Electron Microscopy II

- Transmission Electron Microscopy (TEM)
- Scanning Transmission Electron Microscopy (STEM)
- Scanning Electron Microscopy (SEM)

krumeich@inorg.chem.ethz.ch www.microscopy.ethz.ch

200 nm

1

Electron Microscopy Methods

Transmission Electron Microscopy (TEM)

- Bright / Dark Field (BF/DF)
- High-Resolution Transition Electron Microscopy (HRTEM)
- Energy-Filtered (EFTEM)
- Electron Diffraction (ED)

Scanning Transmission Electron Microscopy (STEM)

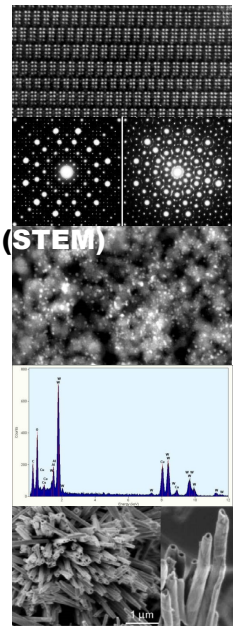
- Bright / Dark Field (BF/DF-STEM)
- High-Angle Annular Dark Field (HAADF-STEM)

Analytical Electron Microscopy (AEM)

- X-ray Spectroscopy
- Electron Energy-Loss Spectroscopy (EELS)
- Electron Spectroscopic Imaging (ESI)

Scanning Electron Microscopy (SEM)

- Secondary Electrons (SE)
- Back-Scattered Electrons (BSE)



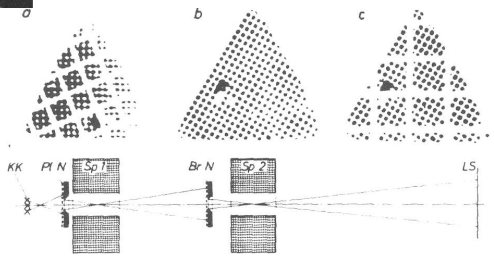
2

Development of the First Transmission Electron Microscope

1927 ***Hans Busch*: Electron beams can be focused in an inhomogeneous magnetic field.**

1931 ***Max Knoll* and *Ernst Ruska* built the first TEM.**

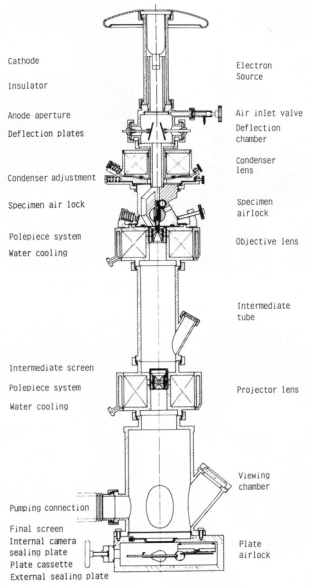
1986 **Nobel prize for *Ruska***

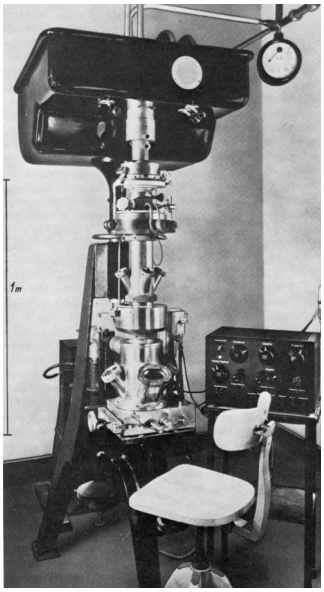


a) Einstufiges Bild eines Platin-Netzes vor Spule 1 durch Spule 1; M 13,0 : 1
b) Einstufiges Bild eines Bronze-Netzes vor Spule 2 durch Spule 2; M 4,8 : 1
c) Zweistufiges Bild des Platin-Netzes vor Spule 1 durch Spule 1 und Spule 2; M 17,4 : 1 zusammen mit dem einstufigen Bild des Bronze-Netzes vor Spule 2; M 4,8 : 1

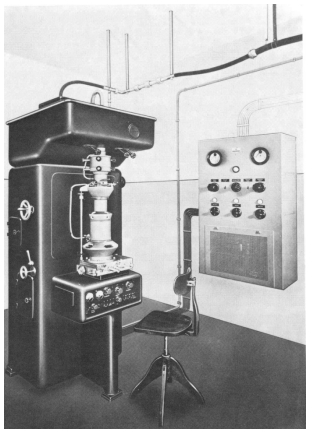
Knoll, Ruska, *Z. Phys.* **78** (1932) 318

1938 First Siemens Electron Microscope (Resolution ca. 13 nm)

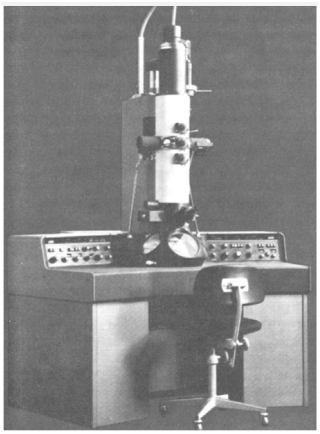




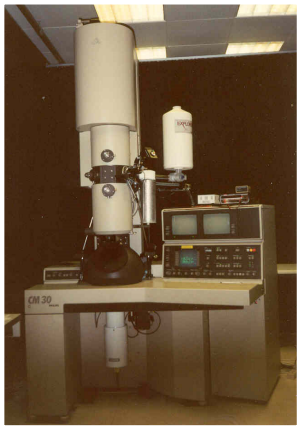
Transmission Electron Microscopes



1939: first TEM serially produced by Siemens resolution ca. 7 nm



~1970: HRTEM Philips EM400, V = 120 kV resolution ca. 0.35 nm



~1990 Philips CM30, V = 300 kV resolution ca. 0.2 nm

History of Electron Microscopy

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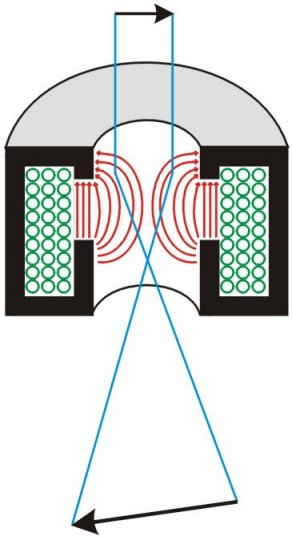
Magnetic Lens



An electron in a magnetic field (here: inhomogeneous, but axially symmetric) experiences the Lorentz force F:

$$\mathbf{F} = -e\,(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

$$|\mathbf{F}| = e\mathbf{v}\mathbf{B}\sin(\mathbf{v},B)$$

E: strength of electric field

B: strength of magnetic field

e/**v**: charge/velocity of electrons

Magnetic lenses
- manipulate the electron beam
- form an image of the object

Transmission Electron Microscopy

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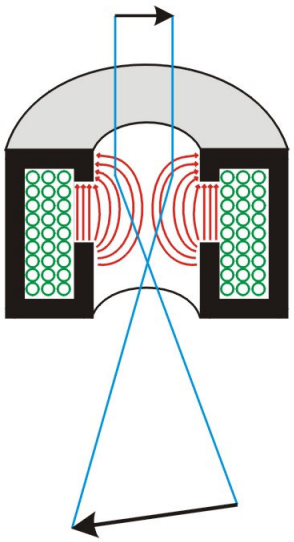
Magnetic Lens



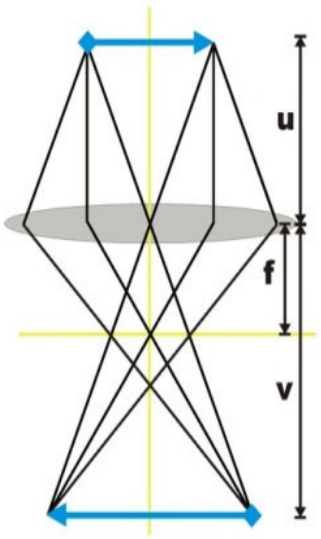
Object plane

Lens

Back focal plane

Lens problems:
spherical aberation C_s
chromatic aberation C_c
astigmatism

Light optical analogue



Lens equation: $1/u + 1/v = 1/f$
Magnification M = v/u

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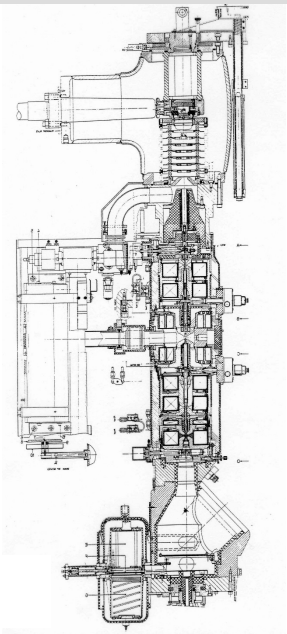
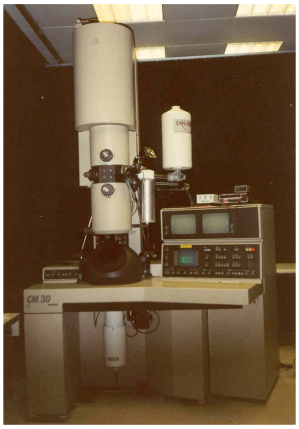
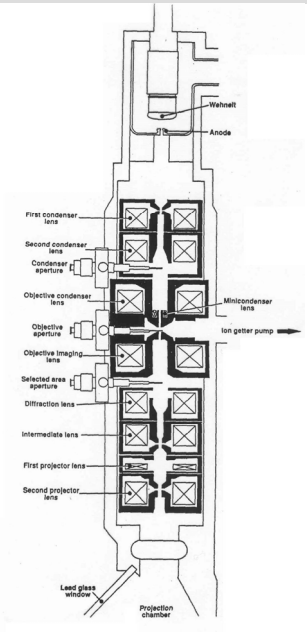
Cross-Section of the Column of a CM30 Microscope







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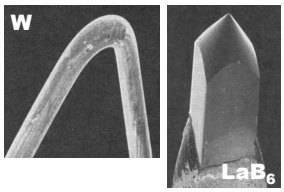
Electron Guns

