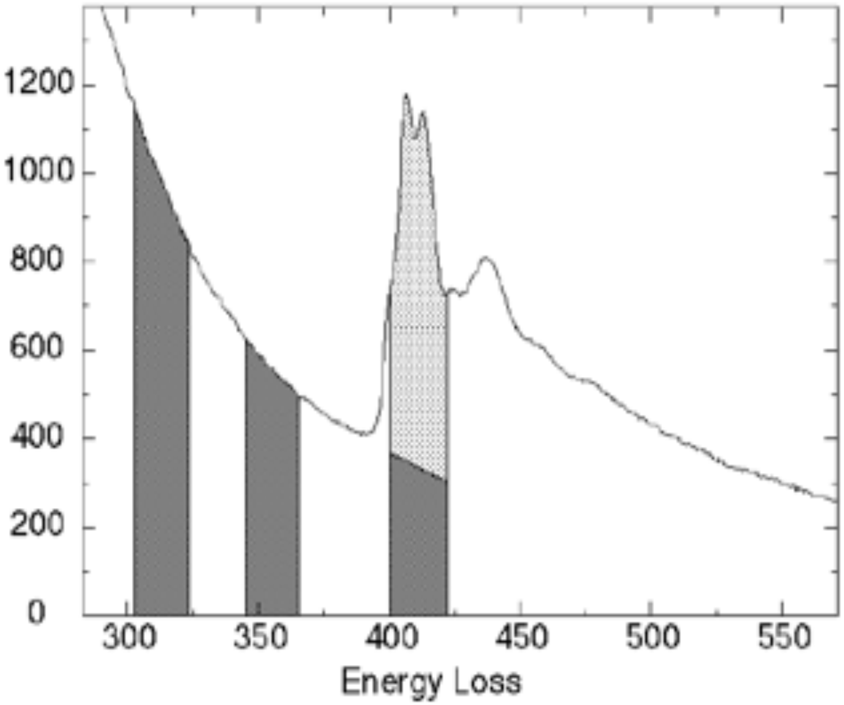
EFTEM



What is EFTEM

- *Energy Filtering Transmission Electron Microscopy*



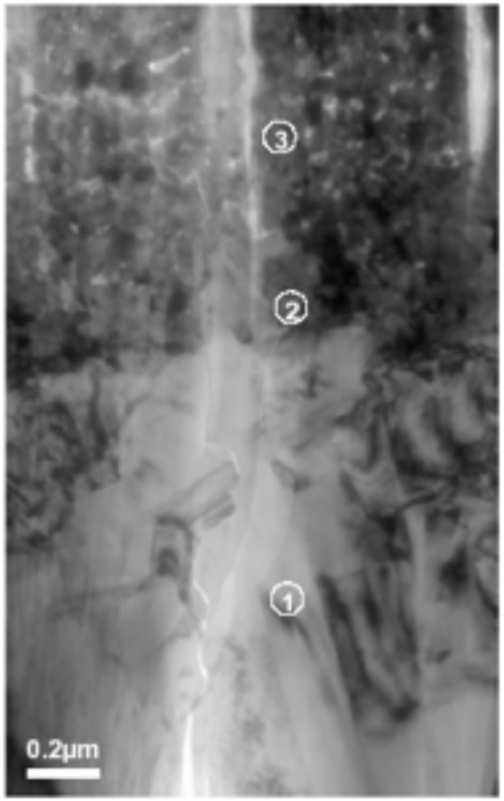


The features of EFTEM

- ***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

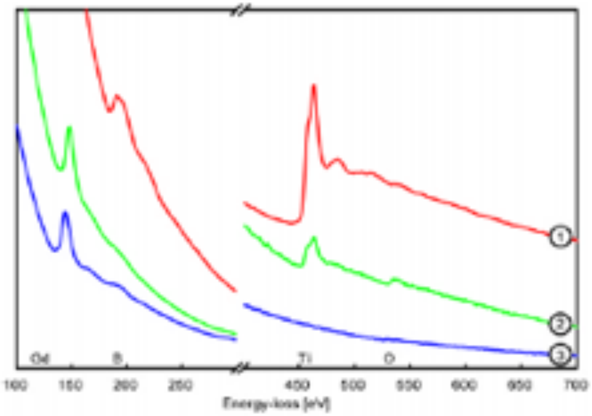


Unfiltered bright field image - structural contrast only

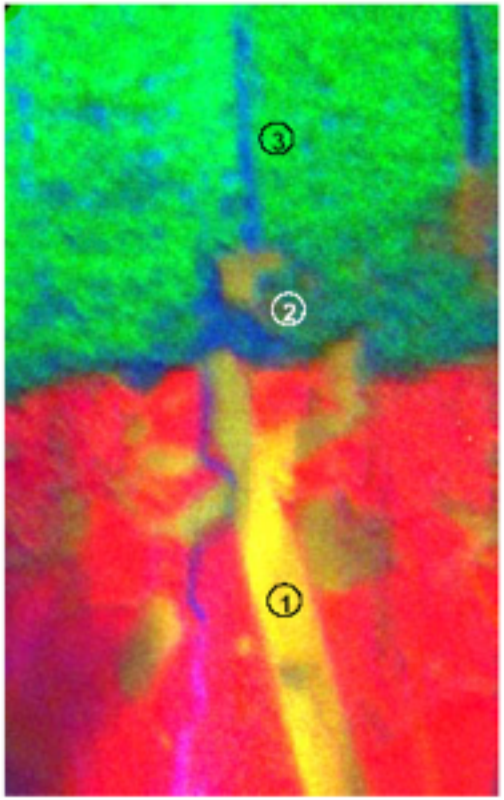
Information gain with EELS + EFTEM

