Nano Sensors

M. Tech. (Sensors and IoT)
Course No.: EEL7450
L-T-P [C]: 3–0–0 [3]

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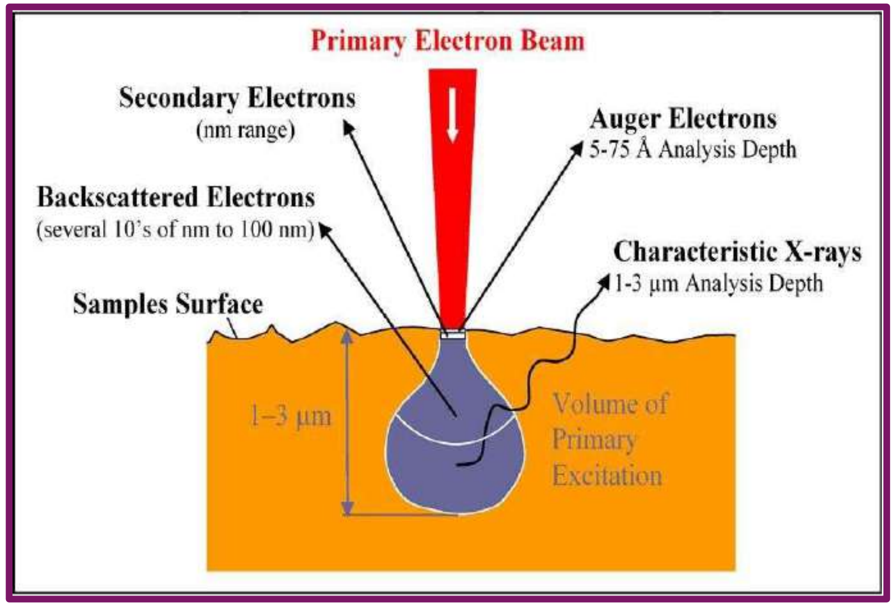
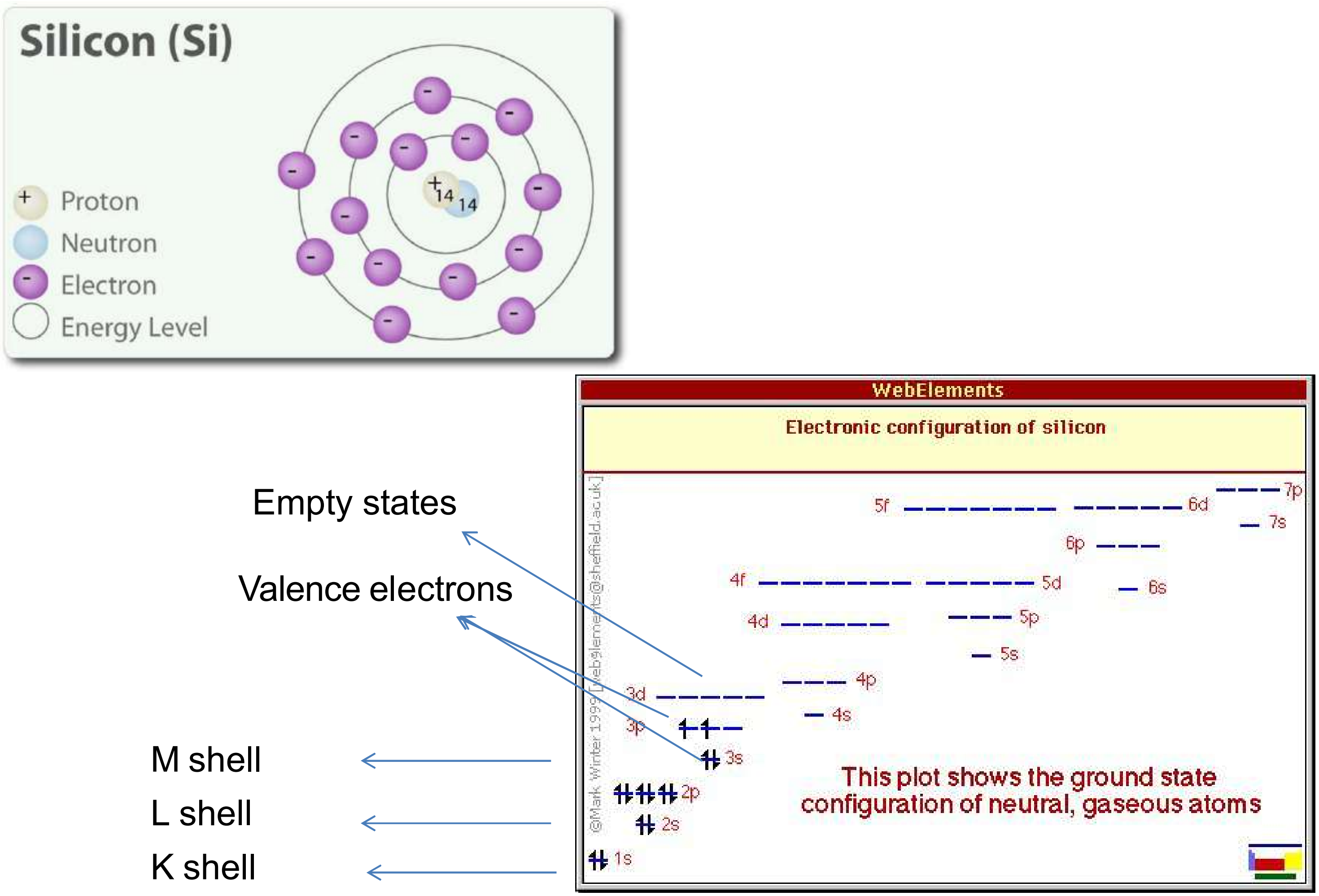
Lecture 16 dated 13th February 2024