Thermoionic Guns

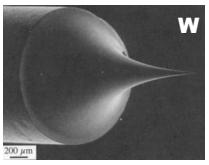
Electron emission by heating



Properties	W	LaB_6	FEG
Work function / eV	4.5	2.4	4.5
Temperature / K	2700	2000	(300-)1800
Energy spread / eV	3-4	1.5-3	0.4-1.5
Source size / nm	30000	5000	3-20
Maximum current / nA	1000	500	(30-)300
Brightness / A/m^2sr	10^9	$5x10^{10}$	10^{13}
Lifetime / h	100	500	>1000

Field Emission Guns (FEG)

Electron emission by applying an extraction voltage



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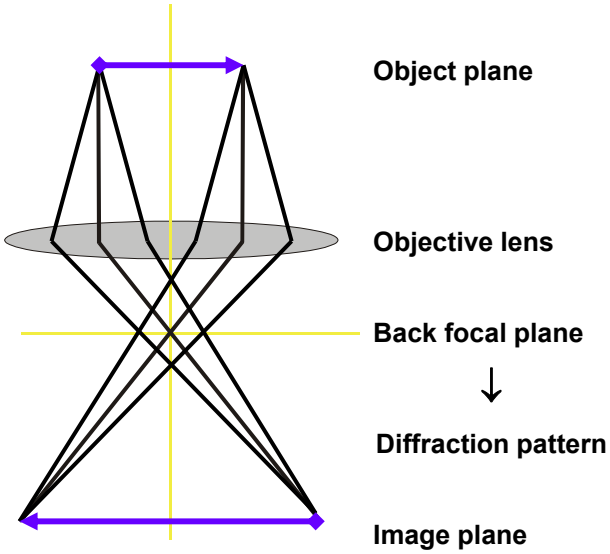
TEM – Imaging and Diffraction



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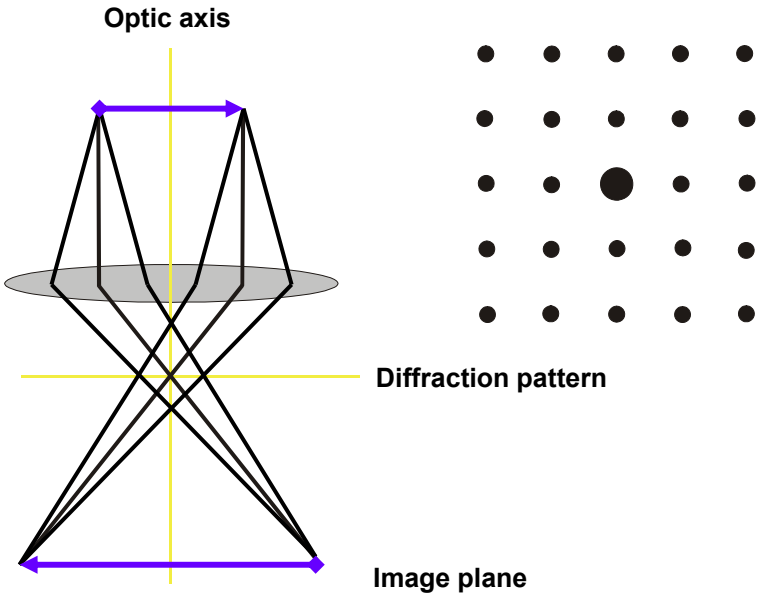
TEM – Imaging and Diffraction



Transmission Electron Microscopy

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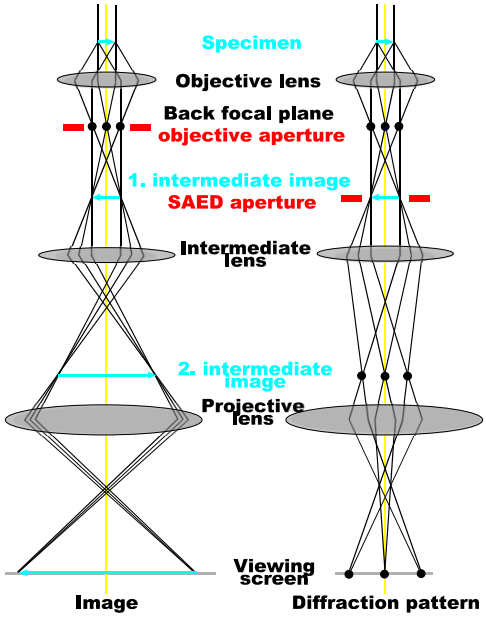
Diffraction and Imaging Mode



Electron Diffraction

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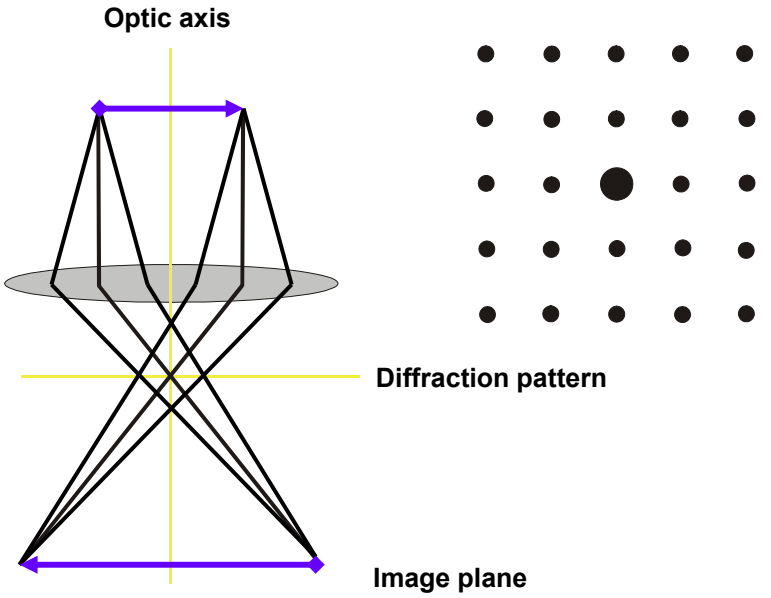
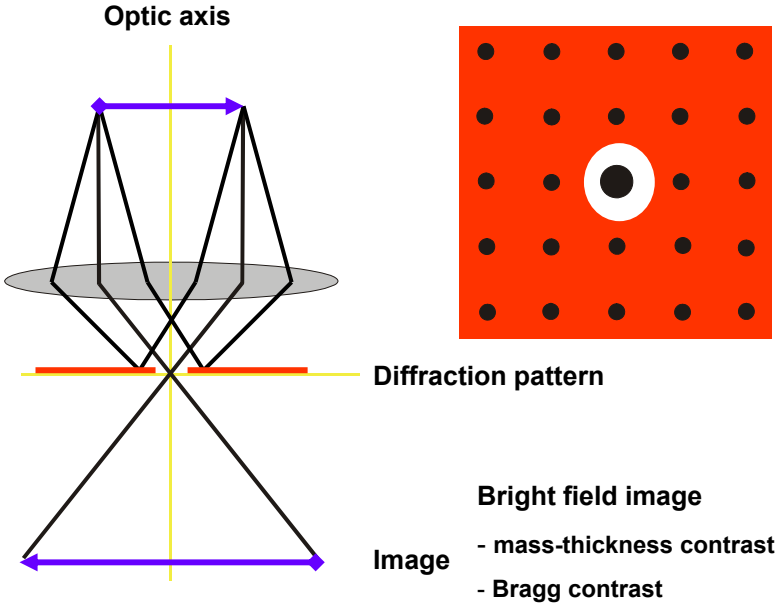
TEM – Imaging and Diffraction



13

TEM – Imaging and Diffraction



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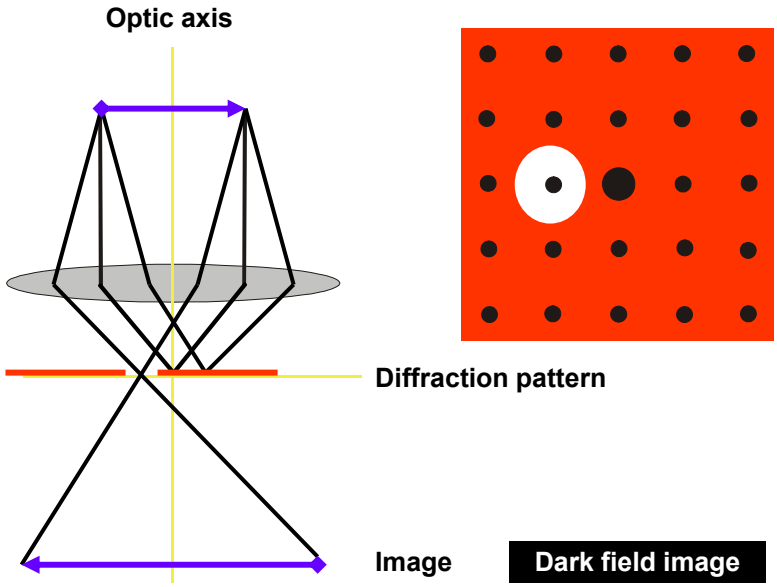
TEM – Imaging and Diffraction



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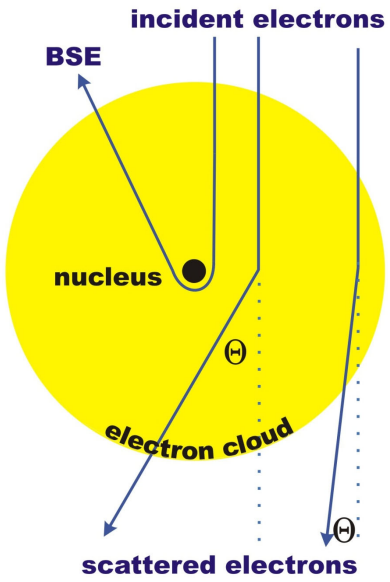
Elastic Scattering of Electrons by an Atom



Weak Coulomb interaction within the electron cloud

⇒ low-angle scattering

Strong Coulomb interaction with the nucleus

⇒ scattering into high angles or even backwards (Rutherford scattering)