Interface Titanium alloy and PVD-grown Gadoliniumboride

EELS spectra



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

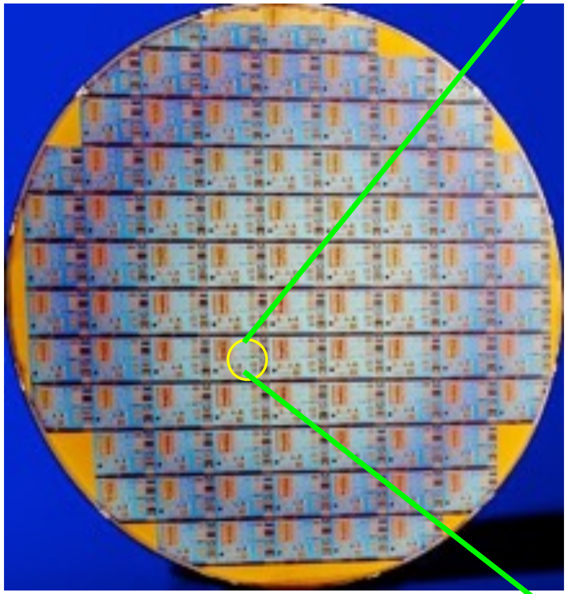


🟥 Titanium 🟩 Boron 🟦 Oxygen

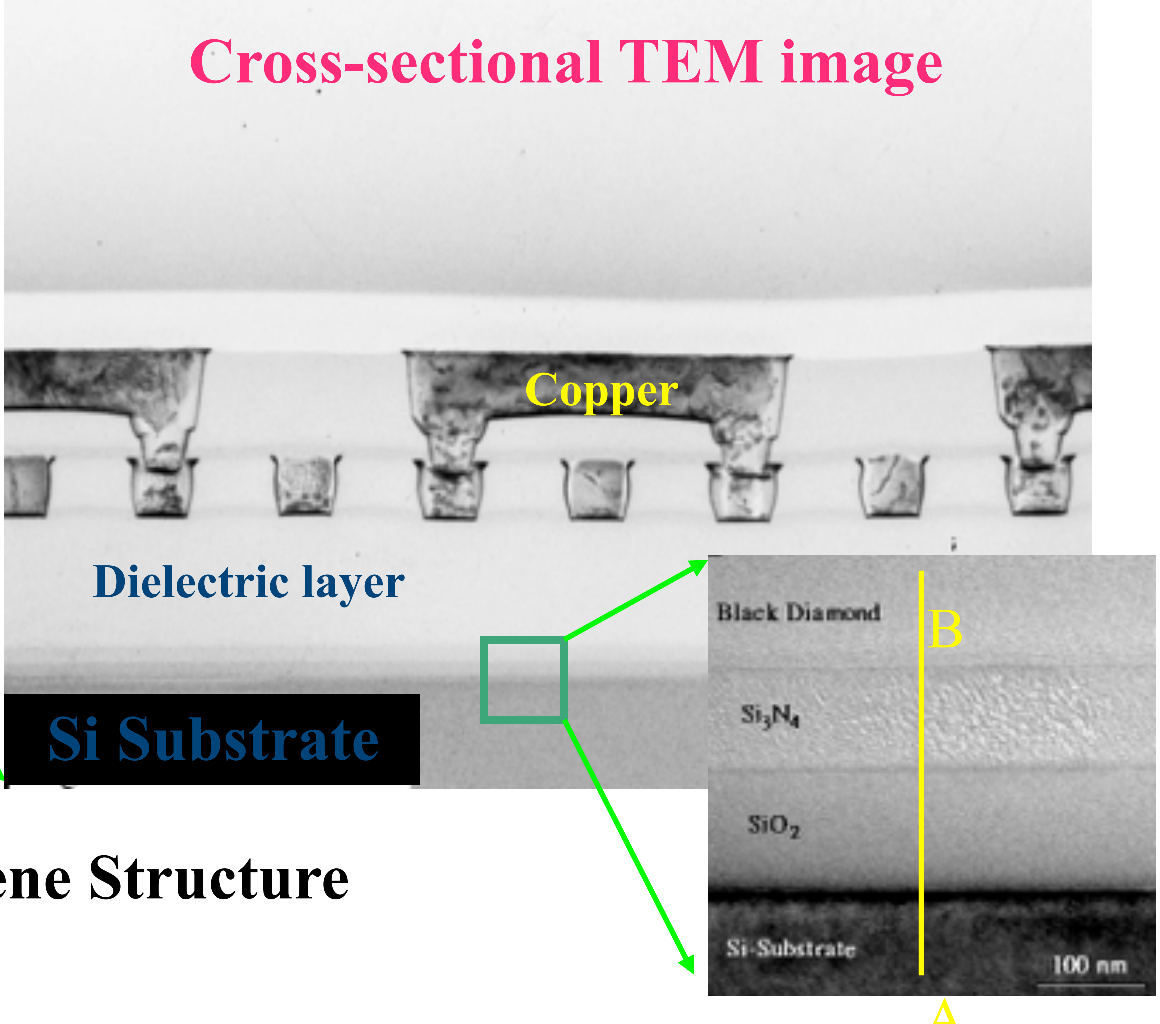
EFTEM - Elemental contrast

•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

如何在具有圖案結構上之試片決定介電材質之介電常數。

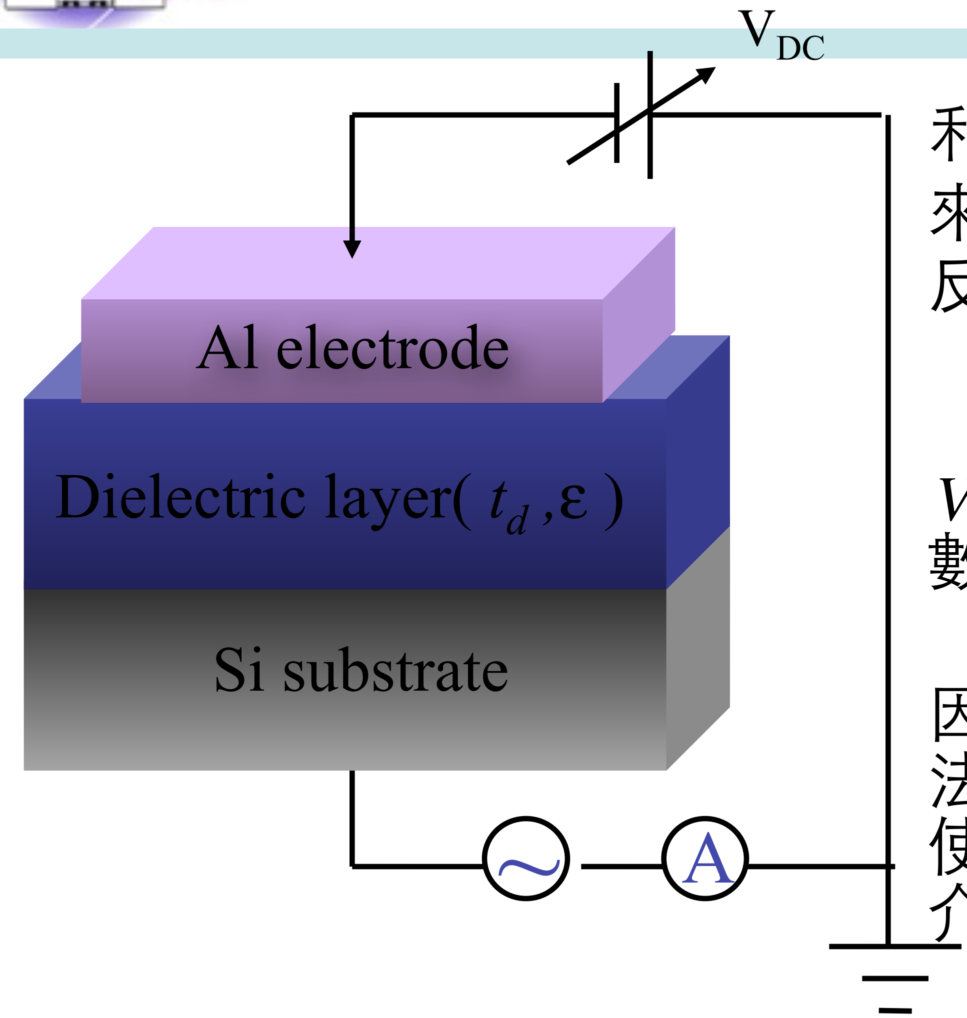


Diameter: (8 inches)



