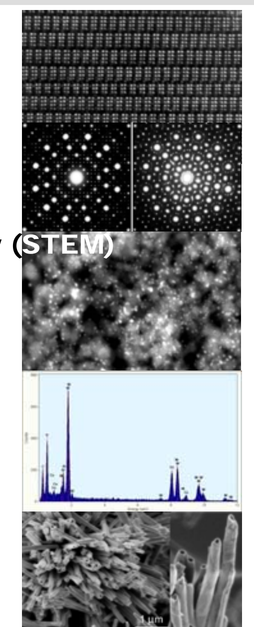
Electron Microscopy Methods



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)

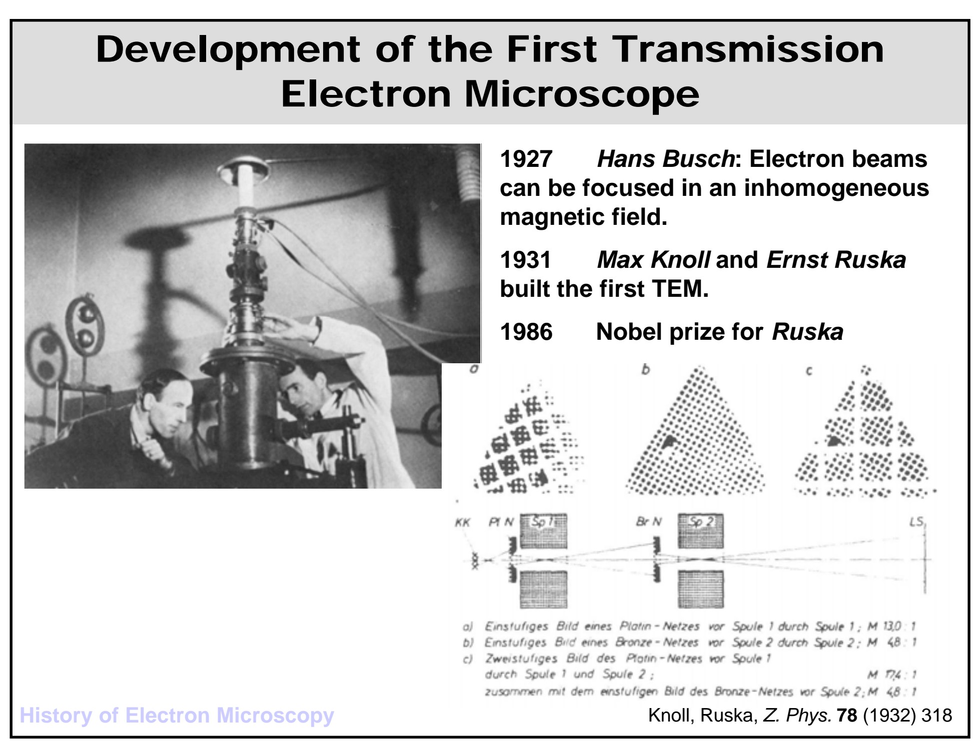
- Bright / Dark Field (BF/DF-STEM)
- High-Angle Annular Dark Field (HAADF-STEM)

Analytical Electron Microscopy (AEM)

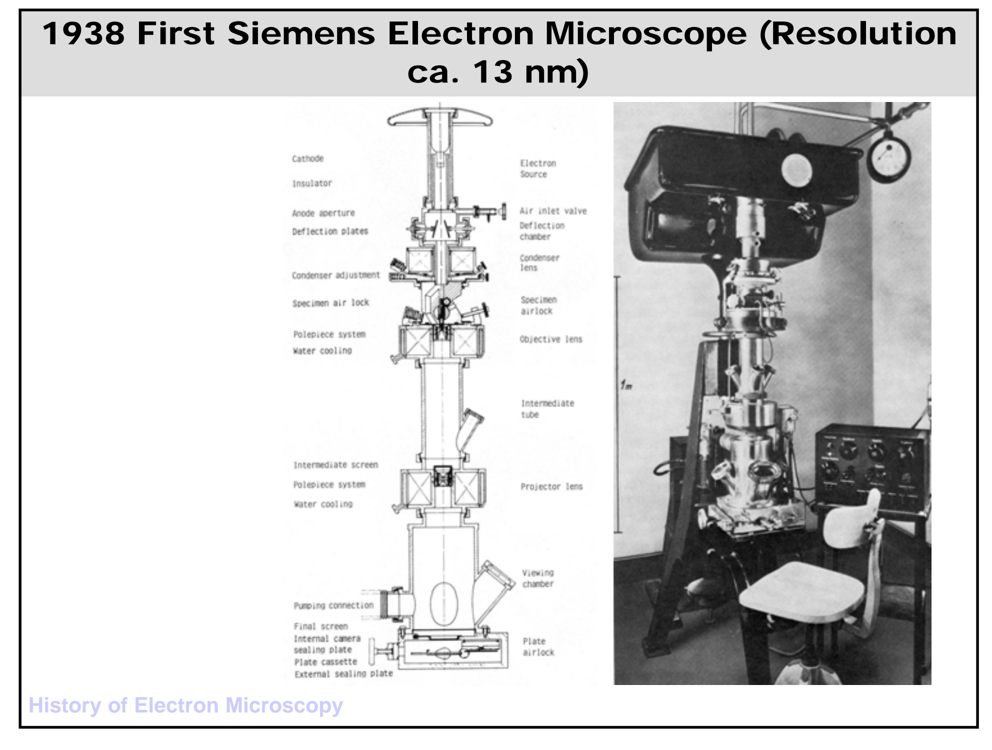
- X-ray Spectroscopy
- Electron Energy-Loss Spectroscopy (EELS)
- Electron Spectroscopic Imaging (ESI)

Scanning Electron Microscopy (SEM)

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



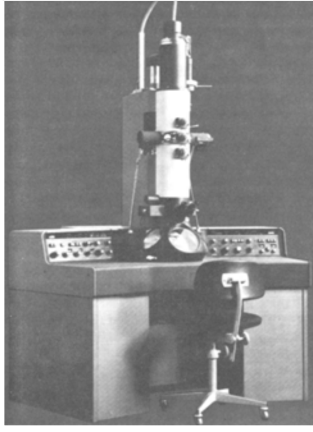
Development of the First Transmission Electron Microscope
1927 Hans Busch: Electron beams can be focused in an inhomogeneous magnetic field.
1931 Max Knoll and Ernst Ruska built the first TEM.
1986 Nobel prize for Ruska
a
b
c
KK
Pl N
Sp 1
Br N
Sp 2
LS
a) Einstufiges Bild eines Platin-Netzes vor Spule 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
History of Electron Microscopy
Knoll, Ruska, Z. Phys. 78 (1932) 318



1938 First Siemens Electron Microscope (Resolution ca. 13 nm)
Cathode
Insulator
Anode aperture
Deflection plates
Condenser adjustment
Specimen air lock
Polepiece system
Water cooling
Intermediate screen
Polepiece system
Water cooling
Pumping connection
Final screen
Internal camera sealing plate
Plate cassette
External sealing plate
Electron Source
Air inlet valve
Deflection chamber
Condenser lens
Specimen airlock
Objective lens
Intermediate tube
Projector lens
Viewing chamber
Plate airlock
1m
History of Electron Microscopy

Transmission Electron Microscopes

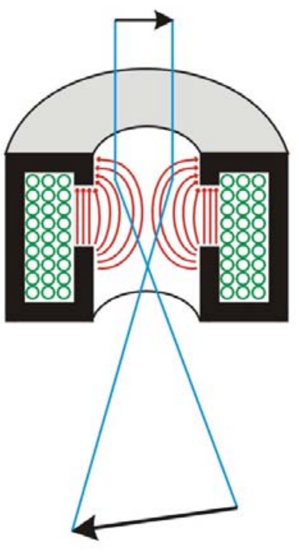
1939: first TEM serially produced by Siemens
resolution ca. 7 nm