⇒ atomic-number (*Z*) contrast

$d\sigma/d\Omega \sim Z^2$

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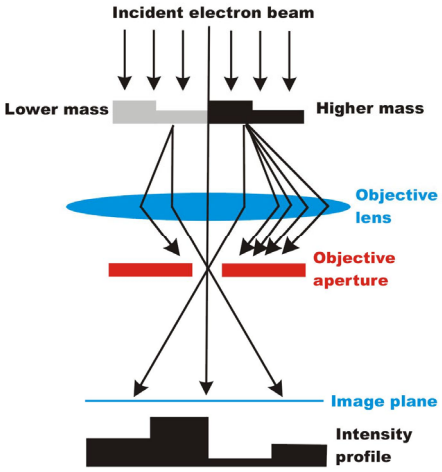
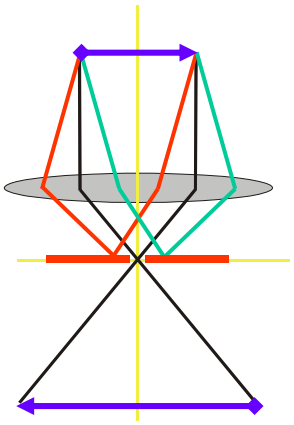
Types of Image Contrast





Diffracted beams do not pass through the objective aperture leading to a decreased intensity of crystalline areas

Mass-Thickness contrast

Bragg contrast

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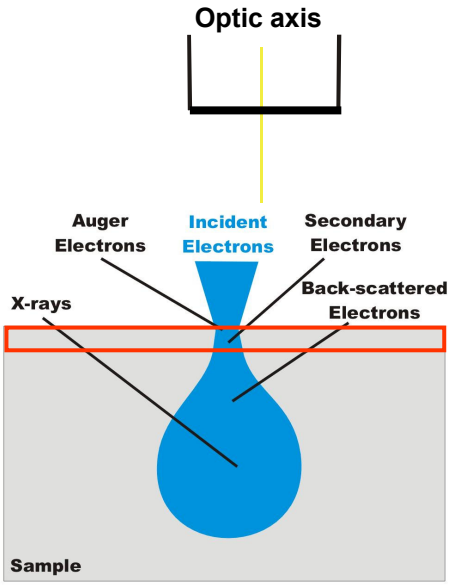
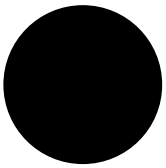
BF TEM Image Contrast





thick sample
⇒ all electrons are absorbed

samples for TEM investigation must be thin (<< 100nm)

⇒ often laborious preparation necessary for compact samples!

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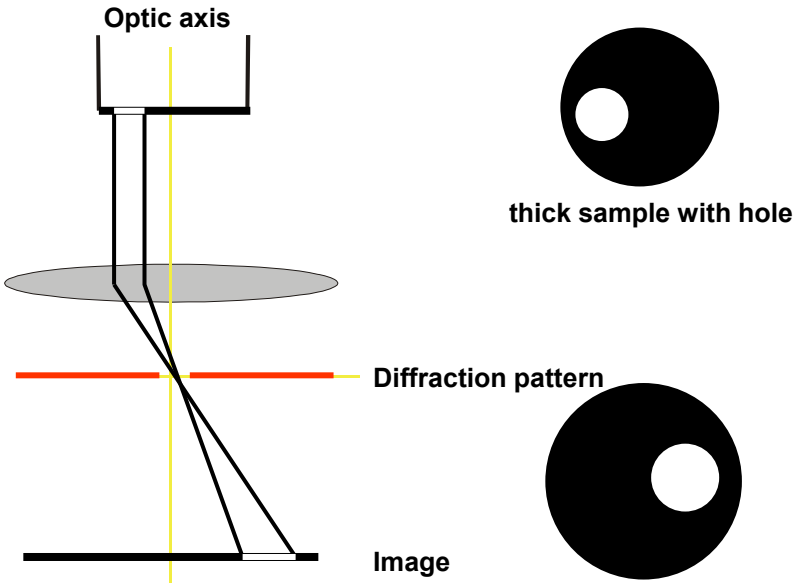
BF Image Contrast



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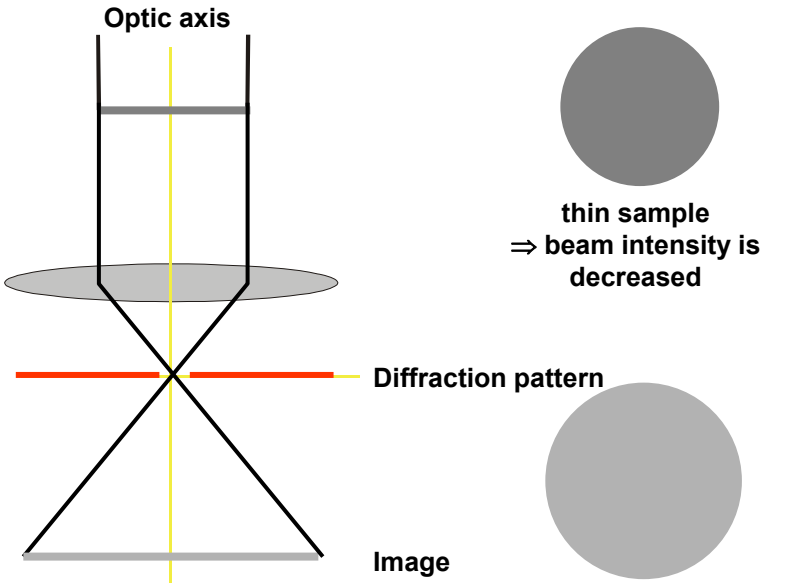
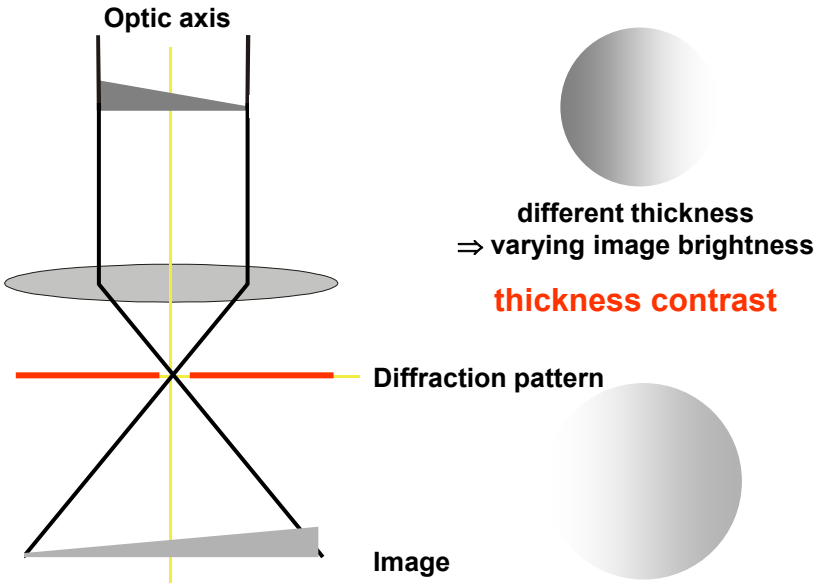
BF Image Contrast



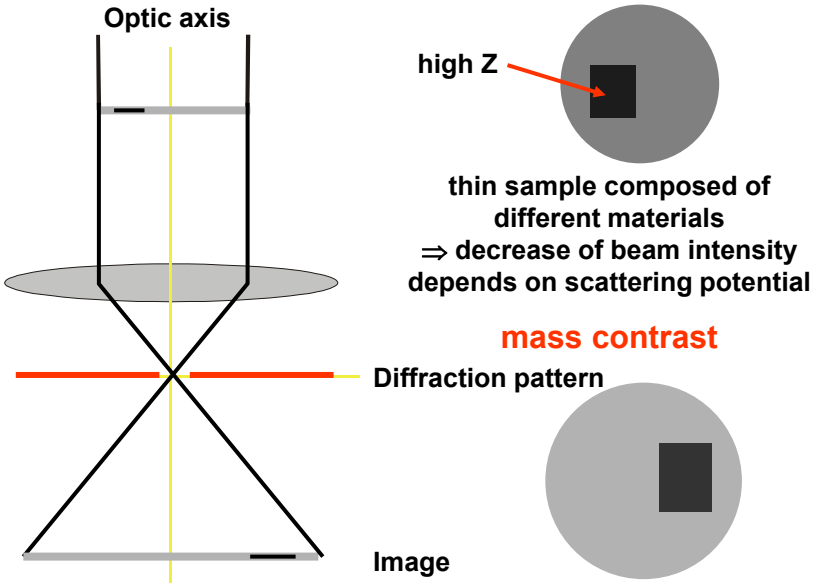
20

BF Image Contrast



21

BF Image Contrast



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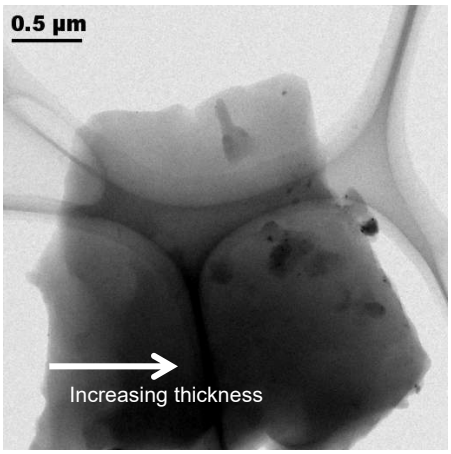
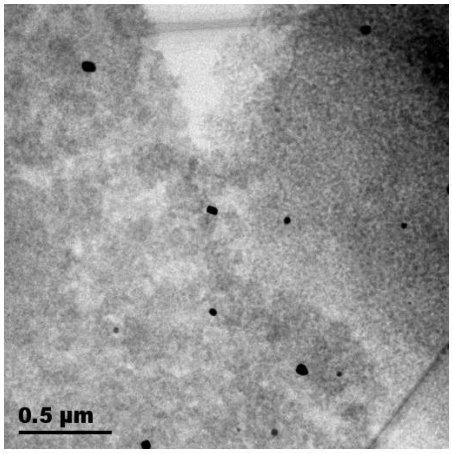
BF Images