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

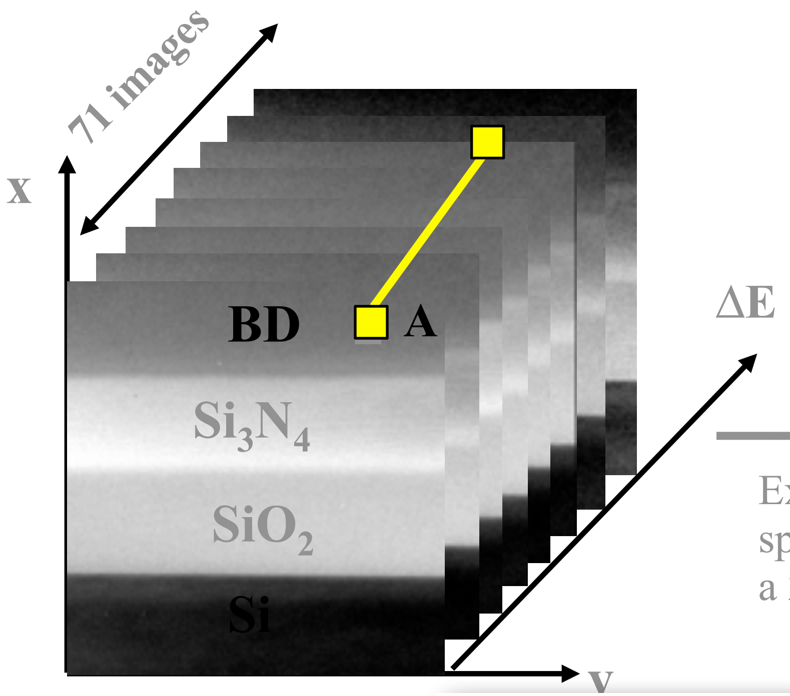
$$V_{DC} = \frac{t_d C_d}{\varepsilon_0}$$

（ε_0：真空介電常數）

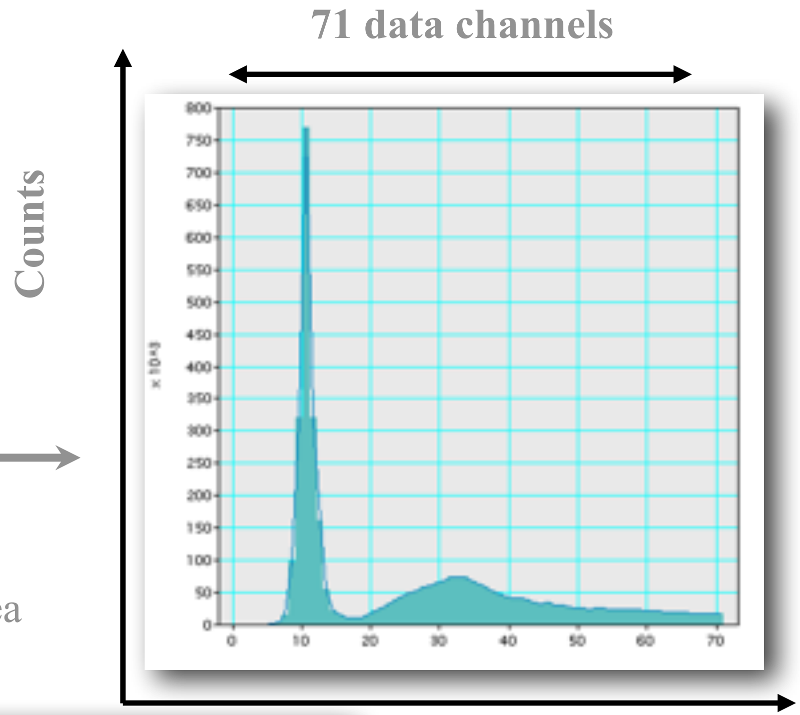
因此對於有結構圖案之試片無法使用此方法量測介電層之介電常數值。

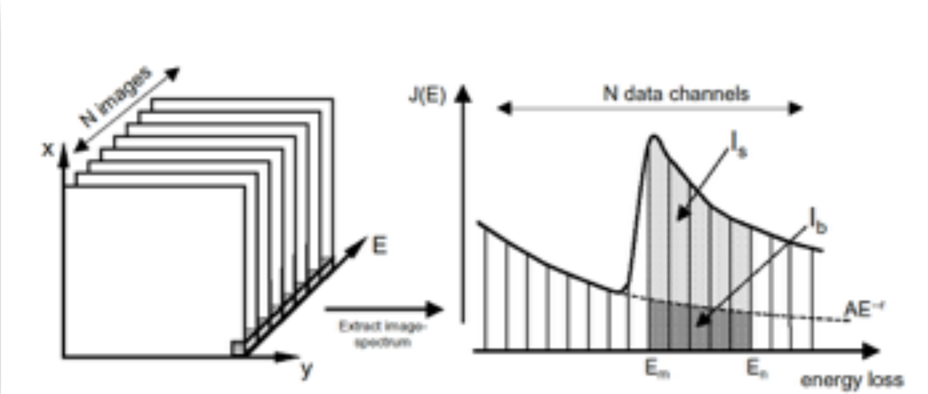
影像能譜(ESI)之擷取
Dielectric Function Imaging