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

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

Magnetic Lens



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

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

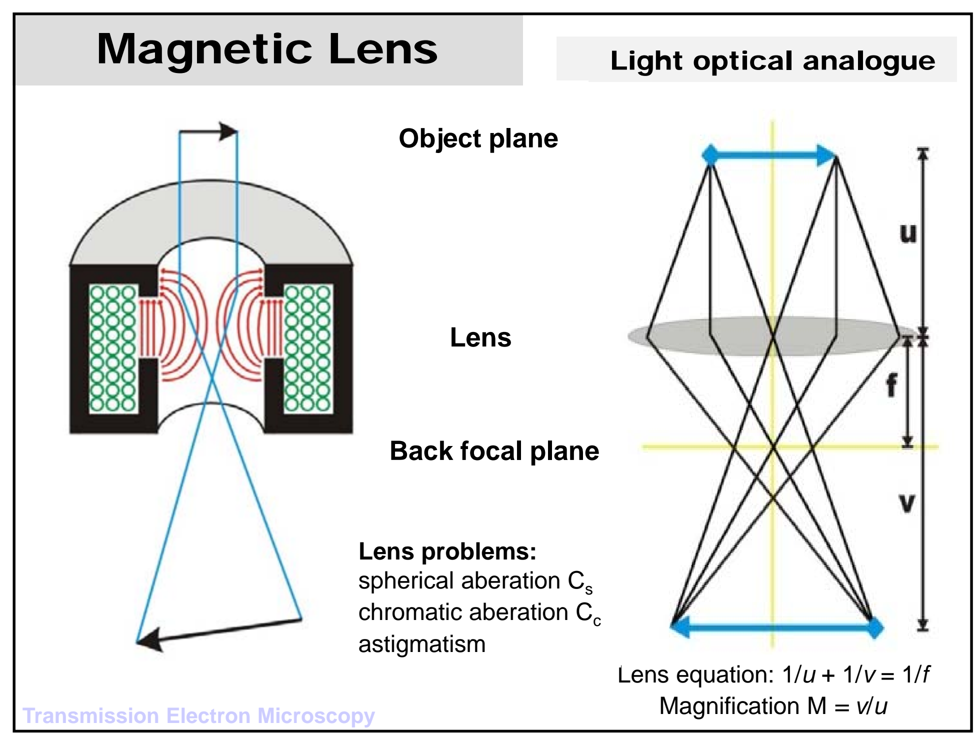
$$|\mathbf{F}| = e\mathbf{v}\mathbf{B}\sin(\mathbf{v},B)$$

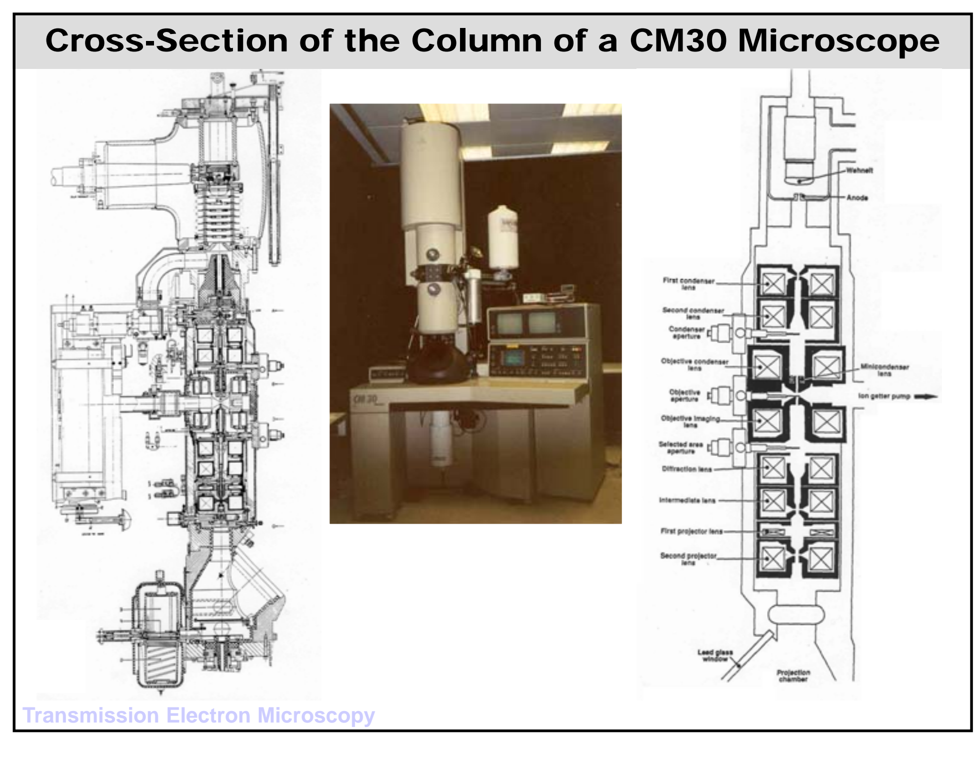
E: strength of electric field

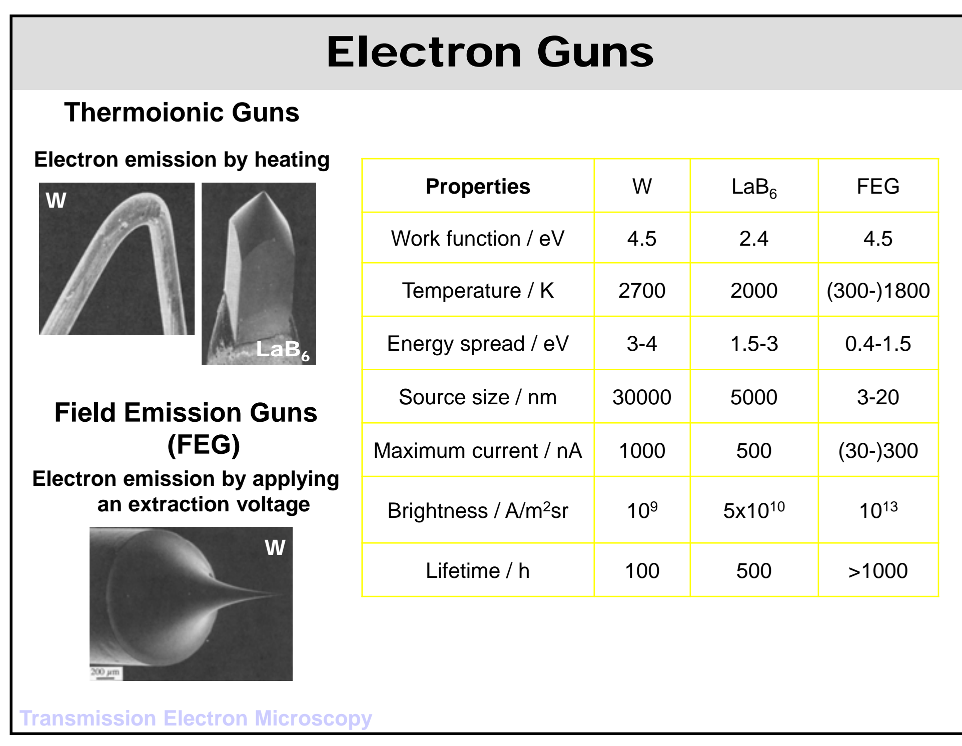
B: strength of magnetic field

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

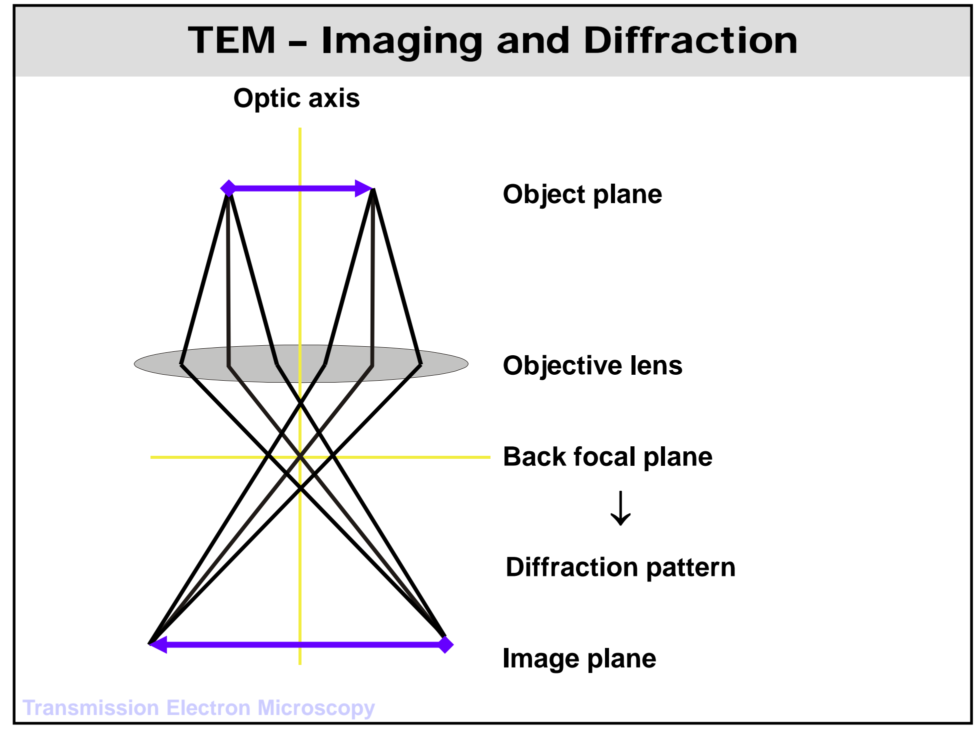
Magnetic lenses
- manipulate the electron beam
- form an image of the object