Amorphous SiO_2 on C foil

Mainly thickness contrast



Au particles (black) on TiO_2

Mainly mass contrast

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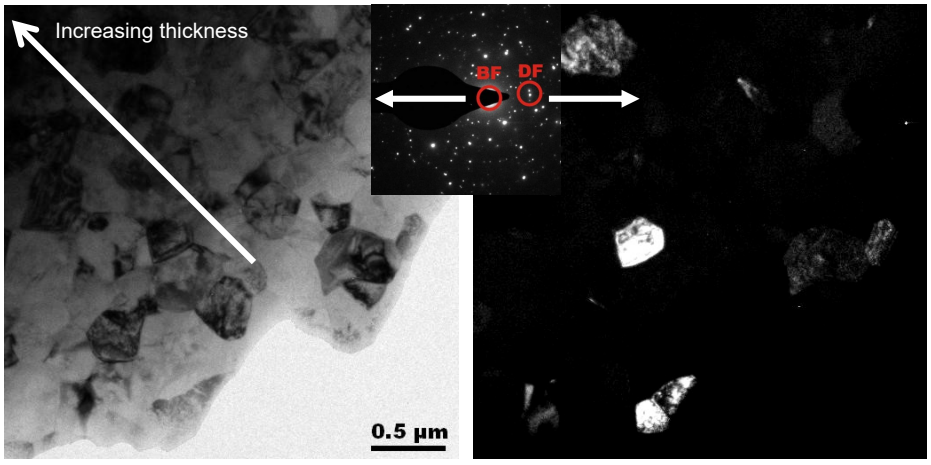
BF and DF Images



ZrO_2 micro crystals; crystals orientated close to a zone axis appear dark in BF and bright in DF

Mainly Bragg contrast

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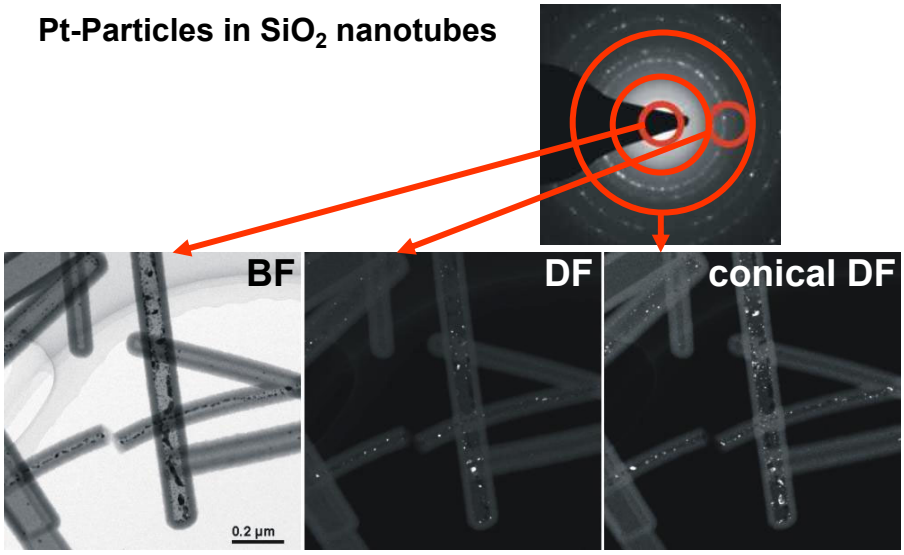
BF and DF Images

Pt-Particles in SiO_2 nanotubes



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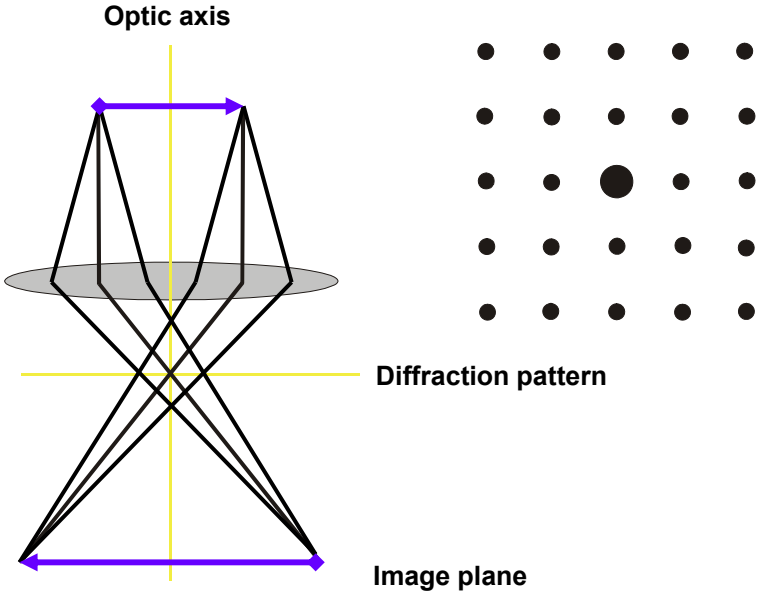
TEM – Imaging and Diffraction



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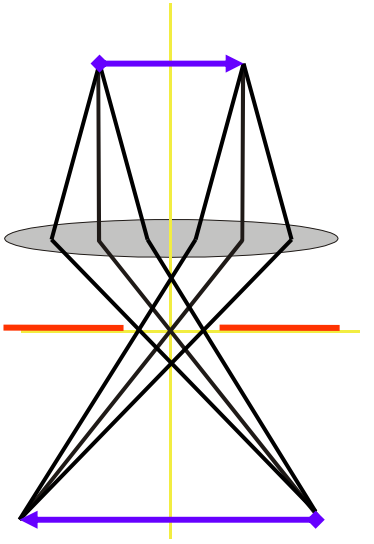
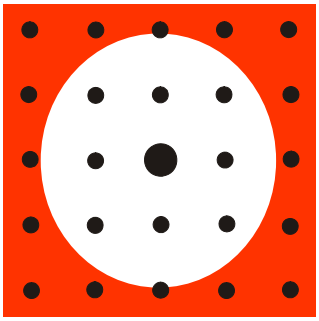
TEM – Imaging and Diffraction





Diffraction pattern

Image

High-resolution image

Interference of several diffracted beams with each other and the direct beam

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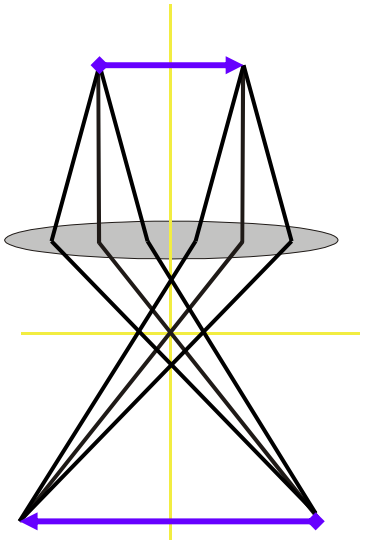
TEM – Imaging and Diffraction



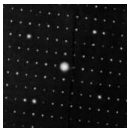
Mathematics

Fourier Transform

$$F\{\mathrm{f(x)}\} = \int_{-\infty}^{+\infty} f(x)\, \mathrm{e}^{-2i\pi qx}\, \mathrm{dx}$$

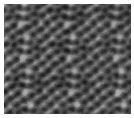
Fourier analysis

Diffraction pattern



Fourier synthesis

Image



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TEM – Imaging and Diffraction

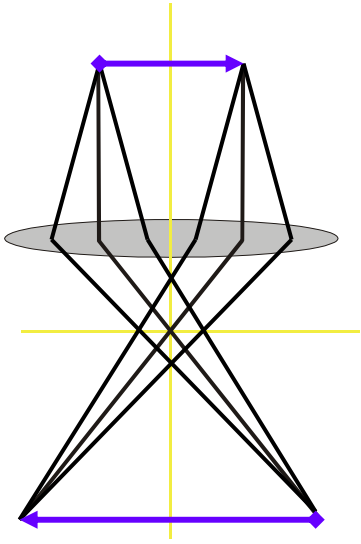

Image Processing

Filtered image

↑ Fourier Transform

Diffraction pattern

↑ Fourier Transform

HRTEM image

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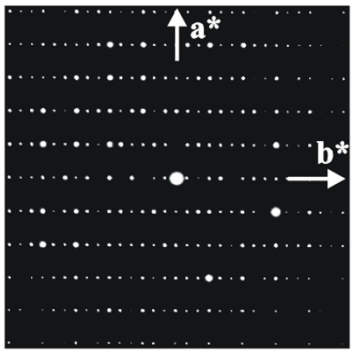
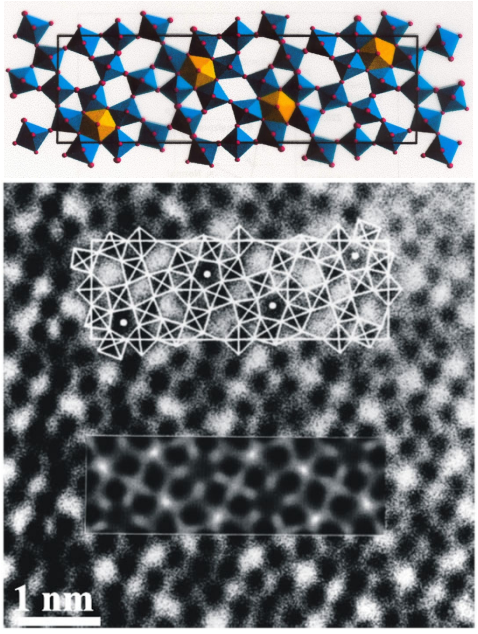
ED + HRTEM



$Nb_7W_{10}O_{47}$ – threefold TTB superstructure



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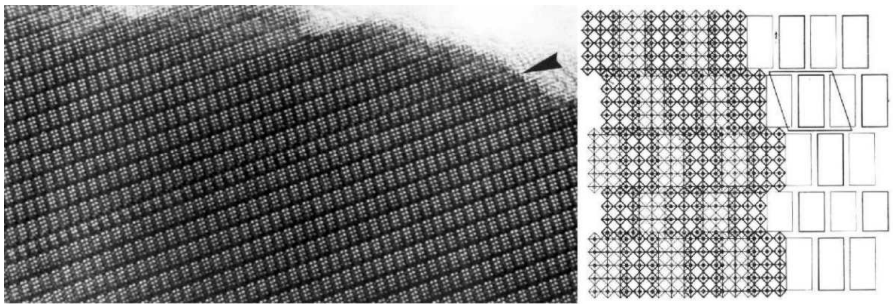
HRTEM: Detection of Defects