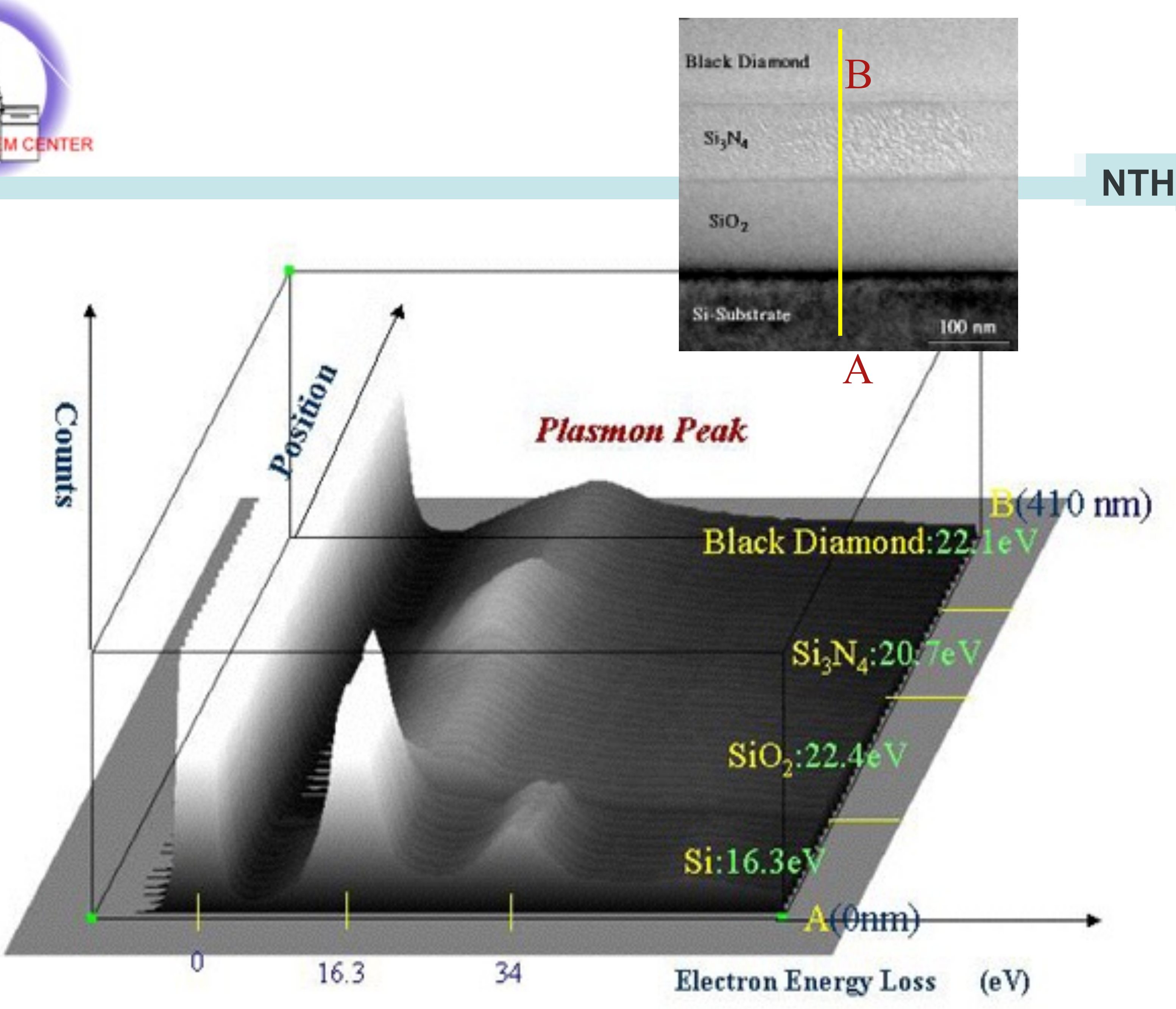
NTHU



Extract image-spectrum from a 2.82^2 nm^2 area

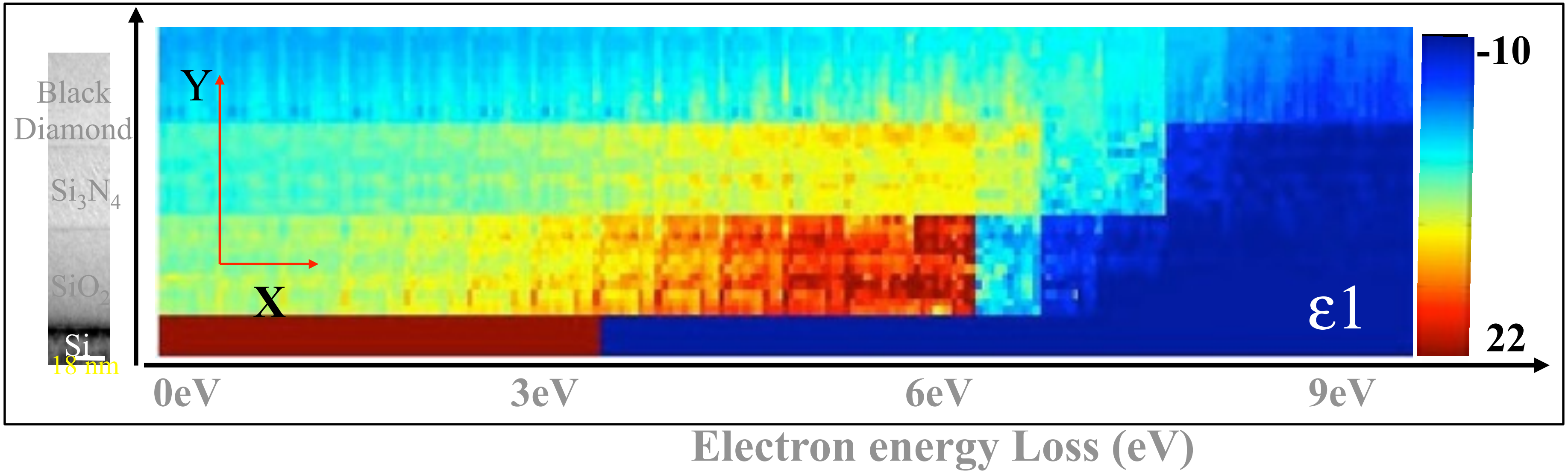


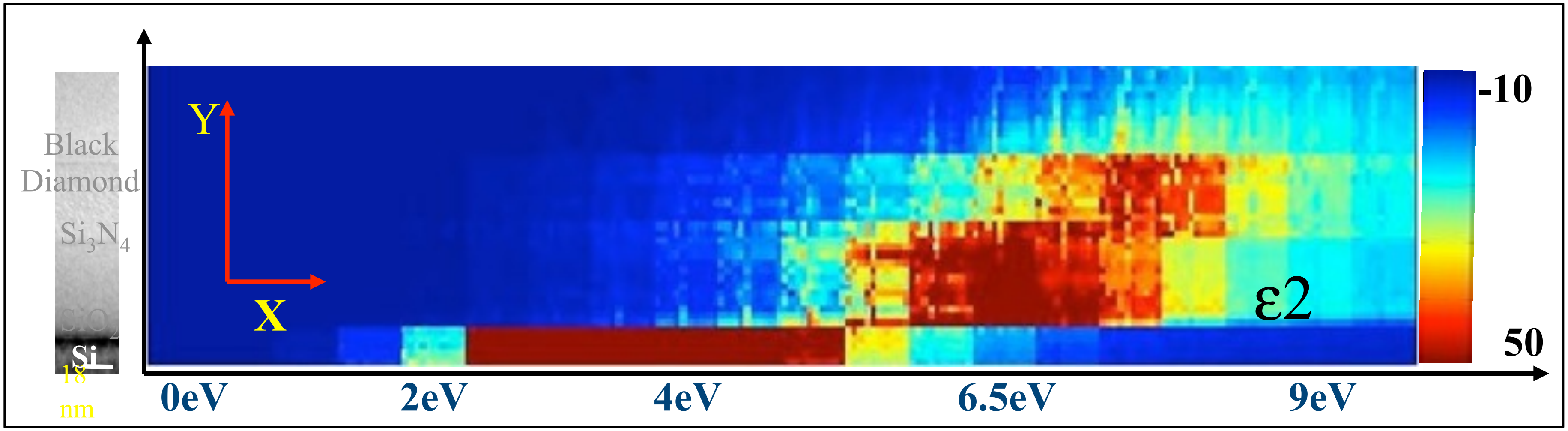



Black Diamond
Si_3N_4
SiO_2
Si-Substrate
100 nm
B
A
Counts
Position
Plasmon Peak
B(410 nm)
Black Diamond:22.1eV
Si_3N_4:20.7eV
SiO_2:22.4eV
Si:16.3eV
A(0nm)
0
16.3
34
Electron Energy Loss (eV)