Energy Dispersive X-Ray Spectroscopy (EDX)

- Chemical characterization in the scanning electron microscope (SEM) is performed non-destructively with energy dispersive X-ray analysis (EDX).
- The electron beam stimulate the atoms in the sample with uniform energy and they instantaneously send out X-rays of specific energies for each element, the so-called **characteristic X-rays**.
- This radiation gives information about the elemental composition of the sample.
- Energy dispersive analysis is a technique to analyze near surface elements and estimate their proportion at different position thus giving a overall mapping of the sample.



- This technique is used in conjunction with SEM.
- In SEM, secondary & backscattered electrons are used for imaging while EDX uses X-rays to give characteristic chemical information of the emitting atoms. The **probed depth in EDX** analysis is around **1-3 µm.**
- By moving the electron beam across the material, an image of each element present in the material can be obtained



Silicon (Si)
Proton
Neutron
Electron
Energy Level
14
14
WebElements
Electronic configuration of silicon
Empty states
Valence electrons
M shell
L shell
K shell
1s
2s
2p
3s
3p
3d
4s
4p
4d
4f
5s
5p
5d
5f
6s
6p
6d
7s
7p
This plot shows the ground state configuration of neutral, gaseous atoms
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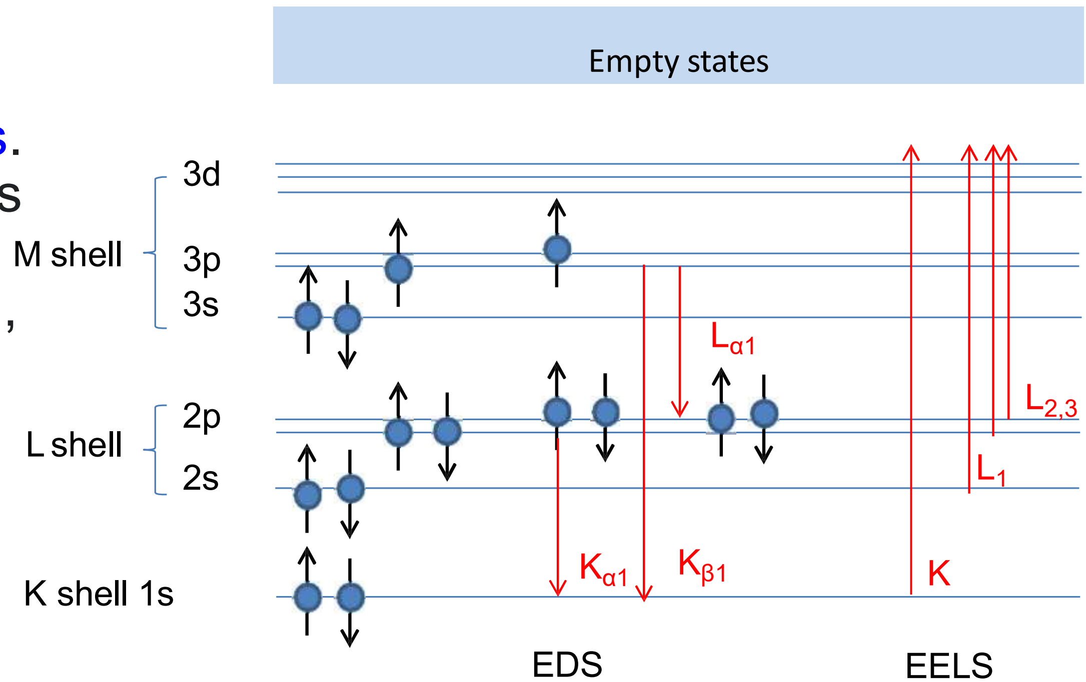
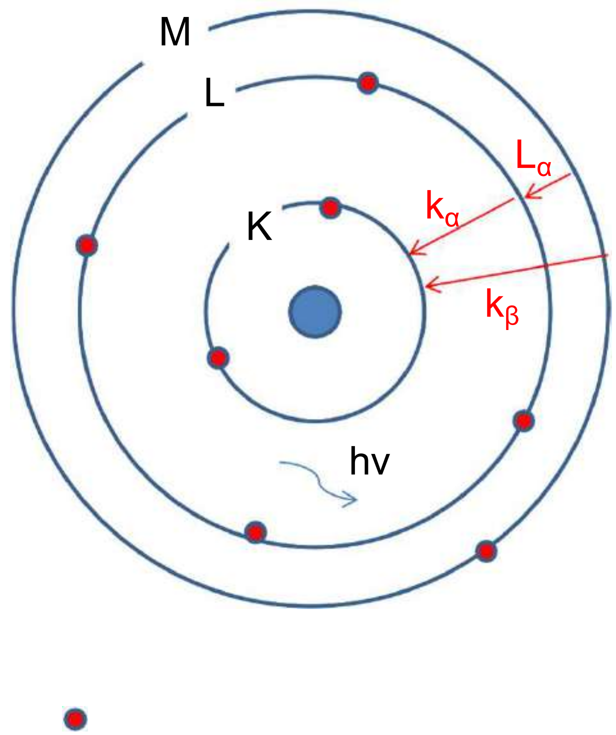
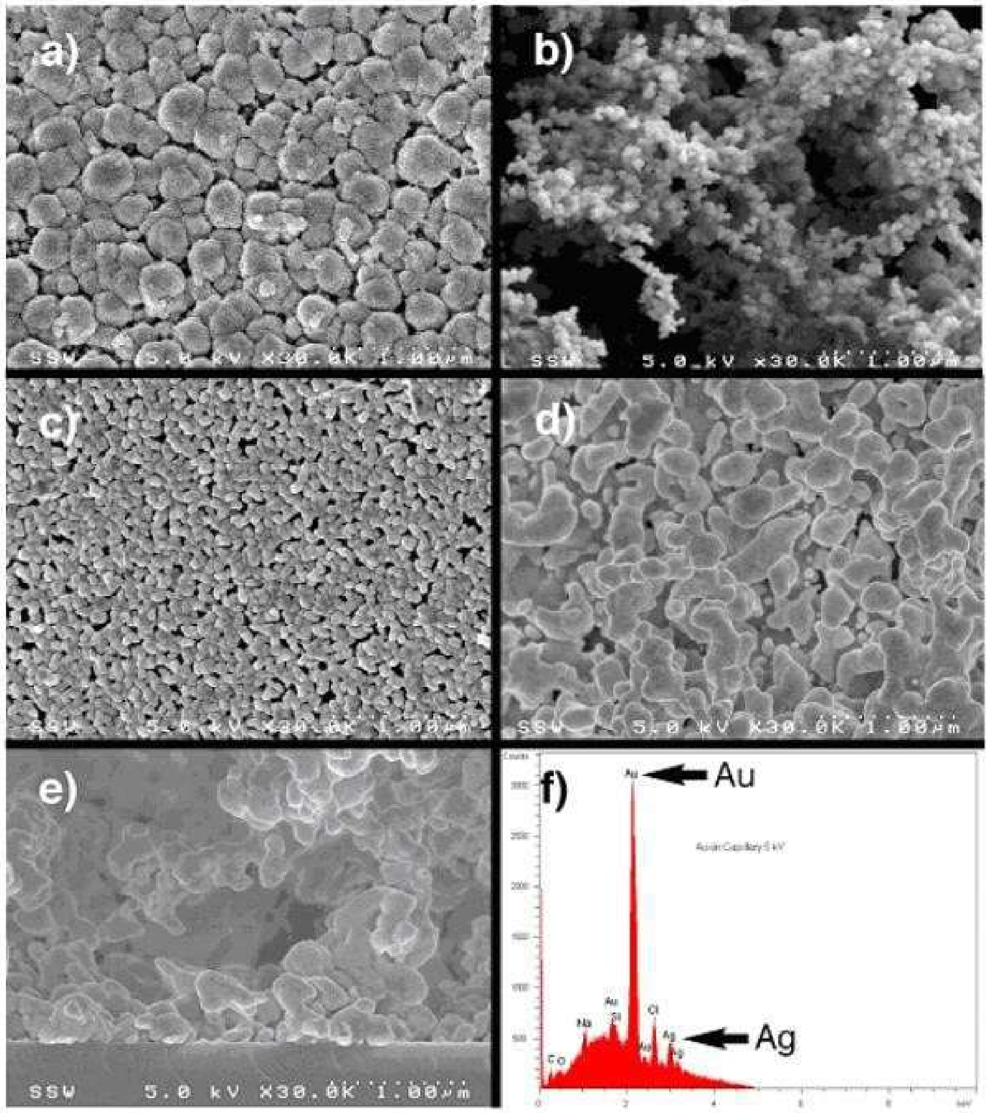
EELS and EDX

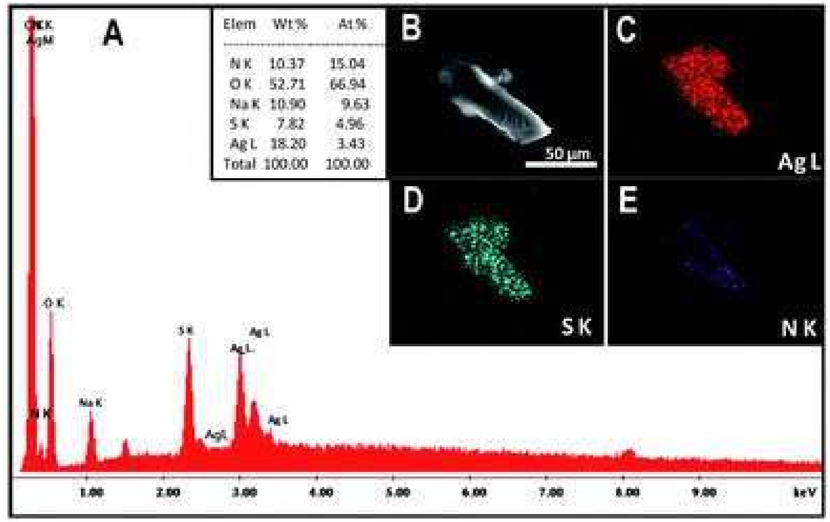
- Electron Energy Loss Spectroscopy (EELS) is a technique that analyzes the composition & structure of materials at the atomic scale.
- **EELS** is complementary to energy-dispersive x-ray spectroscopy (variously called EDX, EDS, XEDS, etc.), which is another spectroscopy technique available on many electron microscopes.
- EDX is used to identify the atomic composition of a material, is easy to use, & is sensitive to heavier elements.
- EELS is more **difficult** technique but is in principle capable of measuring atomic composition, chemical bonding, valence & conduction band, electronic properties, surface properties, & element-specific pair distance distribution functions
- **EELS** works best at relatively **low** atomic numbers