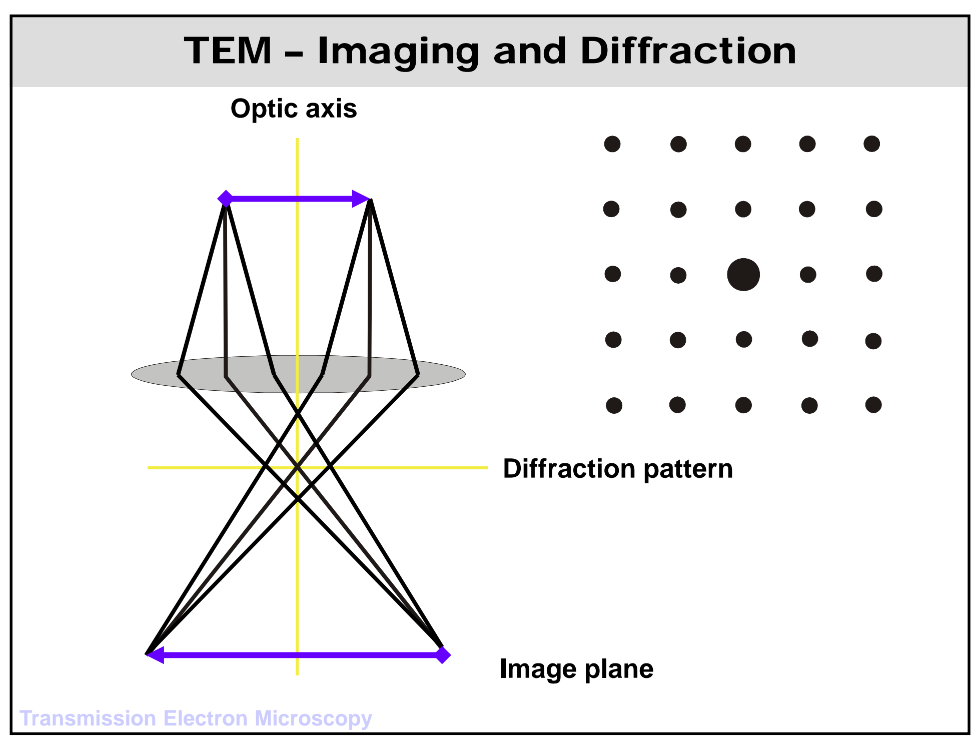

Magnetic Lens
Light optical analogue
Object plane
Lens
Back focal plane
u
f
v
Lens problems:
spherical aberation C_s
chromatic aberation C_c
astigmatism
Lens equation: $1/u + 1/v = 1/f$
Magnification $M = v/u$
Transmission Electron Microscopy

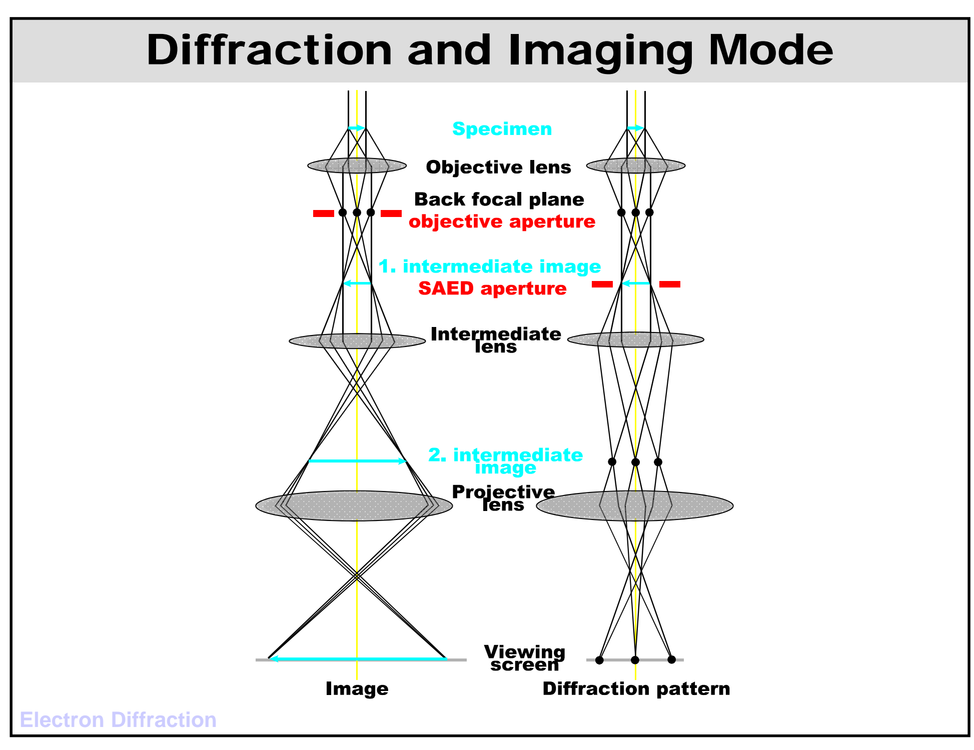

Cross-Section of the Column of a CM30 Microscope
Wehnelt
Anode
First condenser lens
Second condenser lens
Condenser aperture
Objective condenser lens
Minicondenser lens
Objective aperture
Ion getter pump
Objective imaging lens
Selected area aperture
Diffraction lens
Intermediate lens
First projector lens
Second projector lens
Lead glass window
Projection chamber
Transmission Electron Microscopy

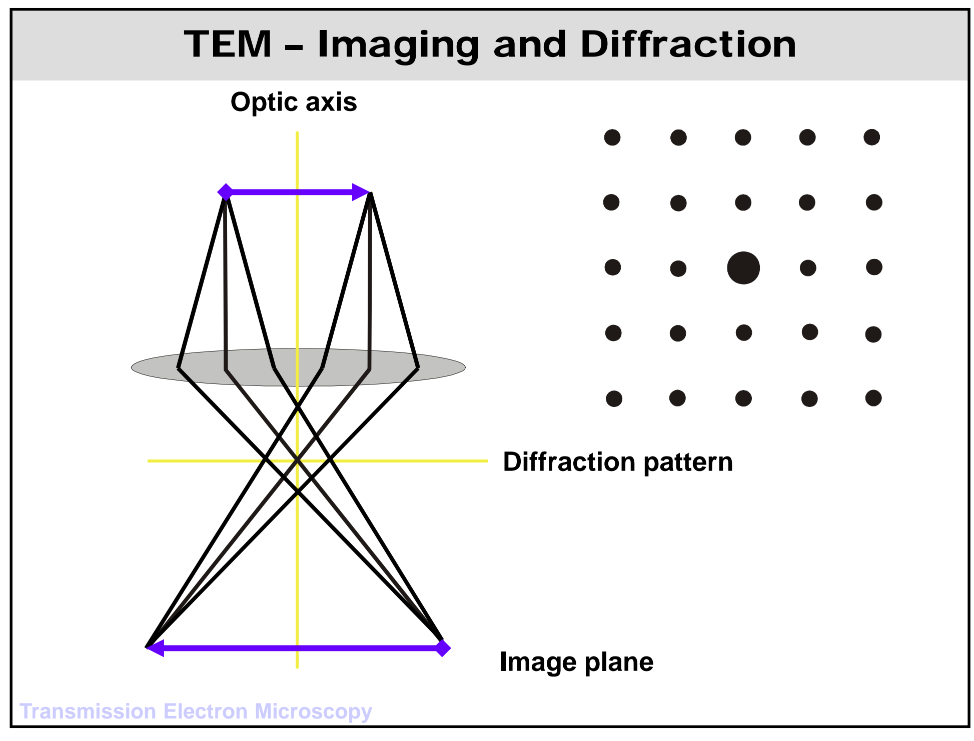


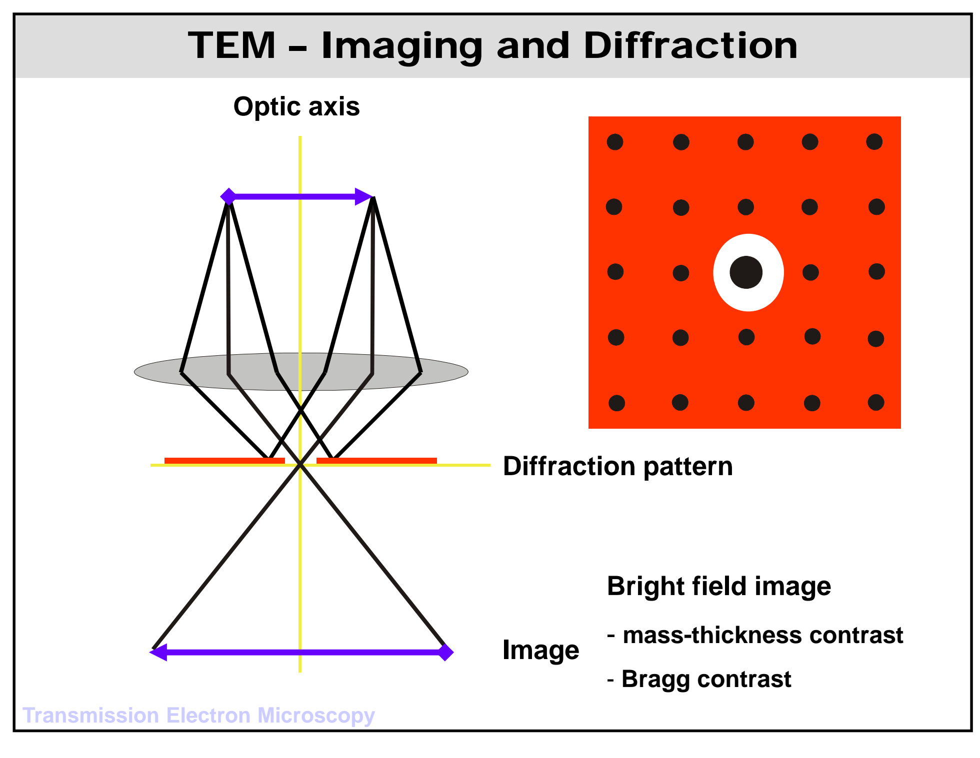
Properties	W	LaB_6	FEG
Work function / eV	4.5	2.4	4.5
Temperature / K	2700	2000	(300-)1800
Energy spread / eV	3-4	1.5-3	0.4-1.5
Source size / nm	30000	5000	3-20
Maximum current / nA	1000	500	(30-)300
Brightness / A/m^2sr	10^9	$5x10^{10}$	10^{13}
Lifetime / h	100	500	>1000