Dielectric Function image

NTHU

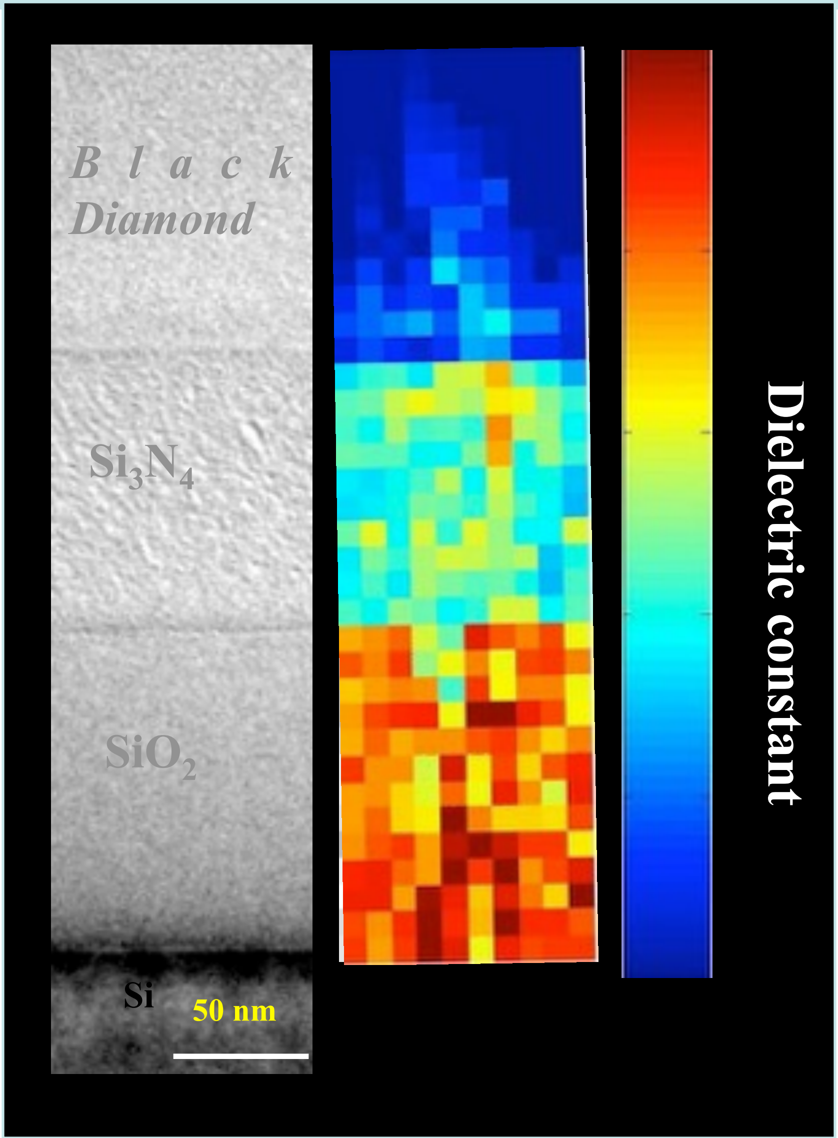




Lo, Chen, L. Chang and Kai et al., Journal of electron Microscopy (2000)

介電常數分佈影像圖(dielectric constant map)

NTHU



Materials	ε_{ref}	ε_{exp}
SiO_2	3.8	4.20±0.31
Si_3N_4	3.6	3.72±0.30
Black Diamond ™	2.5~2.8	2.69±0.27

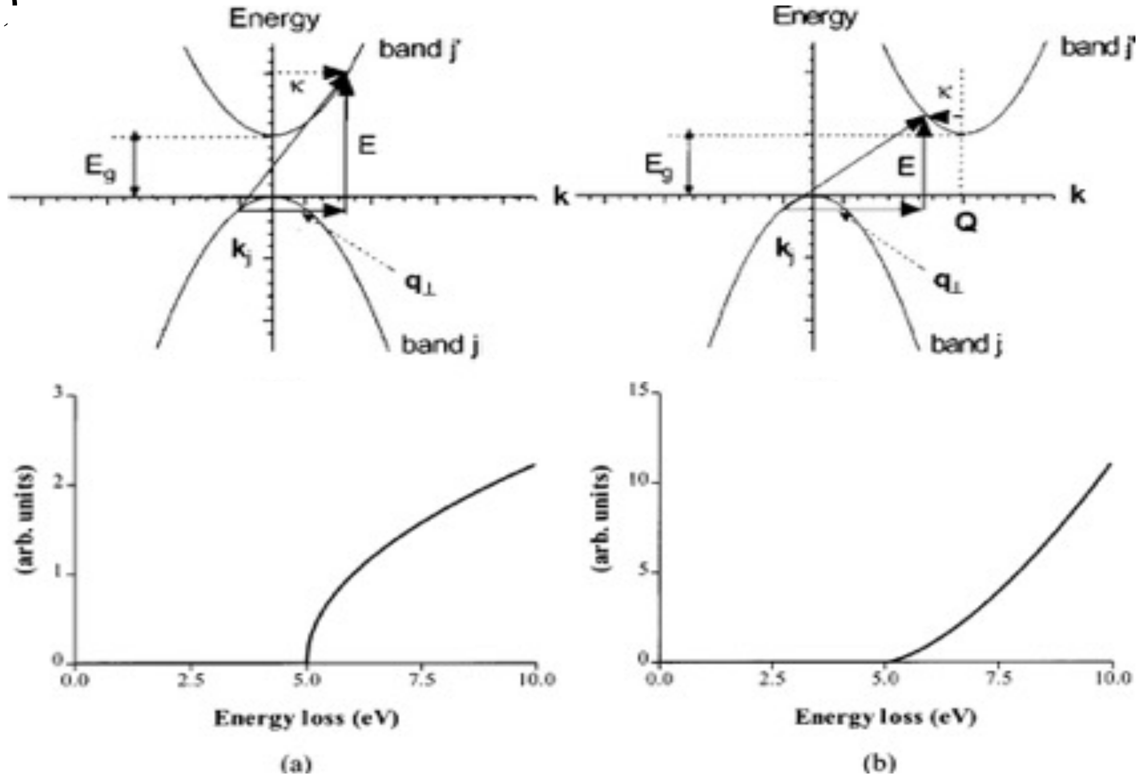
Band gap energy Imaging

$$J^1(E)\propto M^2\rho(E)=(E-E_g)^a$$

- Bruley and Brown (parabolic band)