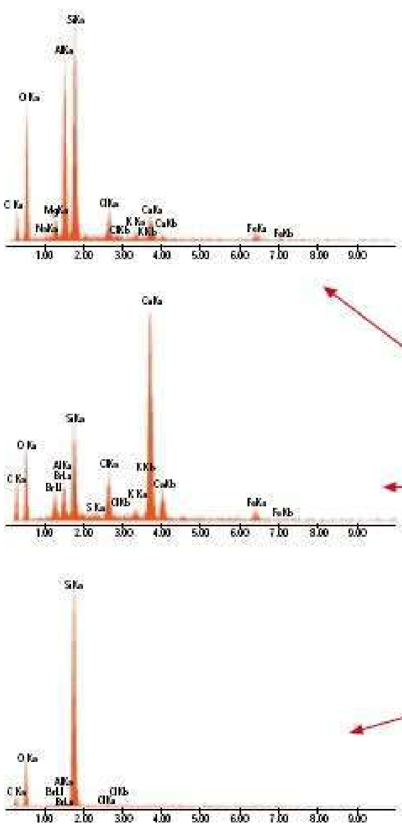
Energy dispersive X-ray spectroscopy

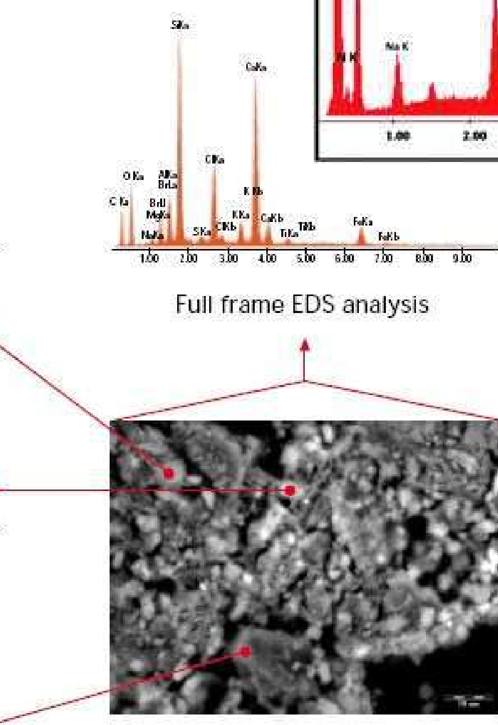



a)
b)
c)
d)
e)
f)
SSW 5.0 kV X30.0K 1.00μm
Au
Ag
Na
Cl
C
O
0
2
4
6
8
500



Elem	Wt%	At%
N K	10.37	15.04
O K	52.71	66.94
Na K	10.90	9.63
S K	7.82	4.96
Ag L	18.20	3.43
Total	100.00	100.00





Full frame and spot analysis of Dead Sea mud, courtesy of AHAVA®. In this case the elements present are: C, O, Na, Br, Mg, Al, Si, S, Cl, K, Ca, Fe and Ti.

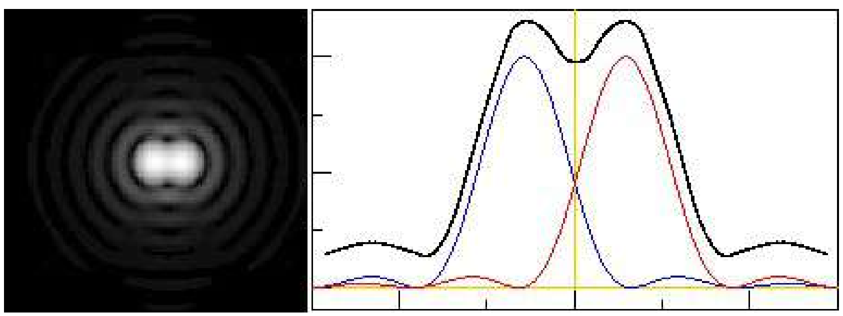
Microstructure (Characterization)

- ✓ **Optical Microscope**
- ✓ **Electron Microscope**
  - ➢ **Scanning Electron Microscope (SEM)**
  - ➢ **Transmission Electron Microscope (TEM)**

Concept of Resolution

TABLE 1.2 Electron Properties as a Function of Accelerating Voltage

Accelerating voltage (kV)	Non-relativistic wavelength (nm)	Relativistic wavelength (nm)	Mass ($\times m_0$)	Velocity ($\times 10^8$ m/s)
100	0.00386	0.00370	1.196	1.644
120	0.00352	0.00335	1.235	1.759
200	0.00273	0.00251	1.391	2.086
300	0.00223	0.00197	1.587	2.330
400	0.00193	0.00164	1.783	2.484
1000	0.00122	0.00087	2.957	2.823



Rayleigh criterion for visible-light Microscope states that **the smallest distance that can be resolved**, δ, is given approximately by:

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

λ is the wavelength of the radiation,

μ the refractive index of the viewing medium, &

β the semi-angle of collection of the magnifying lens.