Planar defect in $ZnNb_{14}O_{35}F_2$

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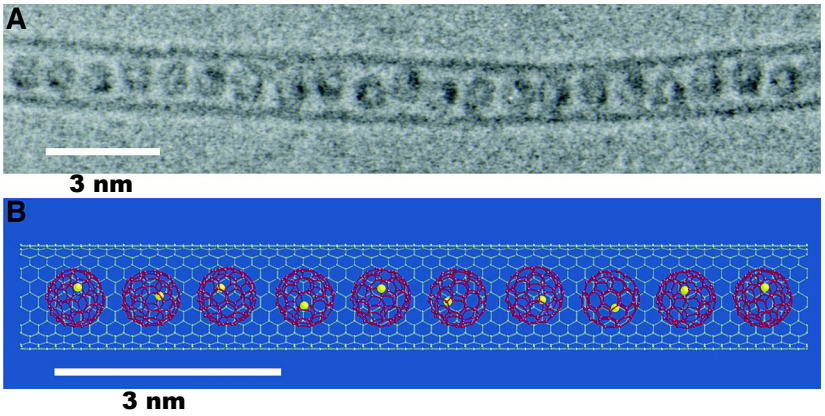
HRTEM: Imaging Single Atoms

$Gd@C_{82}$ in SWCNT



Suenaga et al, *Science* **290** (2000) 2280

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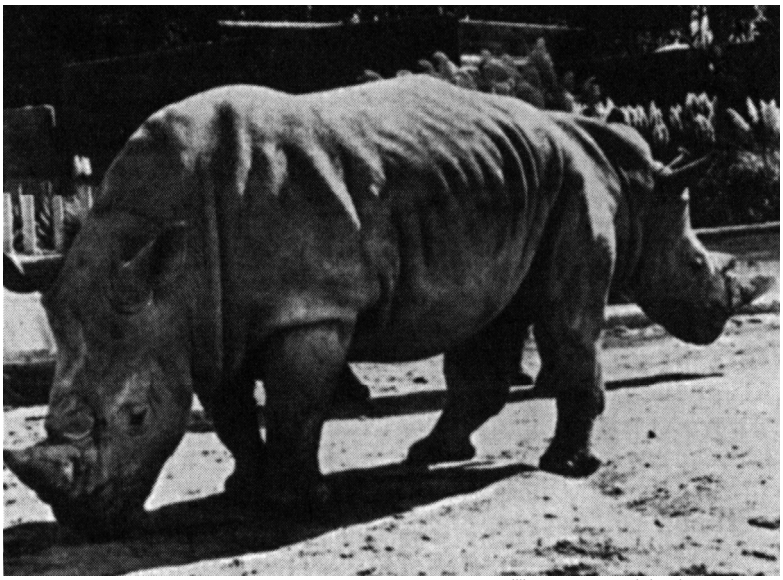
Projection Problem: 3D ⇒ 2D



From: Williams, Carter: Transmission Electron Microscopy

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Transmission Electron Microscopy

Types of contrast:

- Mass-thickness (BF/DF)
- Bragg (BF/DF)
- Phase (HRTEM; resolution limit < 1Å)

Determination of

- Structure: HRTEM
- Defects: HRTEM, TEM
- Lattice constants and symmetry: ED
- Particle size: TEM, HRTEM

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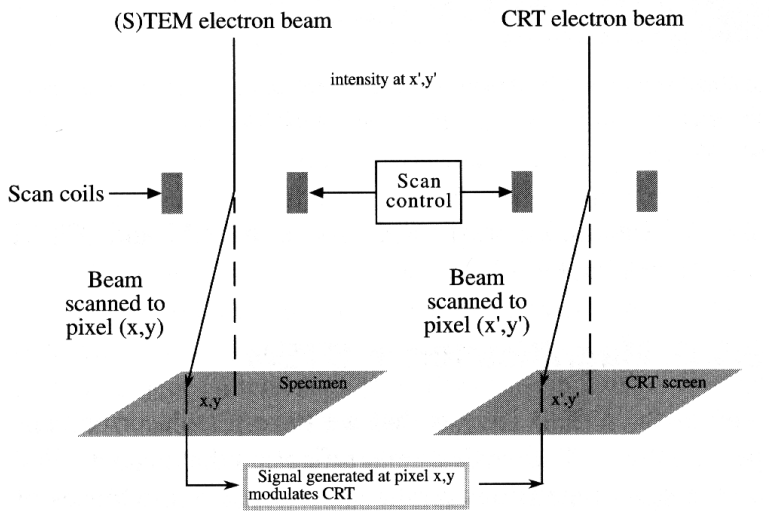
Scanning Transmission Electron Microscopy (STEM)



From: Williams, Carter: Transmission Electron Microscopy

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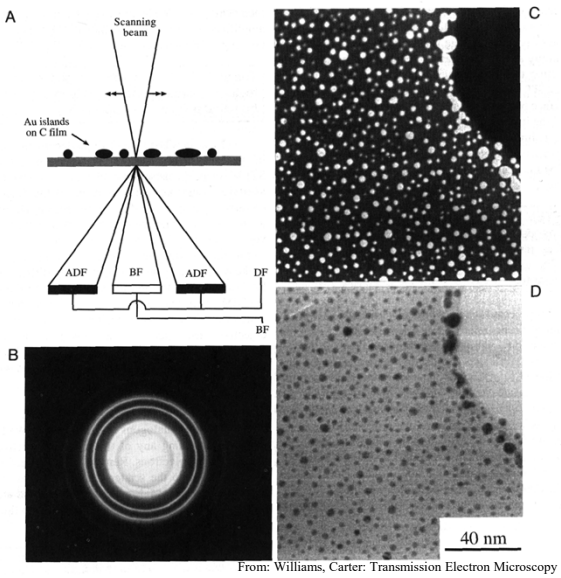
BF and DF Imaging in STEM

Au islands on a C film



DF image recorded by the annular dark field detector

BF image recorded by the bright field detector

From: Williams, Carter: Transmission Electron Microscopy

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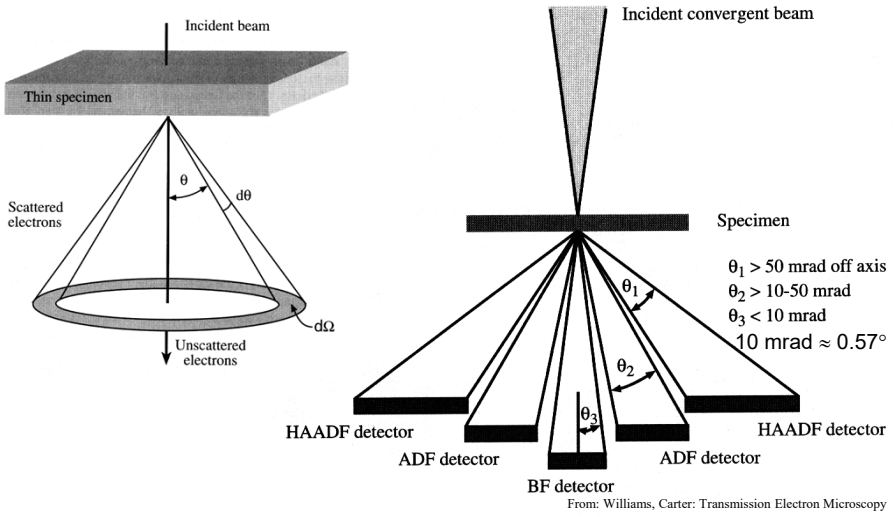


From: Williams, Carter: Transmission Electron Microscopy

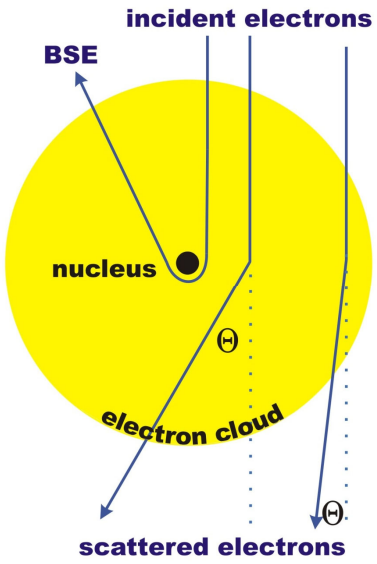
STEM Detectors

BF: Bright Field detector

ADF: Annular Dark Field detector

HAADF: High Angle Annular Dark Field detector

Scattering of Electrons at an Atom



Weak Coulomb interaction within the electron cloud

⇒ low-angle scattering

Strong Coulomb interaction with the nucleus

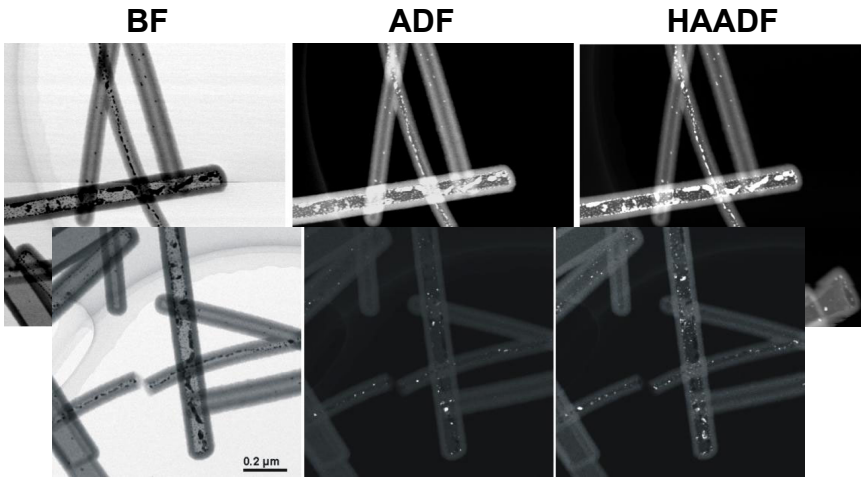
⇒ scattering into high angles or even backwards (Rutherford scattering)