M: transition Matrix from Valence band to conduction band

ρ(E): Density of state of condution band



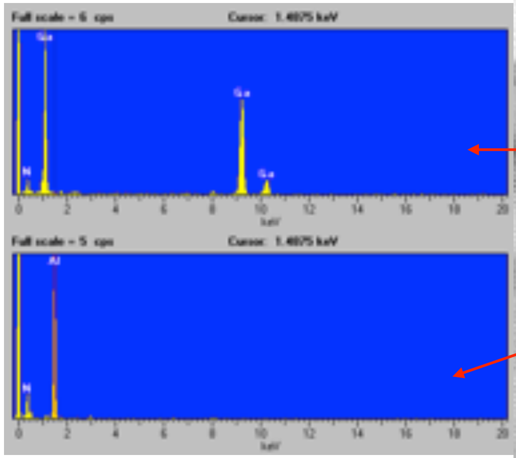
$J^1(E)$: a = 0.5
(direct band gap)

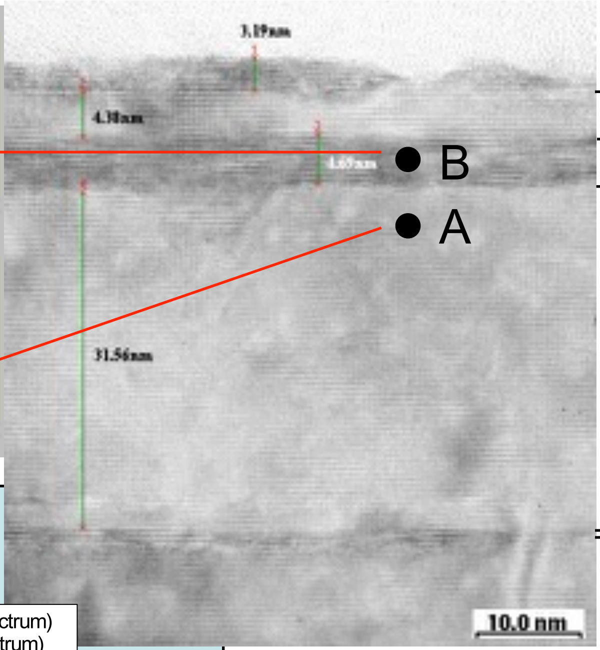
a=1.5
(in-direct band gap)