For the sake of simplicity, we approximate **μ sin β to unity**

So, the **resolution** is equal to about **half the wavelength of light.**

Visible light:

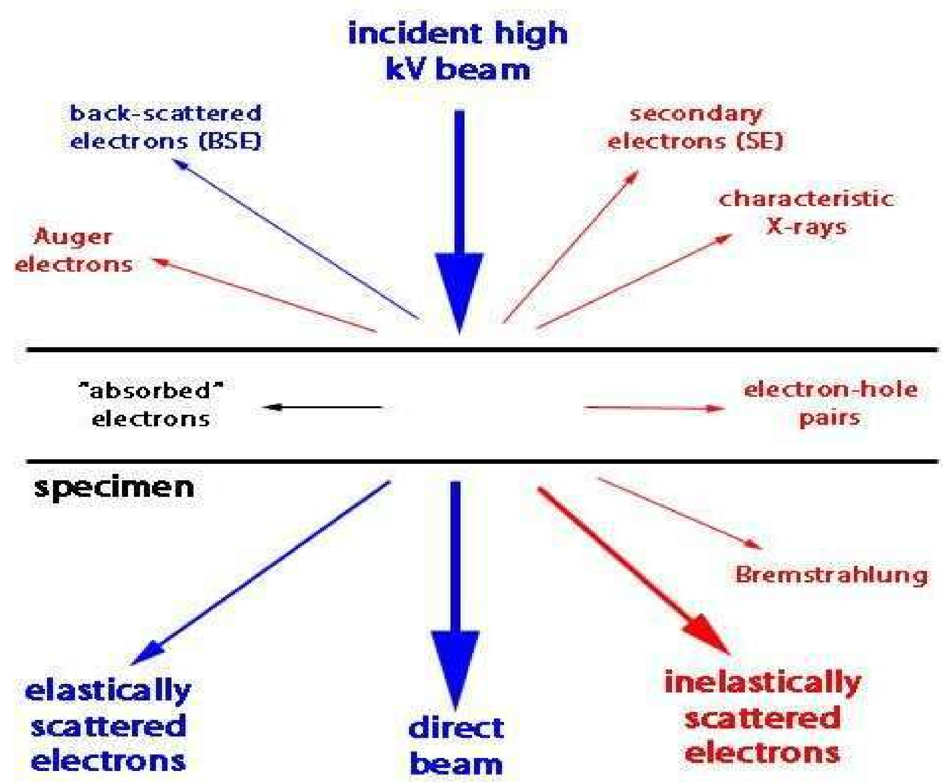
$\lambda = 400$ **nm R= 200nm**

Electrons: λ=4 pm

R= 2 pm << atom diameter

Transmission Electron Microscopy: what can be done?

1. TEM gives images of the internal structure of a specimen sufficiently thin (~1000 Å) to allow transmission of electrons, typically 100-300 kV.
2. Electrons diffraction patterns give detailed *crystallographic information:*
   - Crystal orientation
   - Lattice parameters
   - Specimen thickness
3. ***Chemical analysis*** is also possible with available analytical attachments for x-ray or electron spectroscopy.



modified from Williams & Carter (1996) Fig. 1.3

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Standard TEM Image Modes

BRIGHT FIELD (BF) IMAGE:

Only the **transmitted** beam is allowed to pass through the objective aperture.
Image is therefore bright where **diffraction** in specimen is weak.

DARK FIELD (DF) IMAGE:

Only one diffracted beam passes through objective aperture.
Image is dark where diffraction is weak, bright where diffraction is strong.

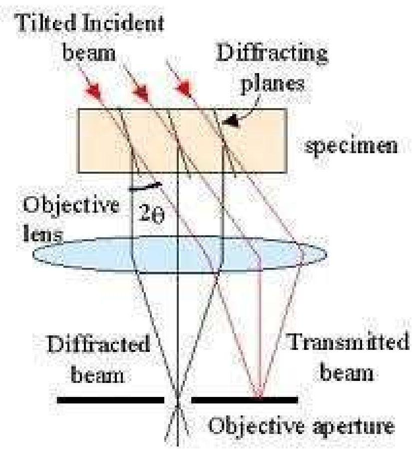
LATTICE IMAGE (High Resolution TEM: HRTEM image):

Interference of transmitted beam (TB) & diffracted beams (DBs) produces an image of the crystal lattice.