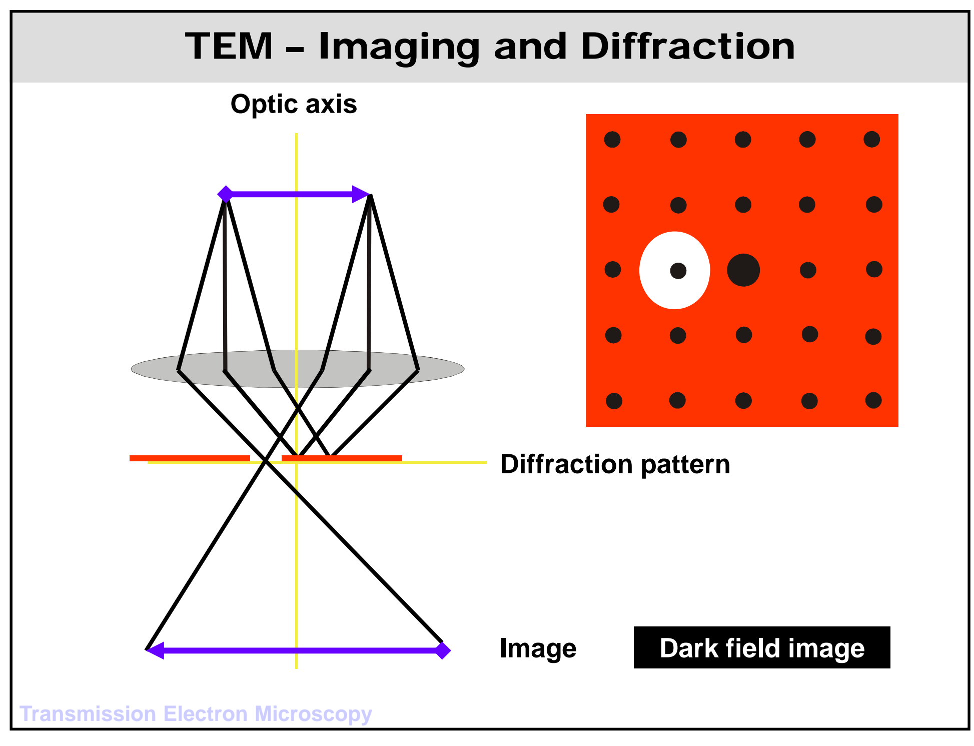


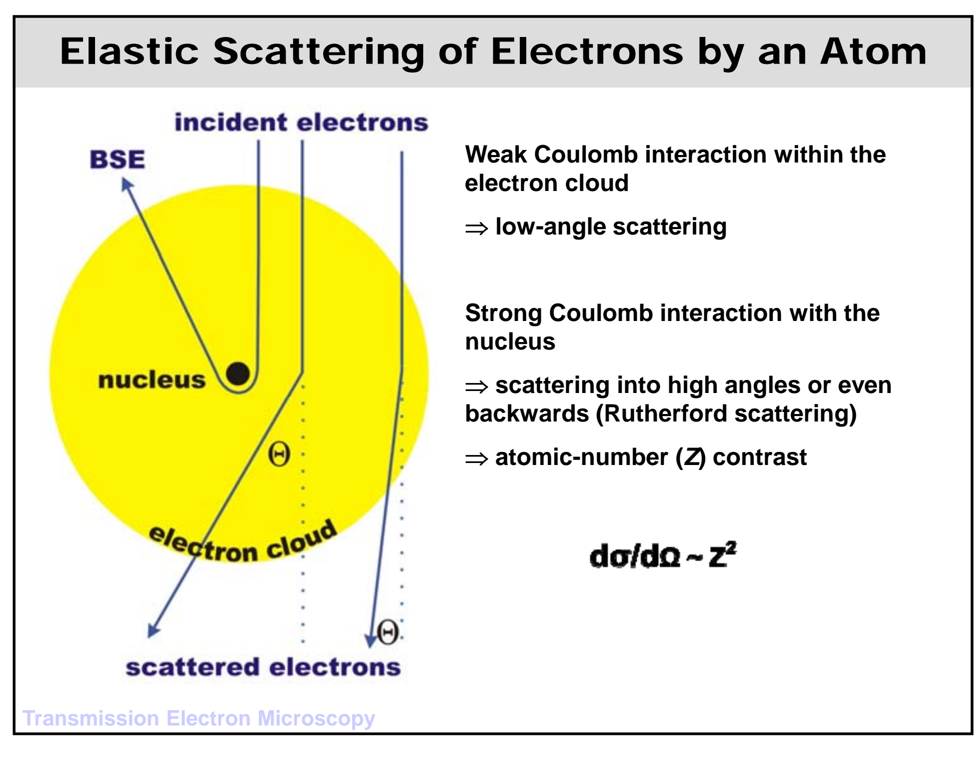

TEM – Imaging and Diffraction
Optic axis
Diffraction pattern
Image plane
Transmission Electron Microscopy

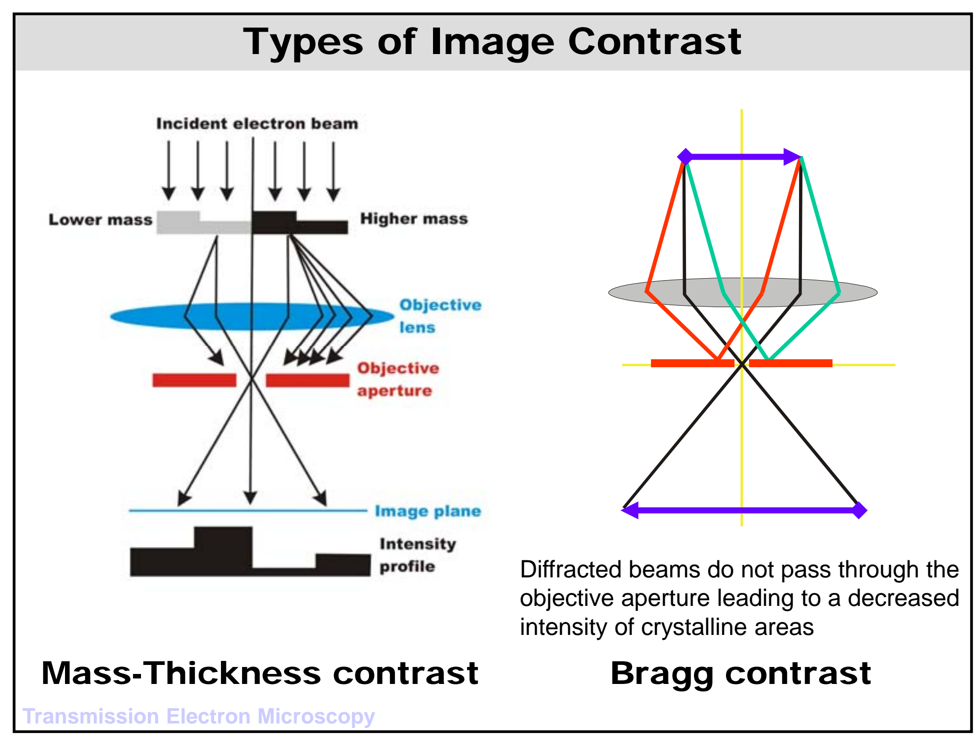

Diffraction and Imaging Mode
Specimen
Objective lens
Back focal plane
objective aperture
1. intermediate image
SAED aperture
Intermediate lens
2. intermediate image
Projective lens
Viewing screen
Image
Diffraction pattern
Electron Diffraction