AlN/GaN Quantum Well

NTHU

EDX

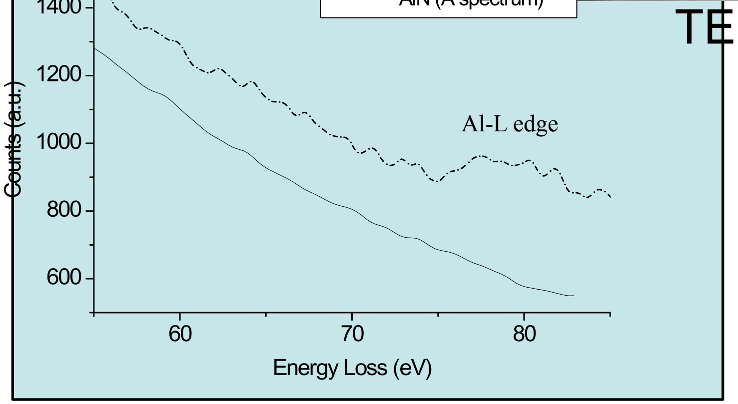




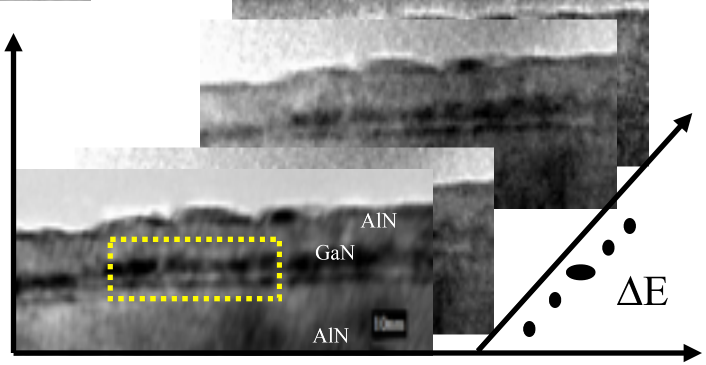
TEM image

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

EELS



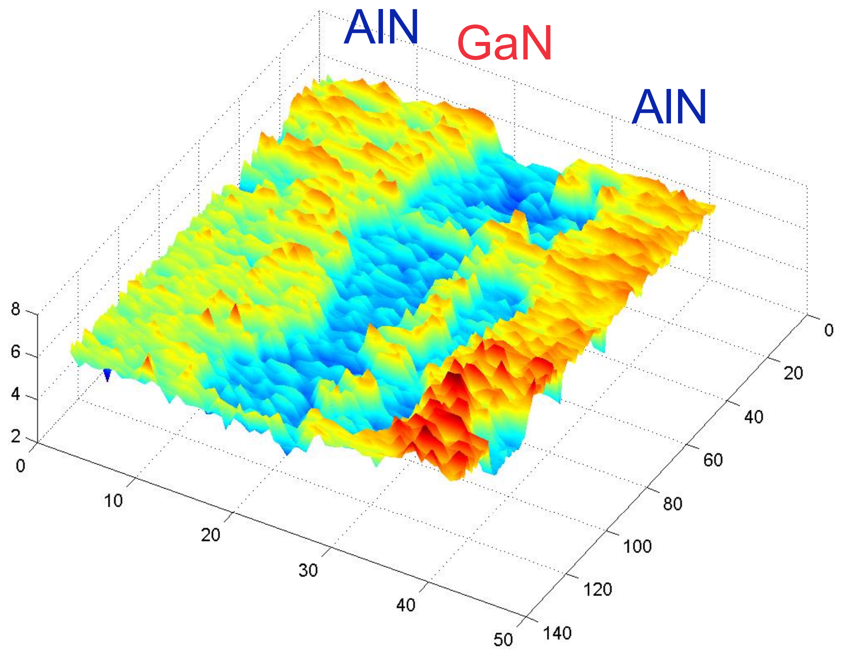
EELS spectra

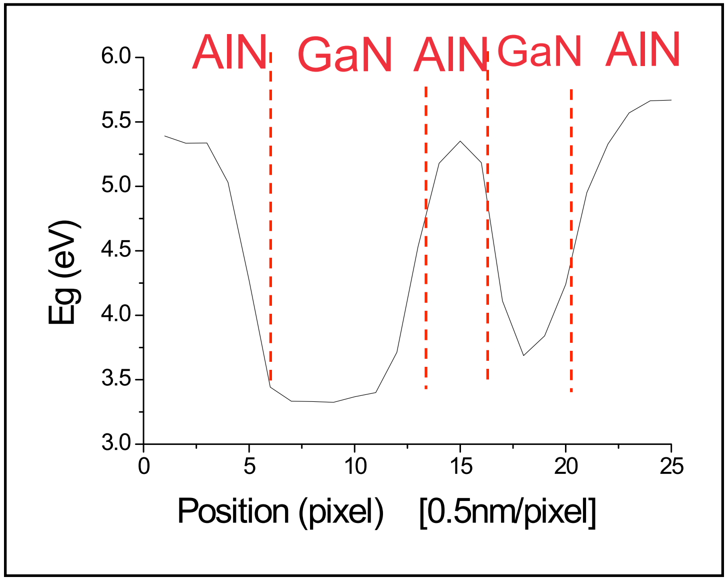


Series ESI images

Band Gap Map

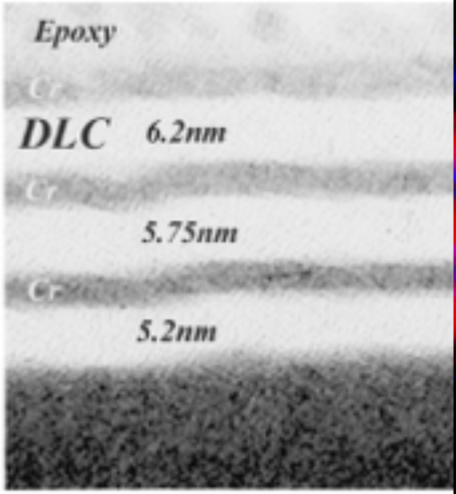
The map of band energy of AlN/GaN layers is obtained using electron spectroscopy imaging (ESI) technique. The average band-gap energy of AlN and GaN is determined to be about 5.62 ± 0.35 eV and 3.47 ± 0.36 eV, respectively.

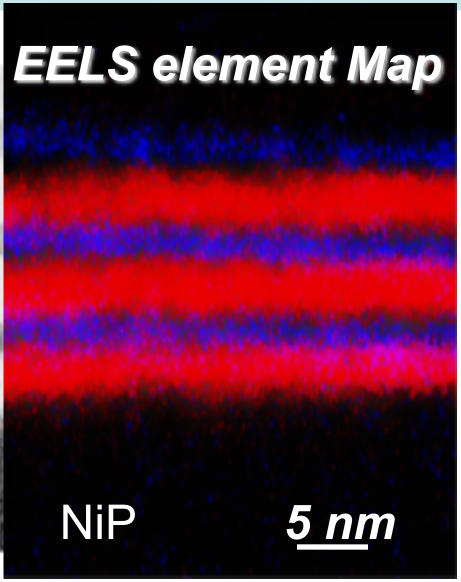


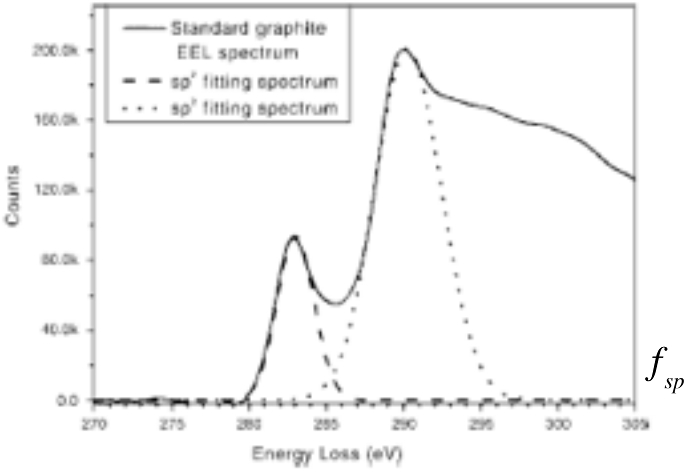


Tsai, Kai,Chen,L. Chang, Journal of Electron Microscopy (2003)

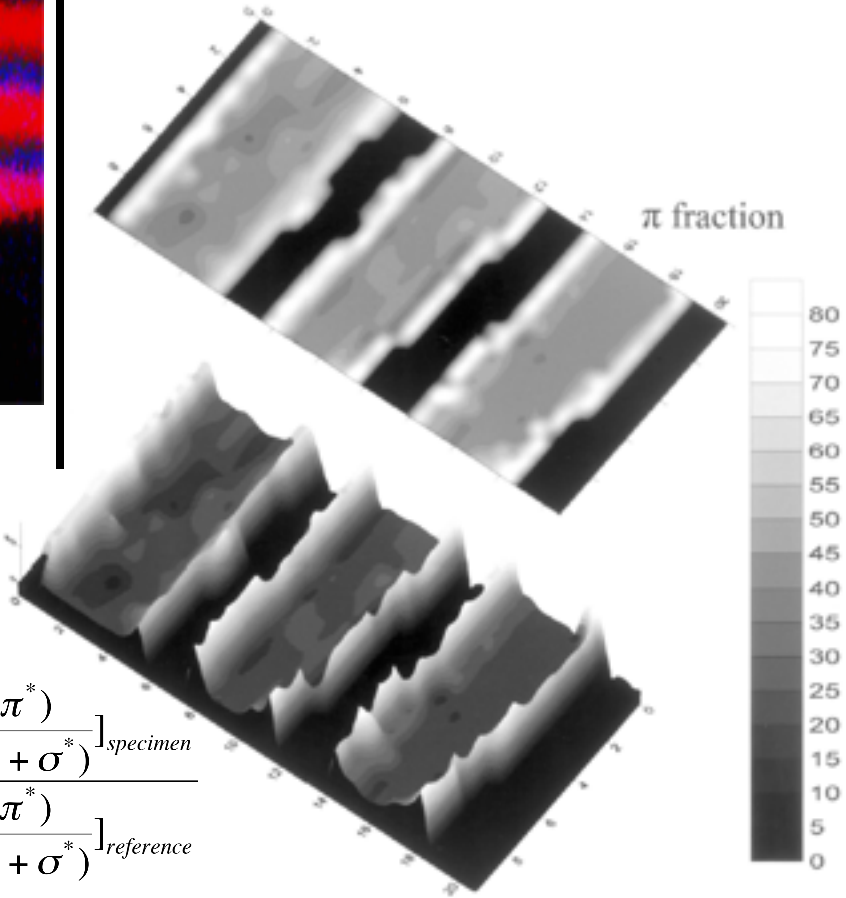
Chemical Bonding sp^2/sp^3 Map







sp^2/sp^3 Map



$$f_{sp^2} = \frac{\left[\dfrac{area(\pi^*)}{area(\pi^* + \sigma^*)}\right]_{specimen}}{\left[\dfrac{area(\pi^*)}{area(\pi^* + \sigma^*)}\right]_{reference}}$$

Yan, Kai, Chen,L. Chang, JEM (2002)

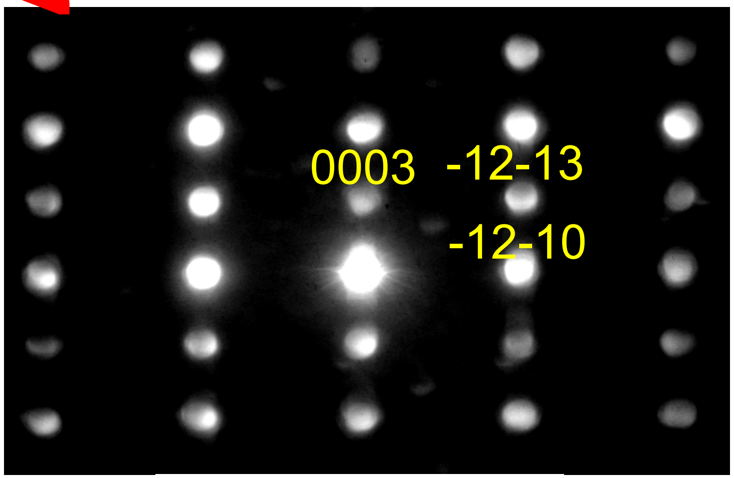
Structure of the specimen

α-Fe_2O_3

Fe

Cu

Si Substrate(100)