⇒ atomic-number (*Z*) contrast

$$d\sigma/d\Omega \sim Z^2$$

BF and DF Imaging in STEM

Pt particles in SiO_2 nanotubes



BF DF conical DF TEM

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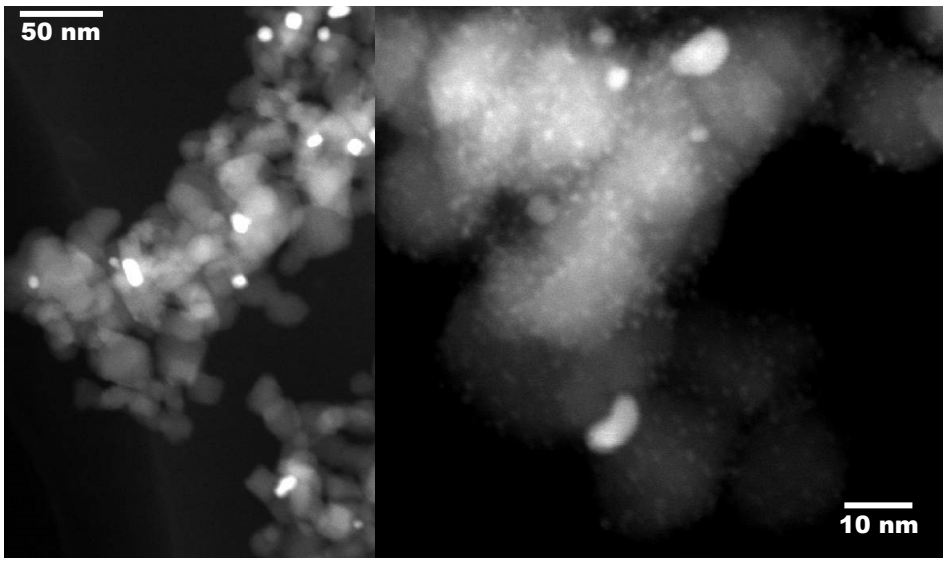
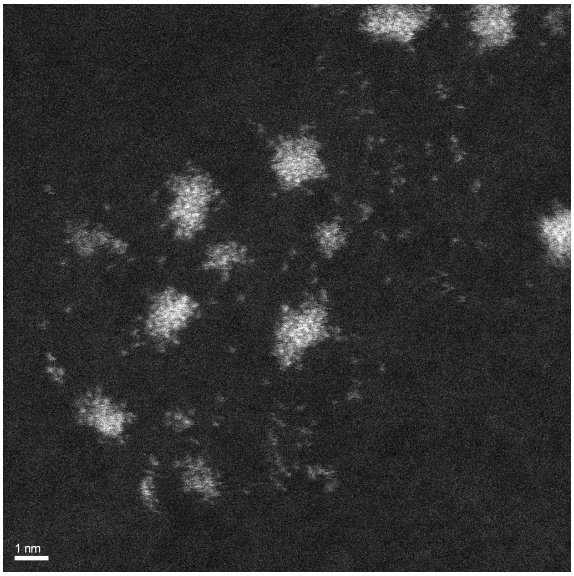
HAADF-STEM or Z contrast Images of Au Particles on Titania



40

HAADF-STEM or Z contrast Images of Pt Clusters and Atoms on Carbon



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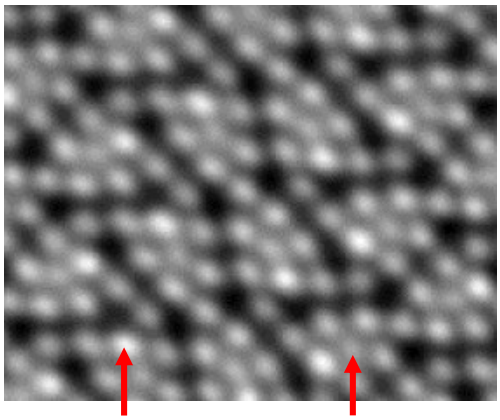
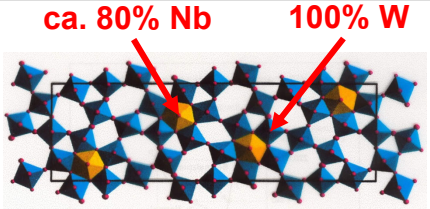
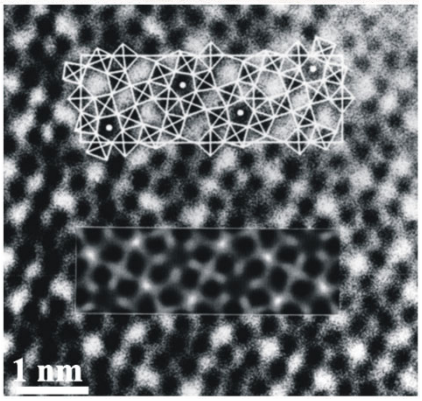
Information about Elemental Distribution in HAADF-STEM or Z contrast images



100% W ca. 80% Nb

HAADF-STEM of $Nb_8W_9O_{47}$

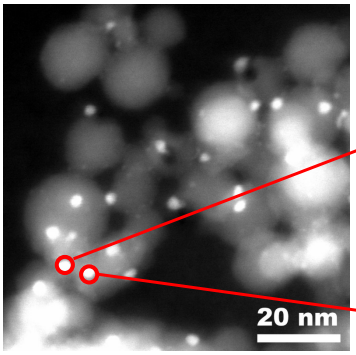




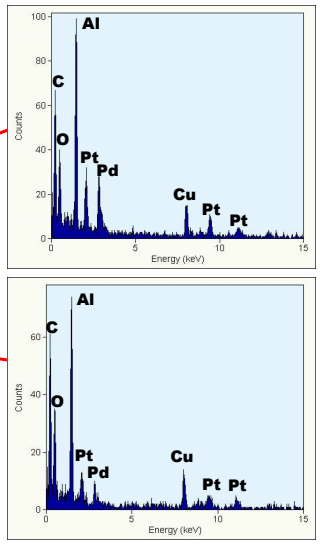
42

Pd and Pt supported on alumina: Size of the particles? Alloy or separated?

STEM + EDXS: Point Analyses



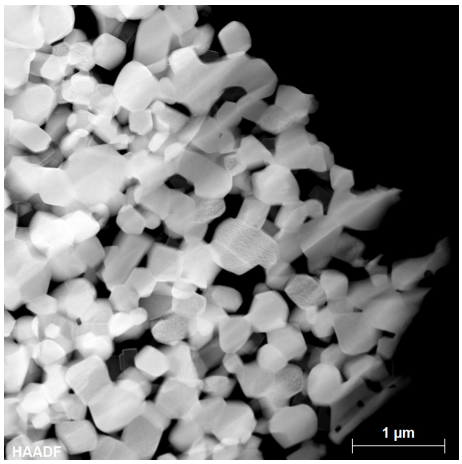
HAADF-STEM image

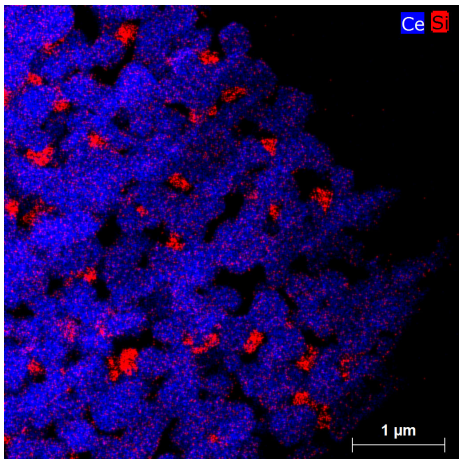


43

Elemental Mapping

STEM + EDXS: Area Analyses: CeO_2 and zeolite

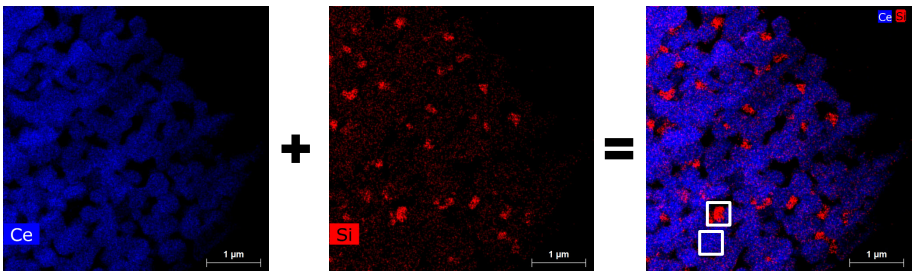




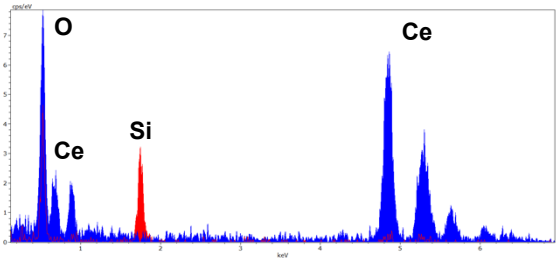
44

Elemental Mapping

STEM + EDXS: Area Analyses: CeO_2 and zeolite



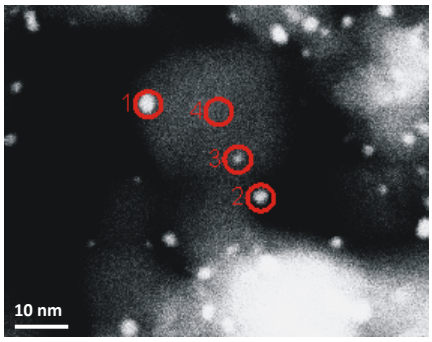
Data cube:
for each pixel in the image, there is an EDX spectrum recorded and stored