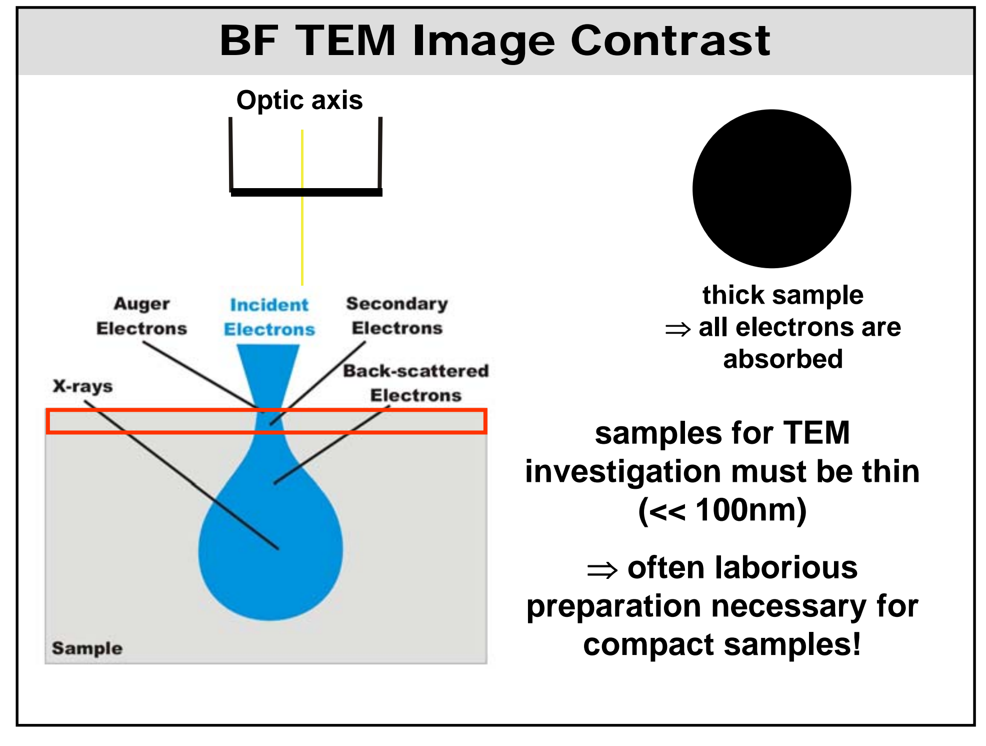

TEM – Imaging and Diffraction
Optic axis
Diffraction pattern
Image plane
Transmission Electron Microscopy

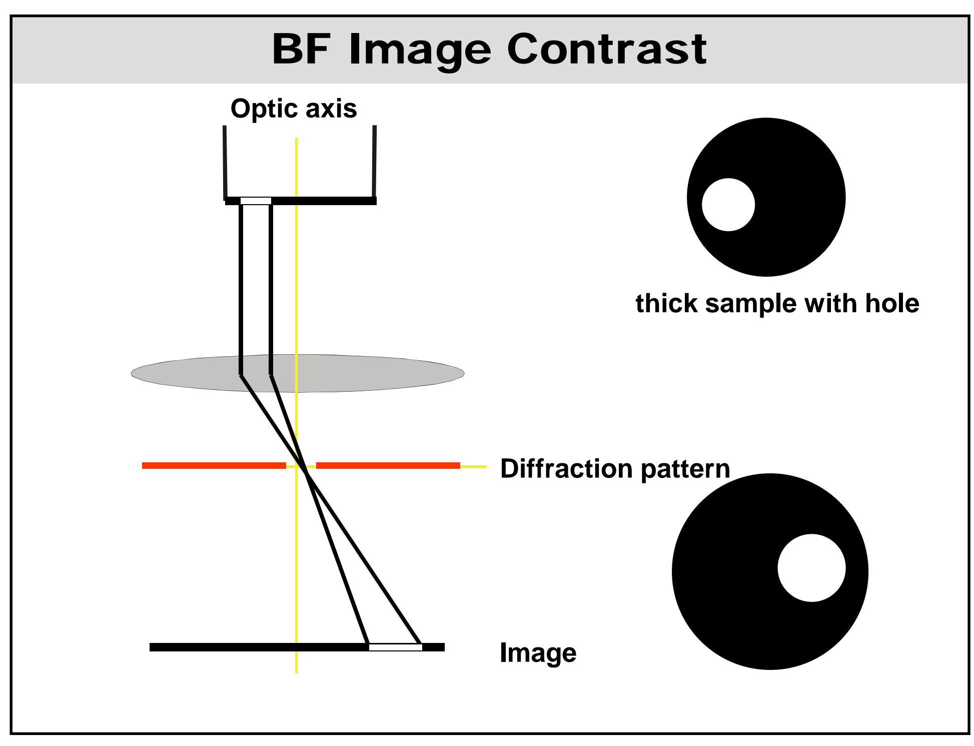

TEM – Imaging and Diffraction
Optic axis
Diffraction pattern
Bright field image
Image
- mass-thickness contrast
- Bragg contrast
Transmission Electron Microscopy

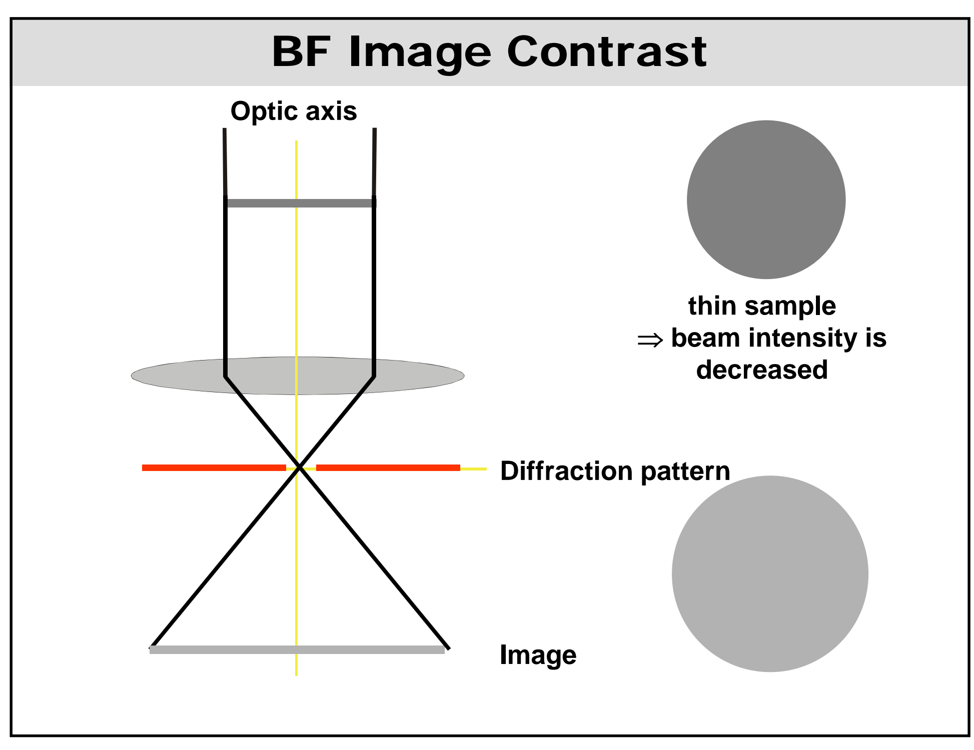

TEM – Imaging and Diffraction
Optic axis
Diffraction pattern
Image
Dark field image
Transmission Electron Microscopy

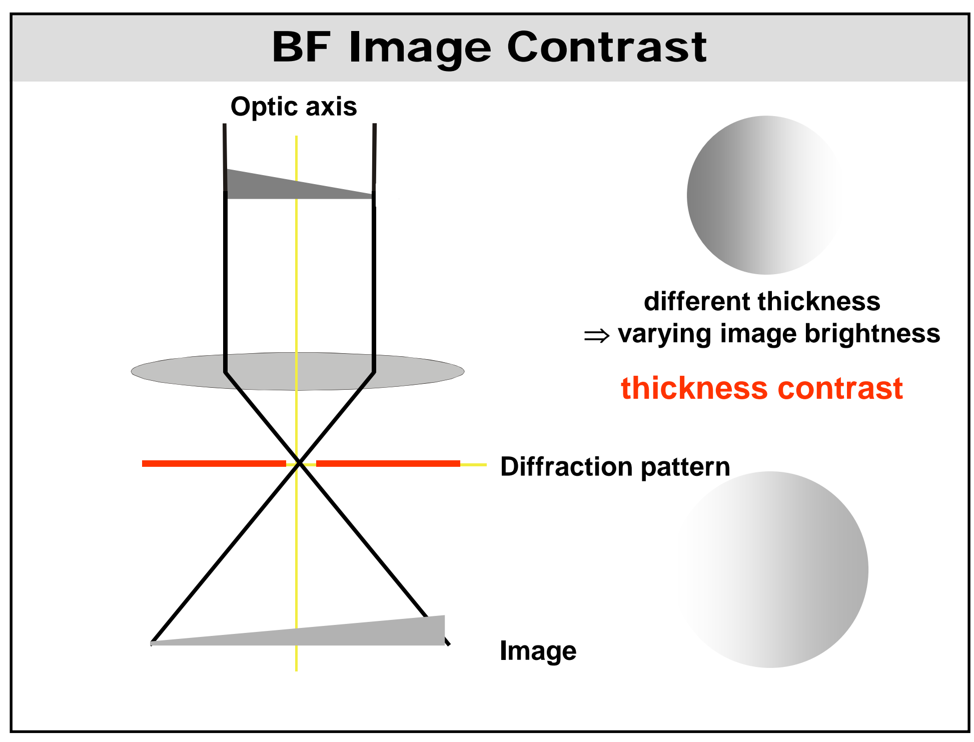

Elastic Scattering of Electrons by an Atom
incident electrons
BSE
nucleus
Θ
electron cloud
Θ
scattered electrons
Weak Coulomb interaction within the electron cloud
⇒ low-angle scattering
Strong Coulomb interaction with the nucleus
⇒ scattering into high angles or even backwards (Rutherford scattering)
⇒ atomic-number (Z) contrast
dσ/dΩ ~ Z²
Transmission Electron Microscopy