Znoe axis(10-10)

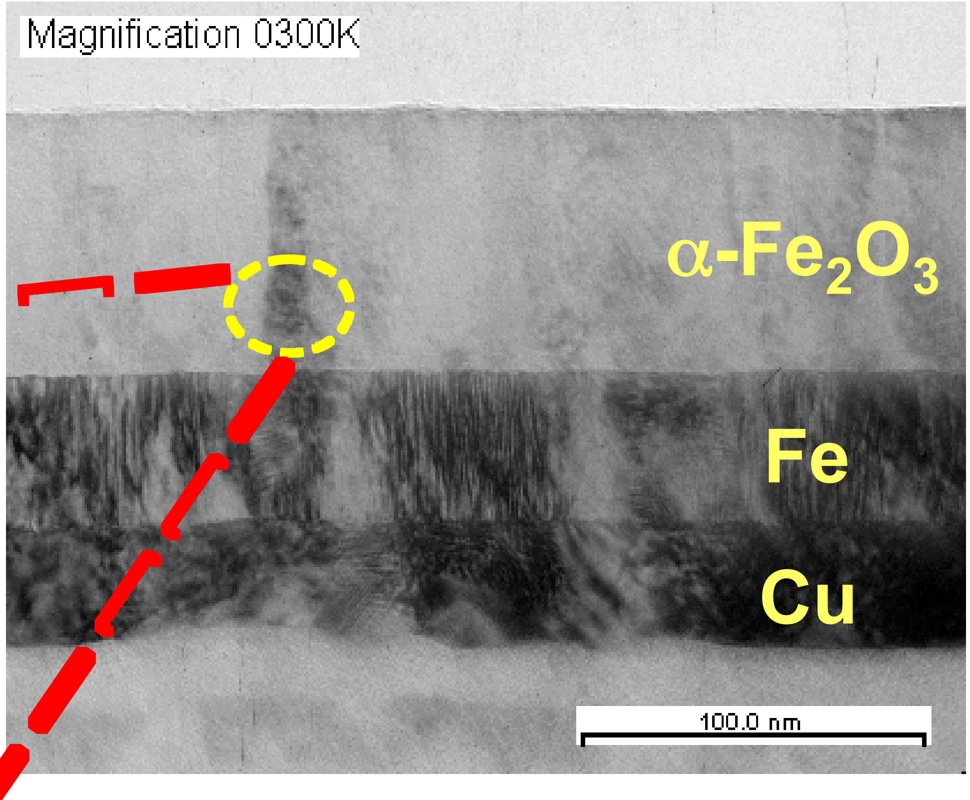
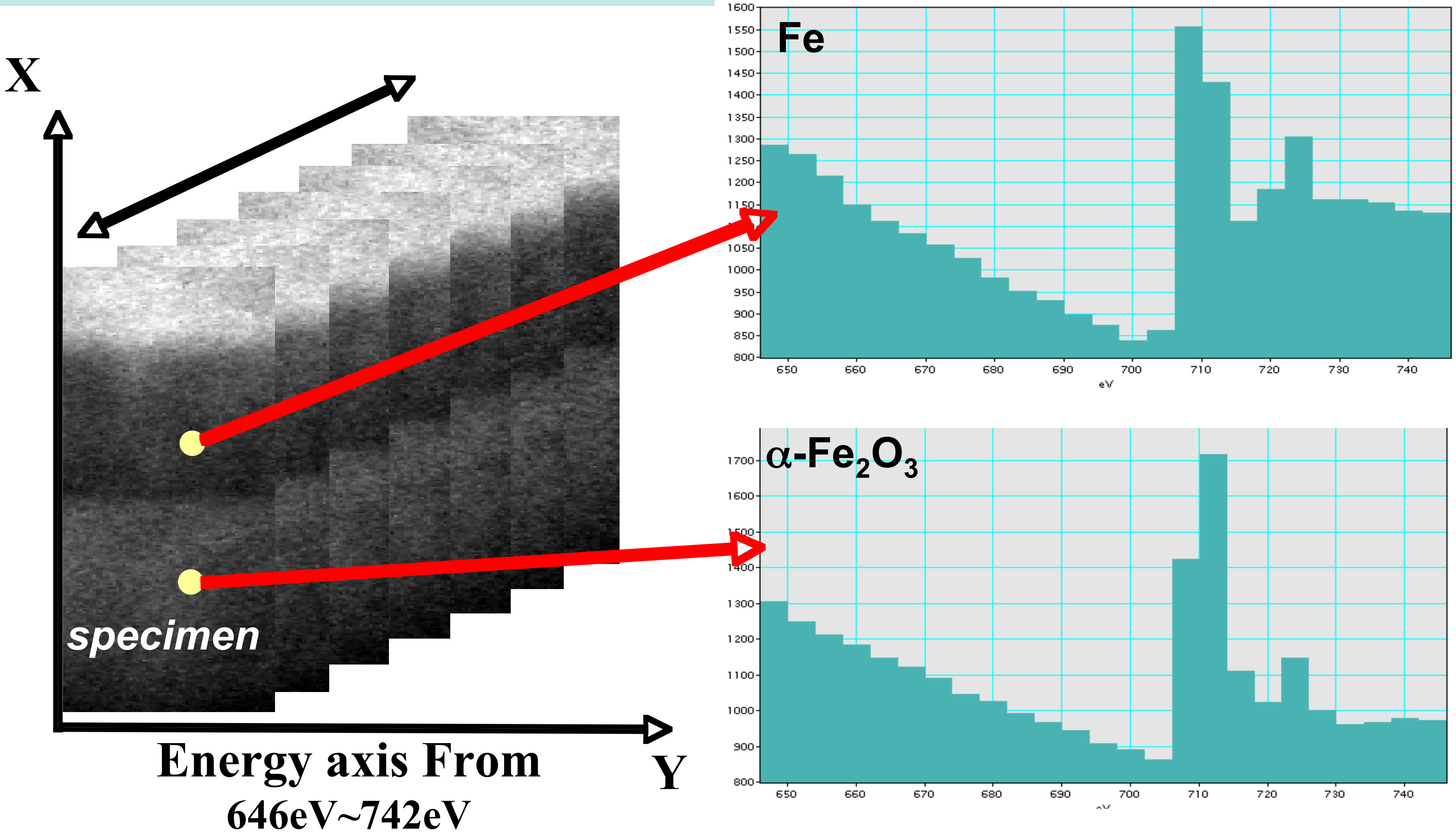


Image to Spectrum



Valence State Mapping