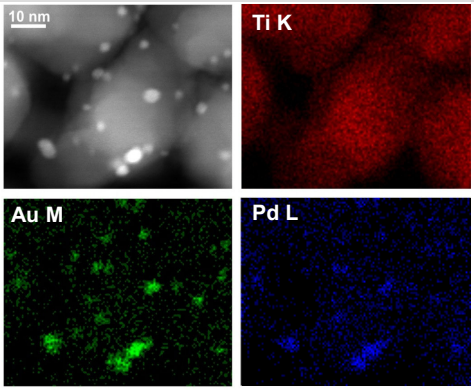


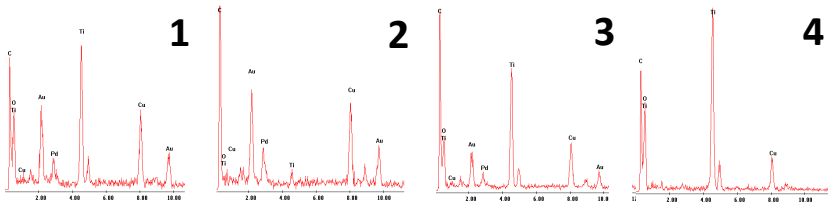
45

STEM+EDXS: spot analyses vs. elemental mapping

Au and Pd on TiO_2







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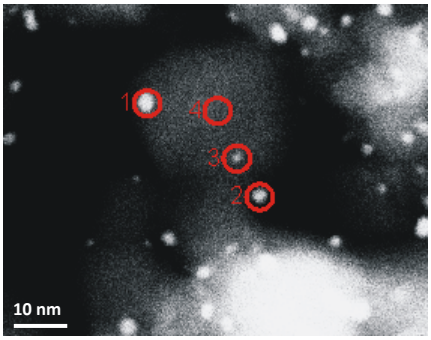
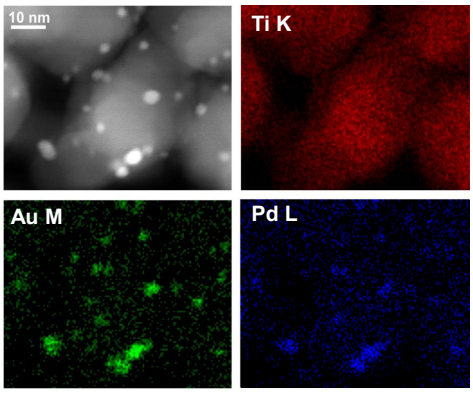
STEM+EDXS: spot analyses vs. elemental mapping





quick and efficient if a clear contrast between the different components appears in STEM

EDX spectra of selected spots with good signal:noise ratio measured in < 1 min

time-consuming but provides the full data cube (1EDXS/pixel)

EDX spectra extracted from selected spots with bad signal:noise ratio

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Scanning Transmission Electron Microscopy

Contrast:

- Mass-thickness (BF/DF)
- Bragg (BF/DF)
- Z^2 (HAADF)

Determination of

- Particles on support : HAADF
- Structure and defects : HR
- Chemical information : HAADF

Important: Combination with EDXS or EELS

Scanning Transmission Electron Microscopy

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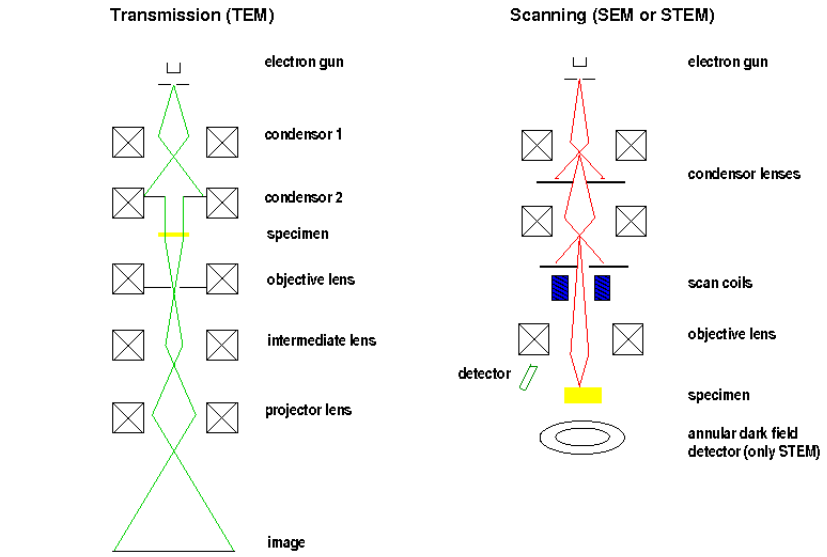
TEM versus STEM



Resolution: $\Delta x = 0.66\ C_s^{1/4}\lambda^{3/4}$ $\quad d = 0.41\ C_s^{1/4}\lambda^{3/4}$

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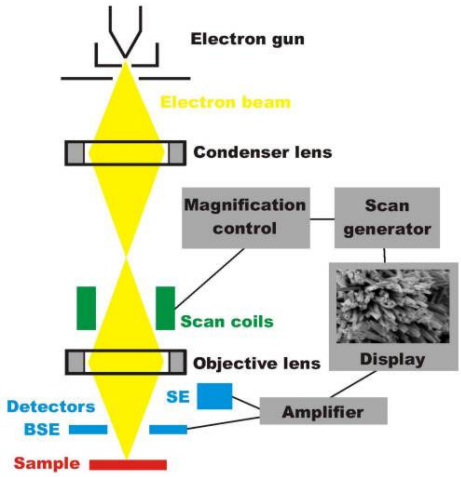
Scanning Electron Microscopy (SEM)



Quanta 200 FEG (FEI)

Scanning Electron Microscopy

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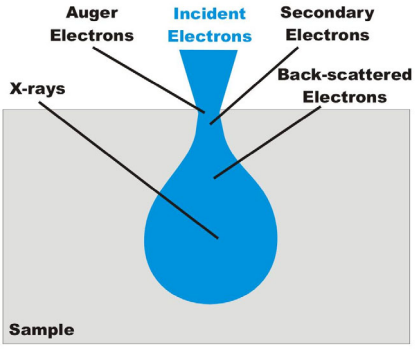
Signals used in the SEM



Secondary Electrons (SE)

- low energy < 100 eV (result of inelastic interactions)
- information about topography and morphology
- escape only when generated close to the surface

Back-scattered Electrons (BSE)

- high energy ≅ E_0 (result of elastic interactions)
- morphology and chemical Information

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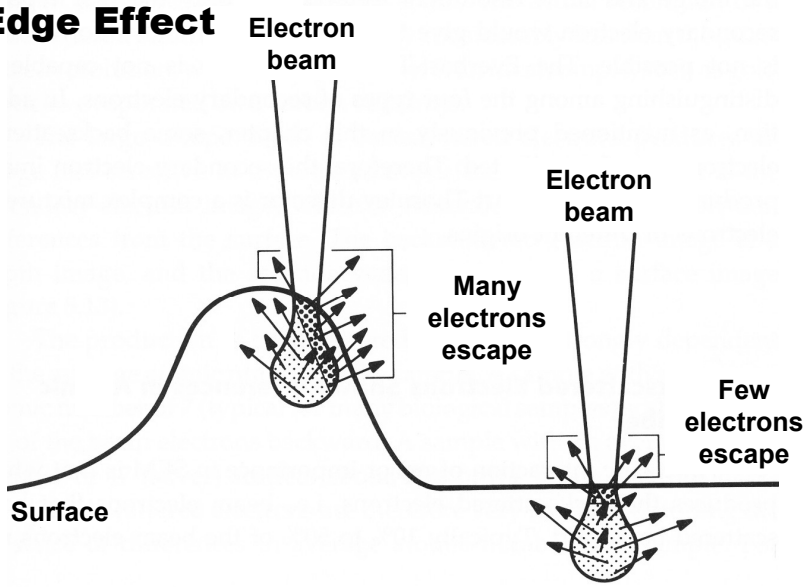
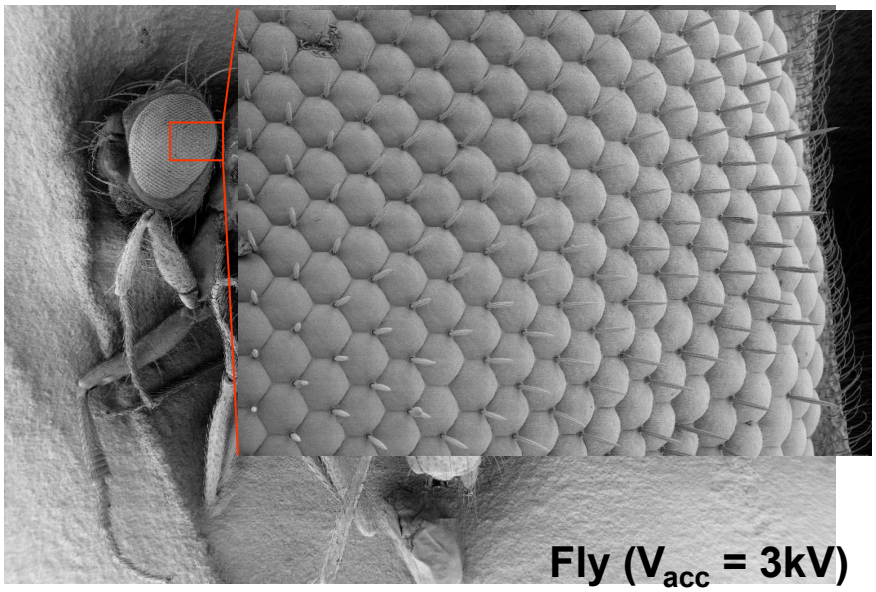
Topographic Contrast in the SEM

Edge Effect



52

SEM: Imaging with Secondary Electrons



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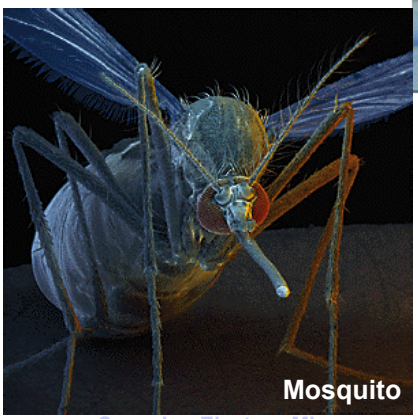
Colorized SEM Images



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www.scharfphoto.com

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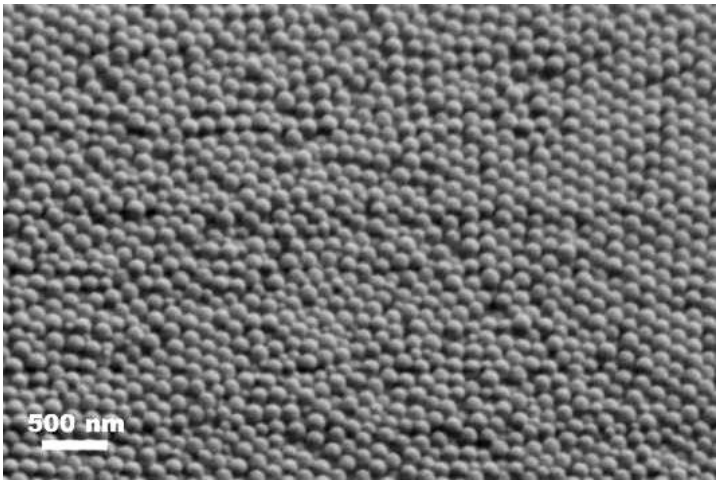
SEM: Imaging with Secondary Electrons