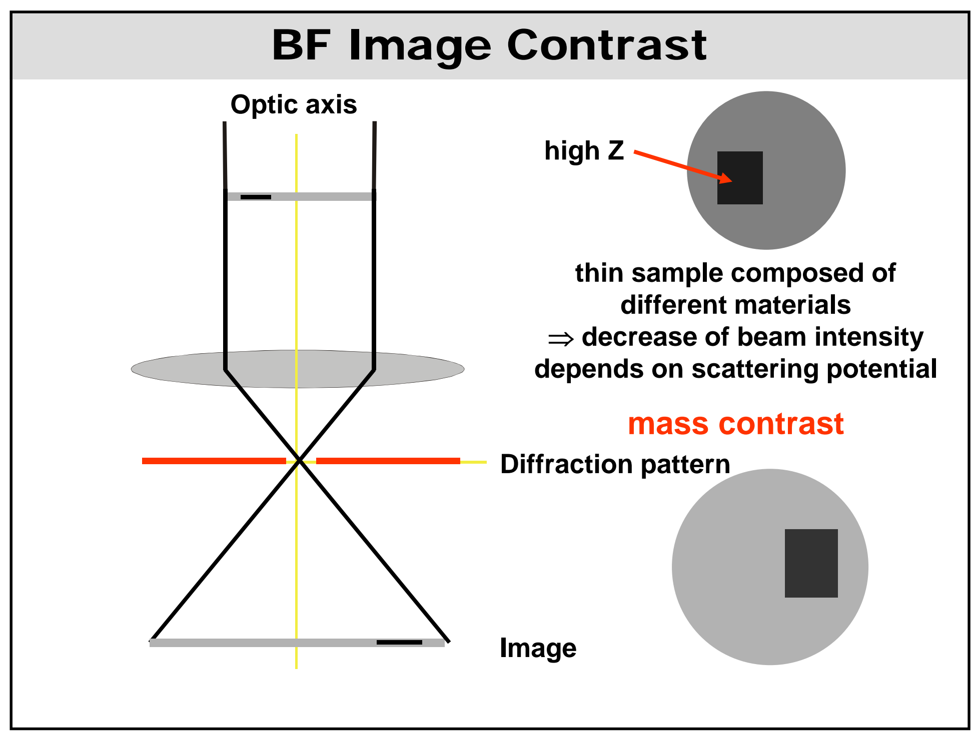

Types of Image Contrast
Incident electron beam
Lower mass
Higher mass
Objective lens
Objective aperture
Image plane
Intensity profile
Diffracted beams do not pass through the objective aperture leading to a decreased intensity of crystalline areas
Mass-Thickness contrast
Bragg contrast
Transmission Electron Microscopy

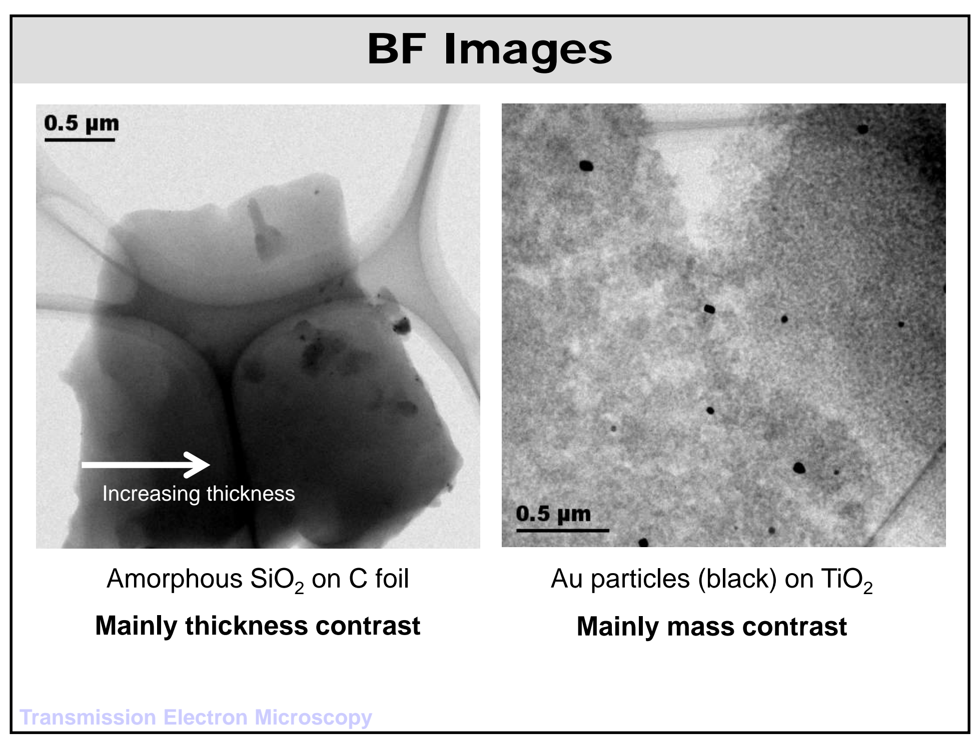

BF TEM Image Contrast
Optic axis
Auger Electrons
Incident Electrons
Secondary Electrons
X-rays
Back-scattered Electrons
Sample
thick sample
⇒ all electrons are absorbed
samples for TEM investigation must be thin (<< 100nm)
⇒ often laborious preparation necessary for compact samples!