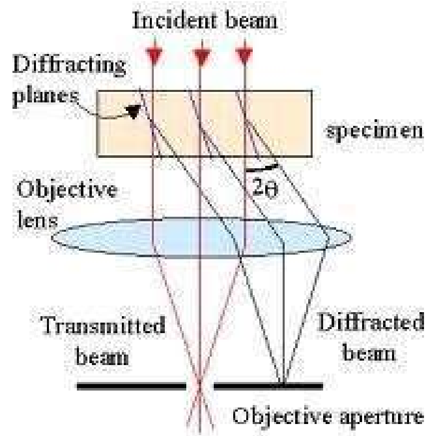
DIFFRACTION PATTERN:

Intermediate lens adjusted to image the diffraction pattern formed in back focal plane (BFP) of objective lens.

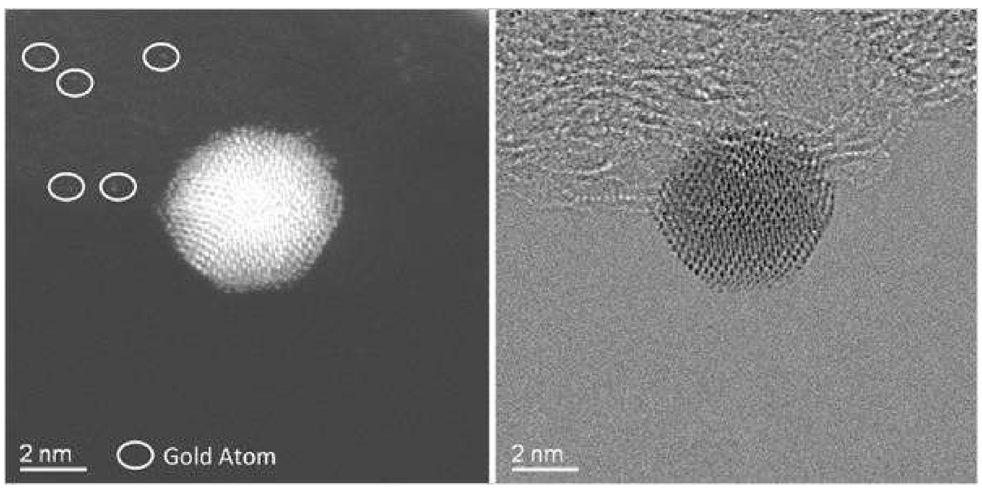
BF & DF Imaging



On-axis Dark Field



Bright Field Imaging

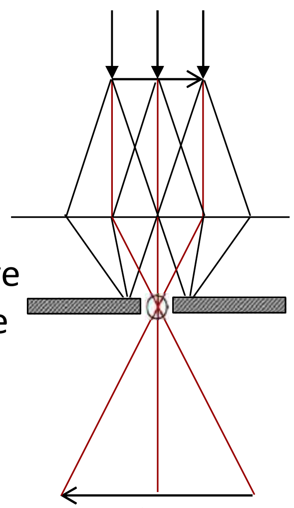


Isolated individual Gold Atoms around Gold Nanoparticles: (left) dark field image, (right) bright field image.

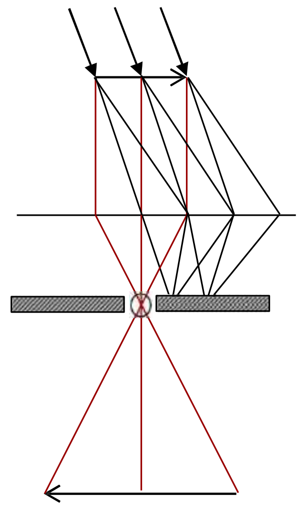
Size of objective aperture

Bright Field (BF), Dark Field (DF) and High-Resolution EM (HREM)