Latex balls (V_{acc} = 1kV)

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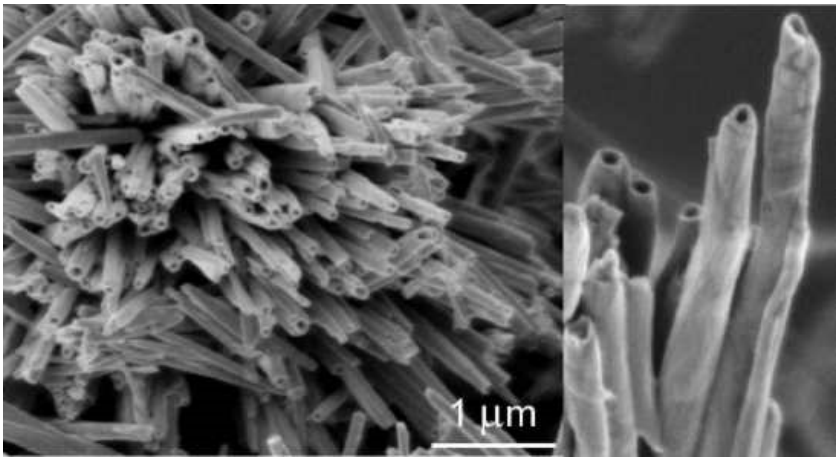
SEM: Imaging with Secondary Electrons



Vanadium oxide nanotubes (V_{acc} = 1kV)

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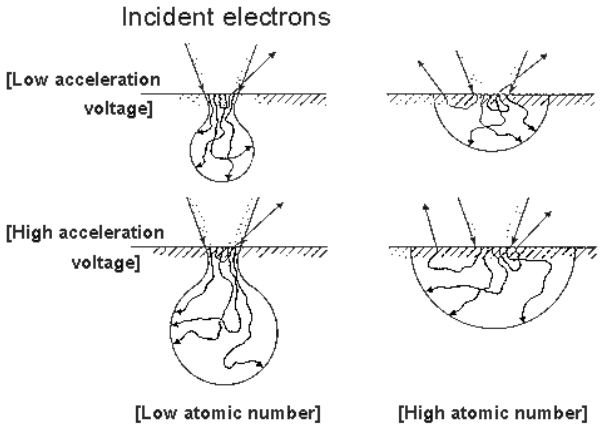
SEM: Dependence on Electron Energy



Penetration depth of electrons in matter

- **increases with increasing V_{acc}**
- **decreases with increasing atomic number**

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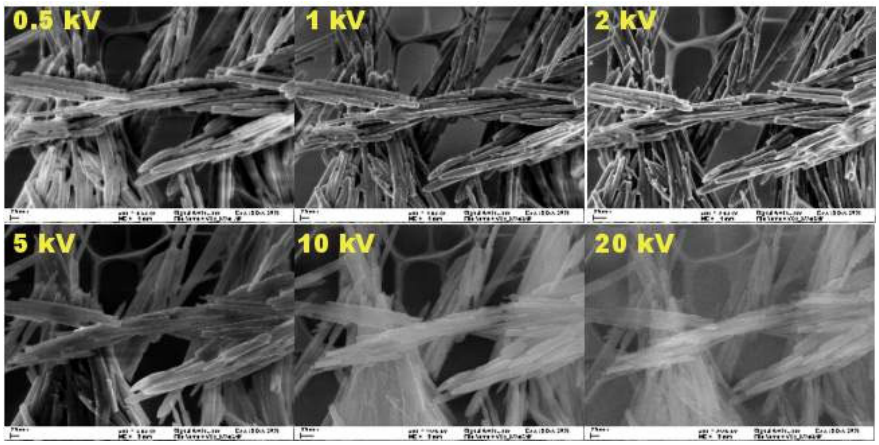
SEM: Dependence on Electron Energy



Resolution (Gemini 1530 FEG):

1 nm at 20 kV 1.5 nm at 10 kV
2.5 nm at 1 kV 5 nm at 0.2 kV

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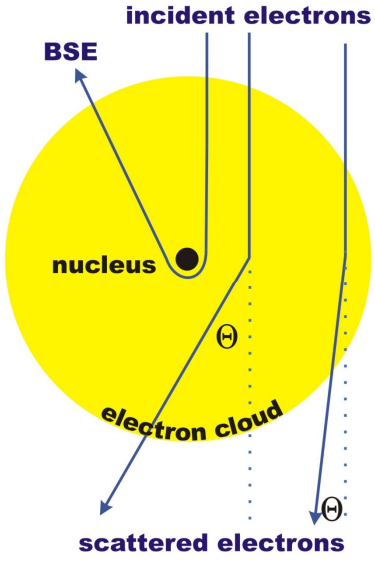
Scattering of Electrons at an Atom



Weak Coulomb interaction within the electron cloud

⇒ low-angle scattering

Strong Coulomb interaction with the nucleus

⇒ scattering into high angles or even backwards (Rutherford scattering)

⇒ atomic-number (Z) contrast

$d\sigma/d\Omega \sim Z^2$

c.f. Z contrast with HAADF-STEM

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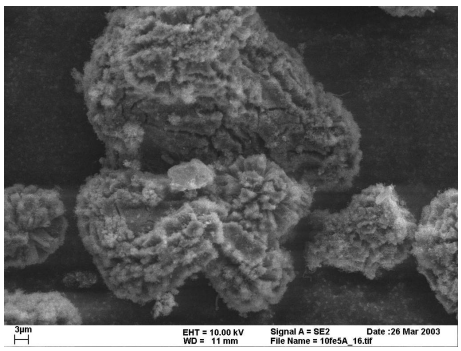
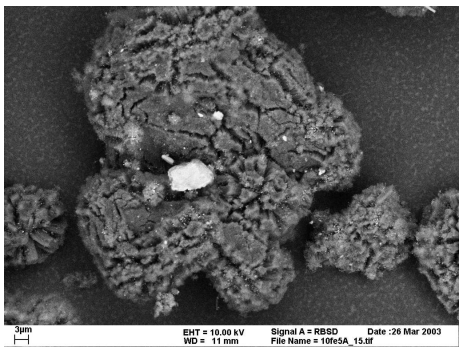
SEM: Detection of SE versus BSE

Fe particles in C



Secondary electron detector



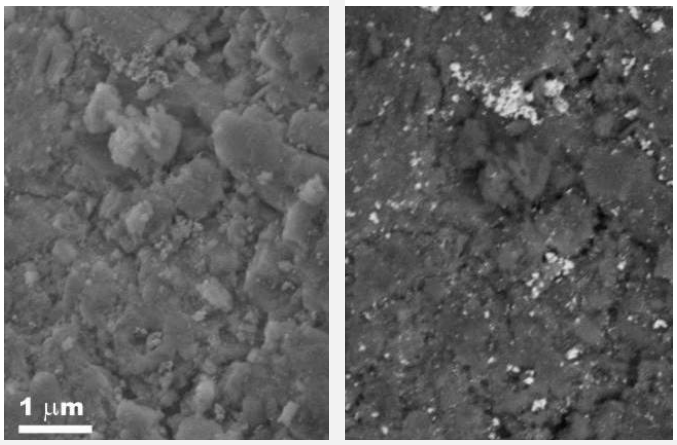
Backscattered electron detector

Fe particles bright (Z contrast)

60

SEM: Detection of SE versus BSE

Pt particles on alumina



Secondary electron detector | Backscattered electron detector

Pt particles bright (Z contrast)

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Scanning Electron Microscopy (SEM)

Detection of:

- Secondary electrons
- Back-scattered electrons

Determination of

- Morphology
- Surface topology
- Particles of heavy elements

Combination with EDXS

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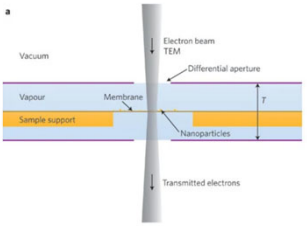
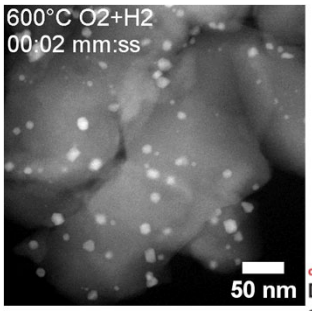
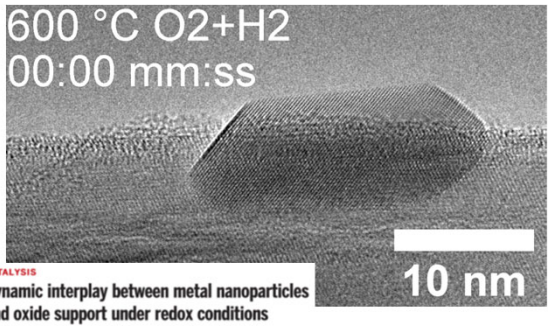
In-situ investigations

- Heating
- Nano-indentation
- Electric conductivity
- Light
- Liquid and gas environment







CATALYSIS

Dynamic interplay between metal nanoparticles and oxide support under redox conditions

H. Frey[1,2]†, A. Beck[2,3]†, X. Huang[1,4]*, J. A. van Bokhoven[2,3]*, M. G. Willinger[2]*†

***Science* 376**, 982-987 (2022)

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Scripts: *Interactions.pdf* and *Introduction into TEM and STEM* on www.microscopy.ethz.ch/downloads

Textbooks:

Williams, Carter, Plenum Press, New York, 1996:
Transmission Electron Microscopy (available in chemistry library)

Thomas, Gemming, Springer, Berlin, 2014:
Analytical Transmission Electron Microscopy – An Introduction for Operators
Analytische Transmissionselektronenmikroskopie – eine Einführung für den Praktiker

Lecture: *Electron Microscopy* (each fall term)

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