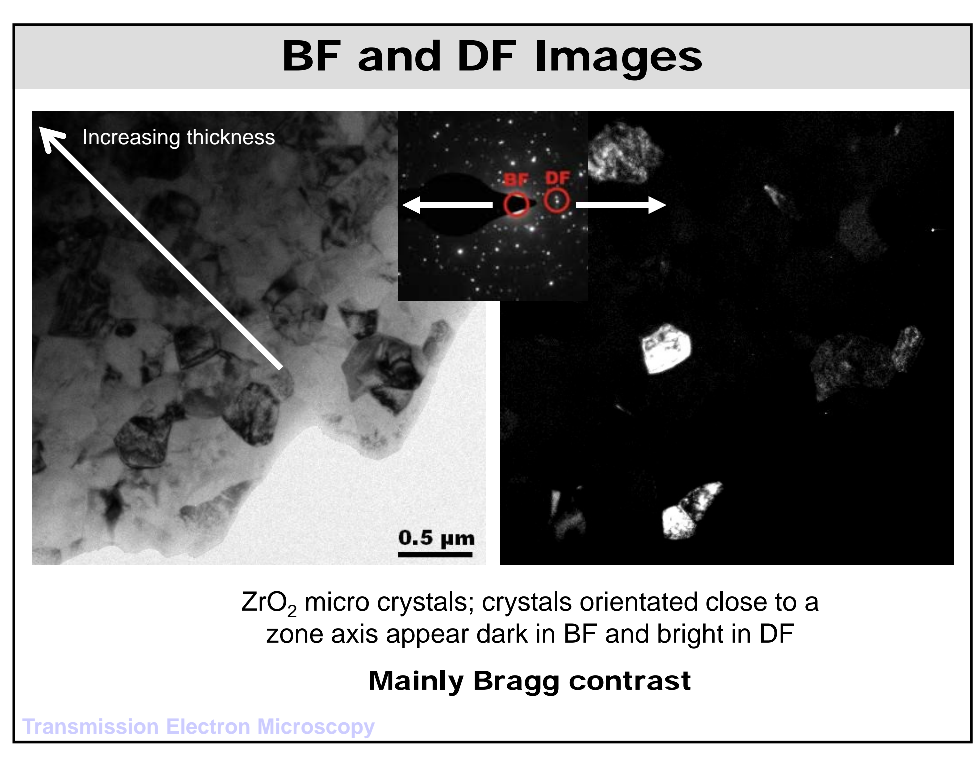

BF Image Contrast
Optic axis
thick sample with hole
Diffraction pattern
Image

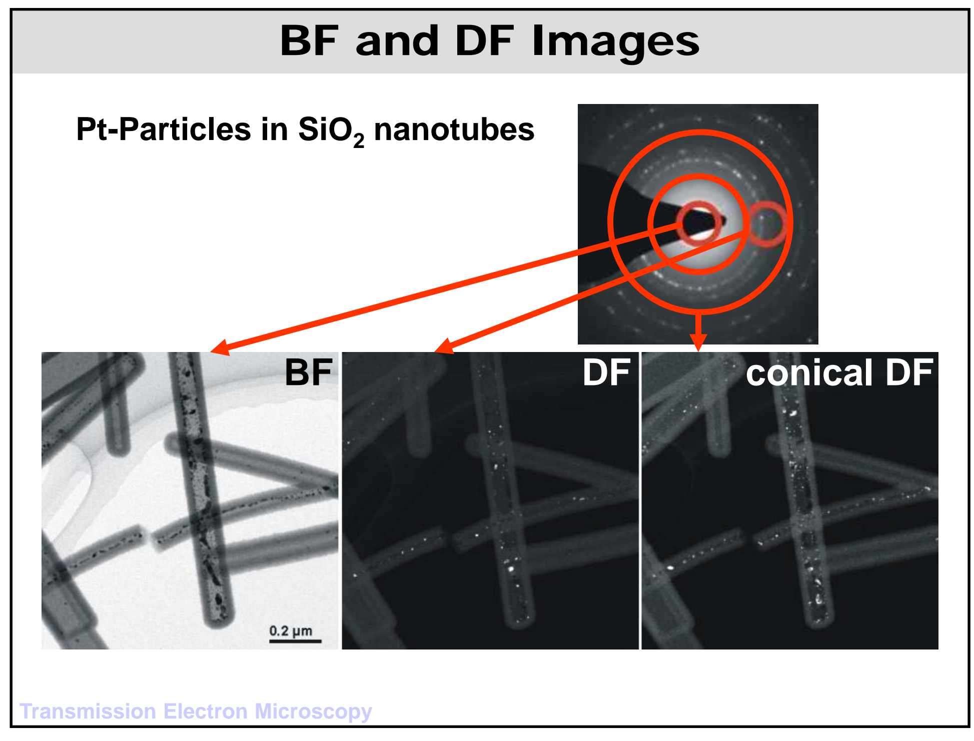

BF Image Contrast
Optic axis
thin sample
⇒ beam intensity is
decreased
Diffraction pattern
Image

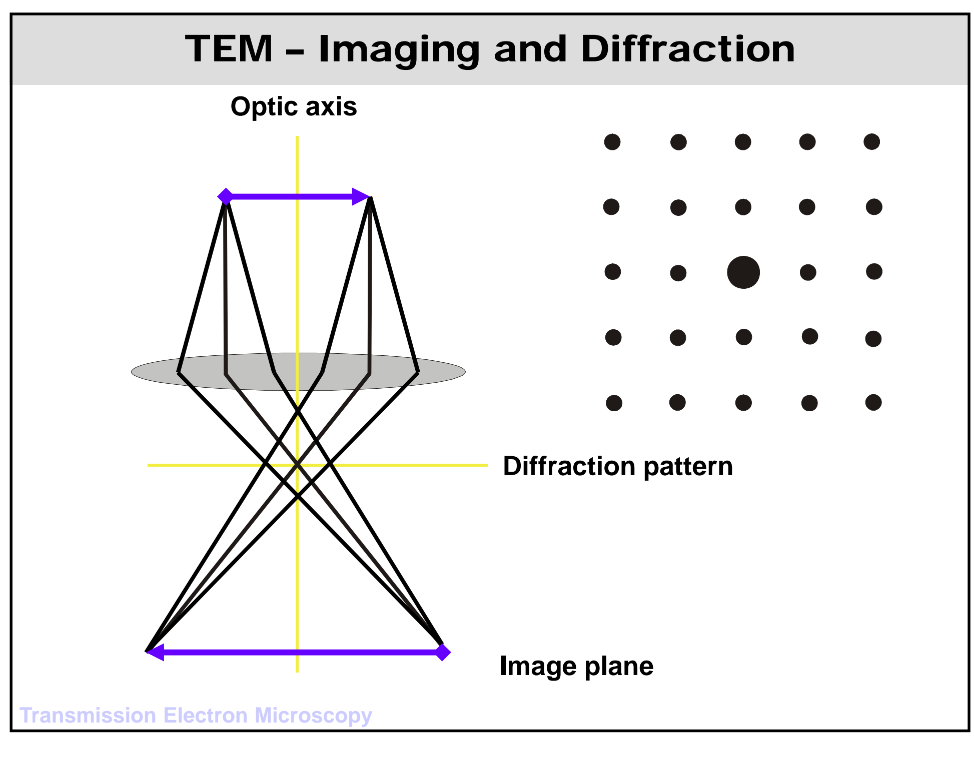

BF Image Contrast
Optic axis
different thickness
⇒ varying image brightness
thickness contrast
Diffraction pattern
Image

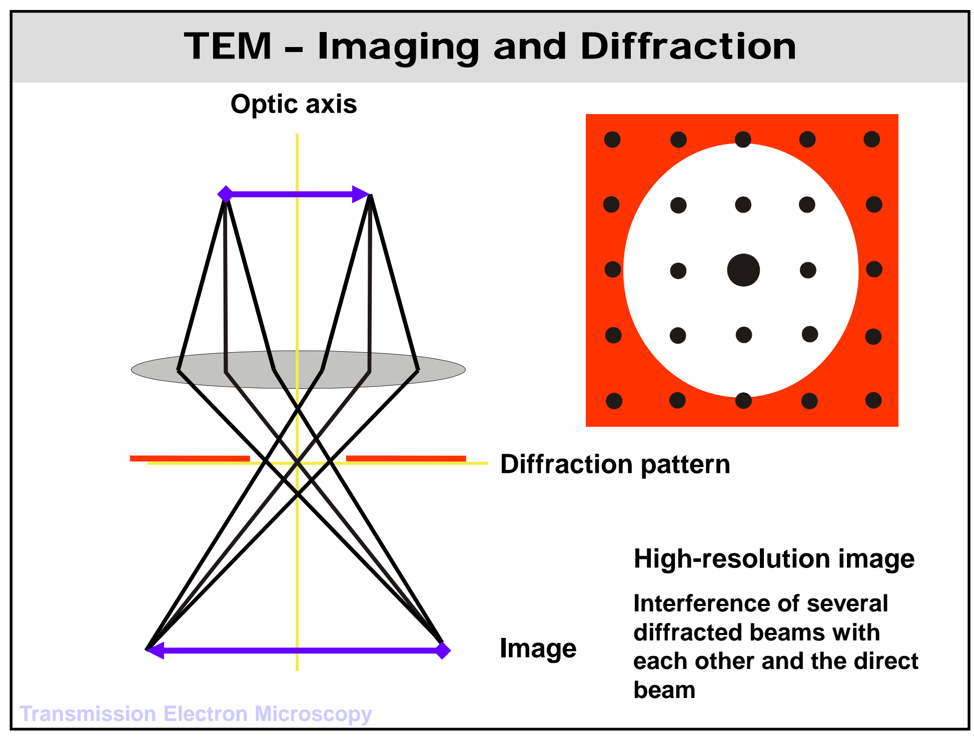

BF Image Contrast
Optic axis
high Z
thin sample composed of
different materials
⇒ decrease of beam intensity
depends on scattering potential
mass contrast
Diffraction pattern
Image