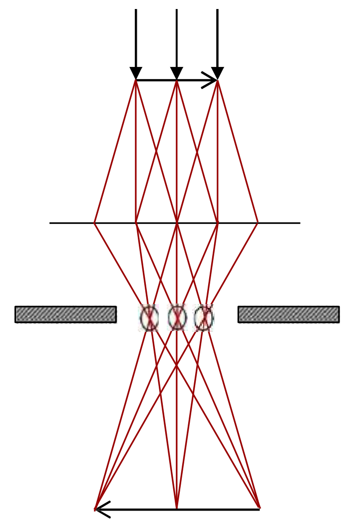
Objective aperture



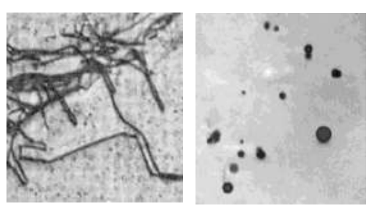
BF image

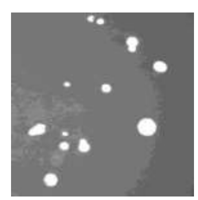


DF image

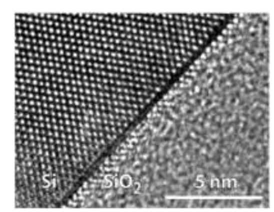


HREM image



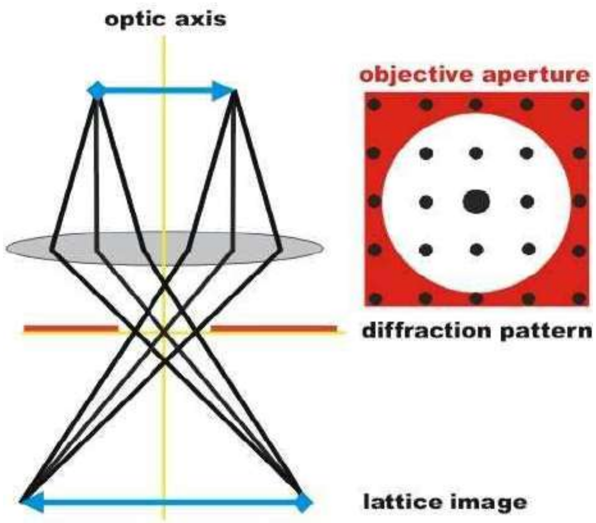


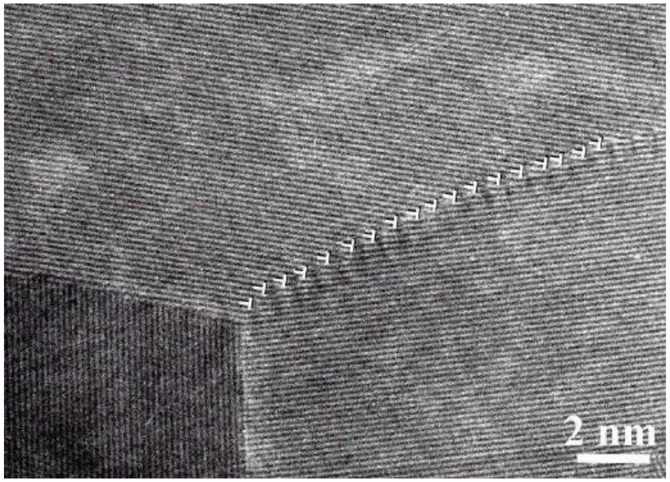
Amplitude/Diffraction contrast



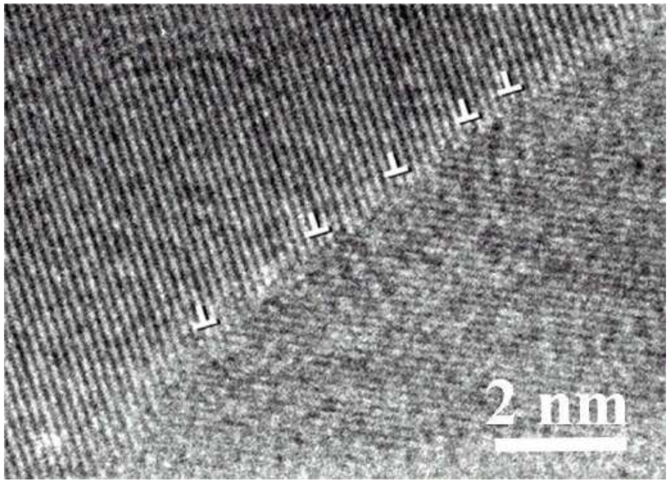
Phase contrast

HRTEM: Lattice Imaging





To obtain lattice images, a large objective aperture has to be selected that allows many beams including the direct beam to pass. The image is formed by the **interference of the diffracted beams with the direct beam** (phase contrast).



Lattice-resolution imaging of Ni_3Al. The image shows three grains at a resolution where the lines are closely related to planes of atoms in the crystalline lattice. **One grain boundary** is being depicted as a **series of edge dislocations**.

Major image contrast mechanisms

Mass-thickness contrast: scattering out of **transmitted** beam creates contrast **due to** difference of atomic number (**Z**) and/or thickness **t**; scattering is proportional to $\mathbf{Z^2t}$. Higher-Z or thicker areas are darker in BF. Applicable to crystalline *or* amorphous materials.

Diffraction contrast: scattering out of transmitted beam creates contrast due to differences in diffracted intensity; **produces contrast** for dislocations, grain boundaries, stacking faults, second phase particles etc. Strongly diffracting objects are darker in **BF**. Applicable *only* to crystalline materials.

Phase contrast: interference between transmitted and diffracted beam produces lattice fringes or **atomic structure images** (typically referred to as HRTEM (high- resolution TEM).

Mass-Thickness Contrast

Rutherford Scattering is the scattering of alpha particles when they pass through thin metal foils.

Mass thickness contrast arises from incoherent elastic scattering (Rutherford scattering)

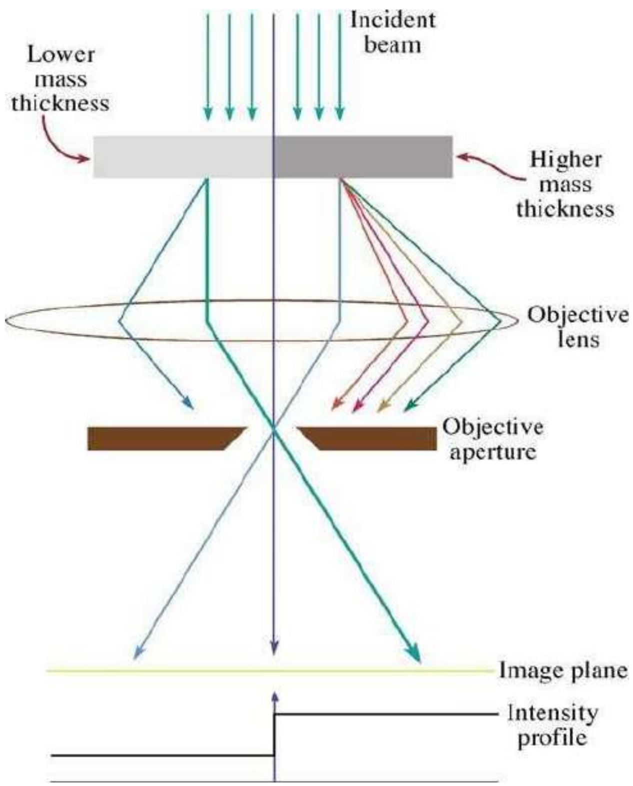
- Peaked in the forward direction in thin samples
- t and Z-dependent

Differential cross-section for high angle scattering:

$$\sigma_R(\theta) = \frac{e^4 Z^2}{16(4\pi\varepsilon_0 E_0)^2} \frac{d\Omega}{\sin^4\frac{\theta}{2}} \qquad (3.3)$$

1. Cross-section for elastic scattering is a function of Z
2. As t increases, more elastic scattering because the mean elastic free path is fixed

Mass-thickness contrast in TEM



Williams and Carter, TEM, Part 3 Springer 2009

Incoherent elastic scattering (Rutherford scattering): peaked in the forward direction, t and Z-dependent

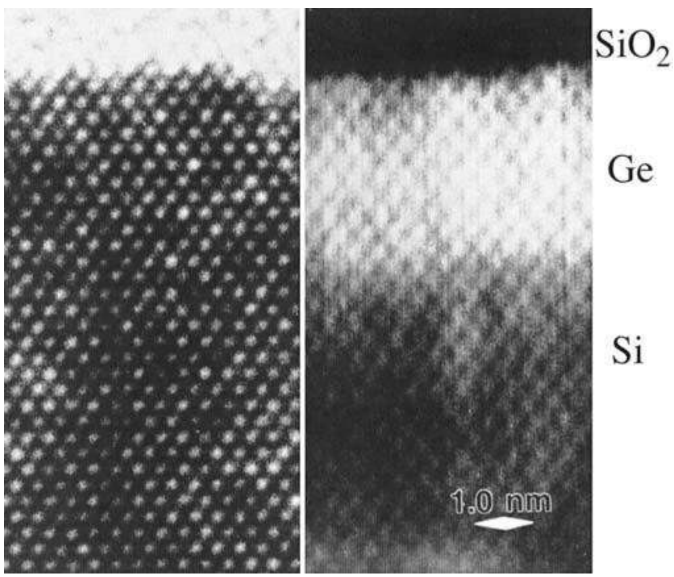
Areas of greater Z and/or t scatter electrons more strongly (in total).

TEM variables that affect the contrast:

-The objective aperture size .

-The high tension of the TEM.

Example of HR Z-contrast with the High-Angle Annular Dark-Field (HAADF) detector



HREM-TEM HR Z-contrast STEM

Atomic structures are visible in both HREM and HAADF images:

HAADF image:
noisier but Z-contrast.

Relate the intensity differences to an absolute measure of the Bi concentration:

Contrast

Cross-section for elastic scattered by matrix A

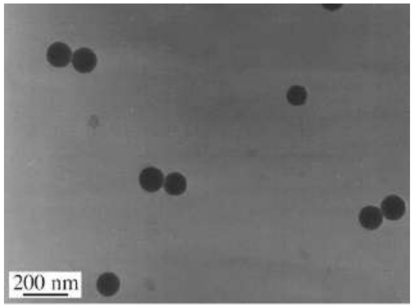
Fraction of the alloying element that sub.
For matrix atoms

$$C = \left(\frac{\sigma_A}{\sigma_B} - F_B\right) c_B \qquad (22.10)$$

Alloying/dopant B

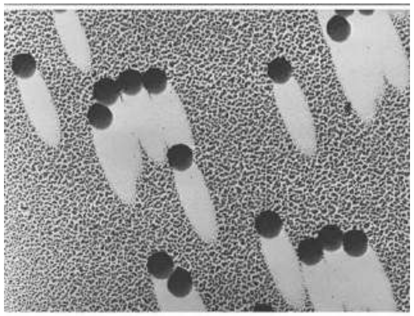
Atomic concentration of alloying element

Example of mass-thickness contrast in TEM mode - Metal shadowing



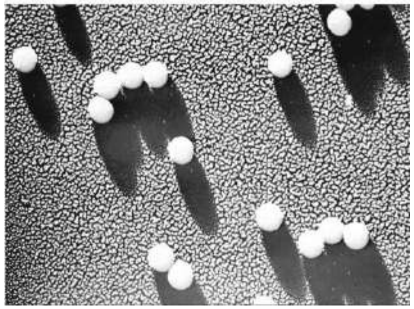
BF-TEM image of latex particles on an amorphous C-film.

- The contrast is t-dependent.
- What is the shape of the particles?



Effect of evaporation of a heavy metal (Au or Au-Pd) thin coating at an oblique angle.

What is the contrast due to in the image?



Effect of inversing the contrast of the image.

The uneven metal shadowing increases the mass contrast and thus accentuates the topography.

Questions / Discussions