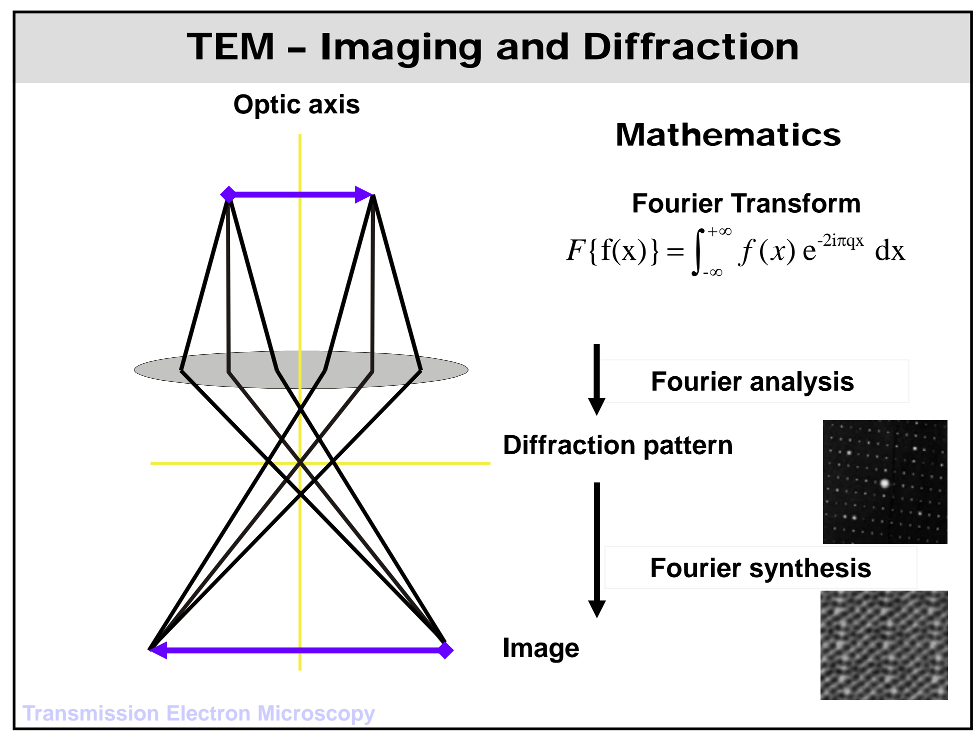

BF Images
0.5 µm
Increasing thickness
0.5 µm
Amorphous SiO2 on C foil
Mainly thickness contrast
Au particles (black) on TiO2
Mainly mass contrast
Transmission Electron Microscopy

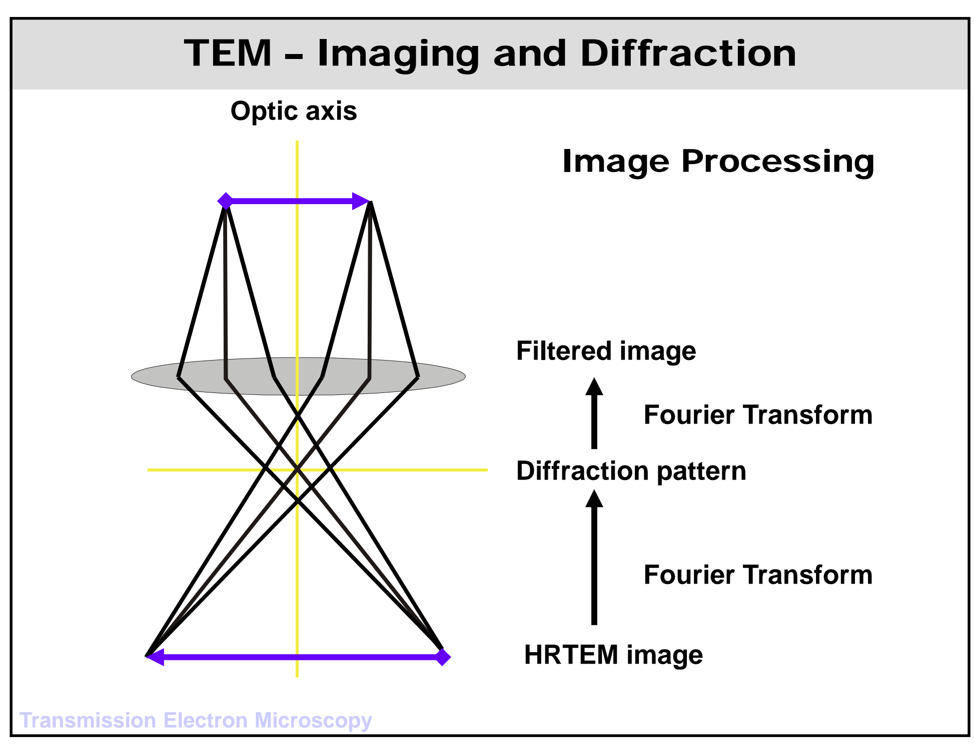

BF and DF Images
Increasing thickness
BF
DF
0.5 µm
ZrO2 micro crystals; crystals orientated close to a zone axis appear dark in BF and bright in DF
Mainly Bragg contrast
Transmission Electron Microscopy

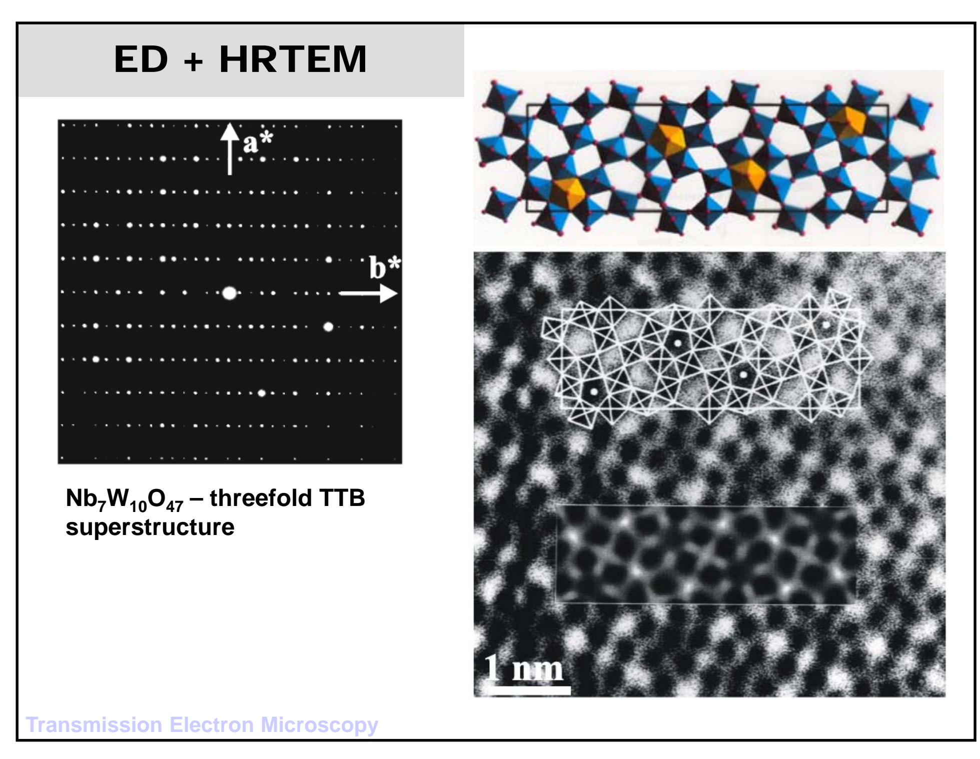

BF and DF Images
Pt-Particles in SiO_2 nanotubes
BF
DF
conical DF
0.2 µm
Transmission Electron Microscopy

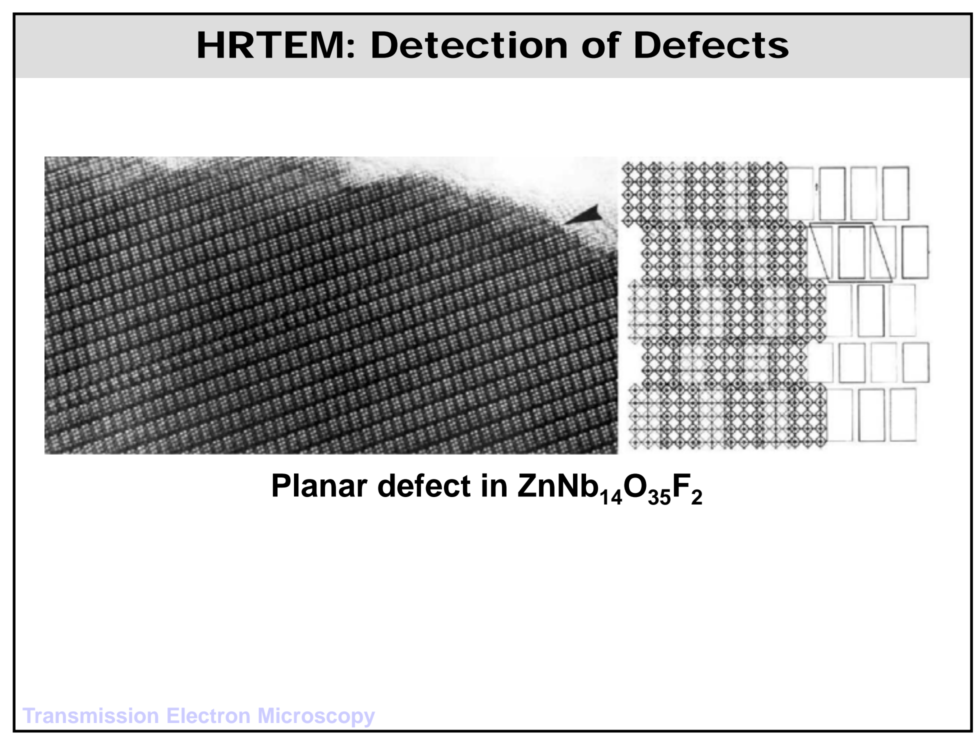

TEM – Imaging and Diffraction
Optic axis
Diffraction pattern
Image plane
Transmission Electron Microscopy

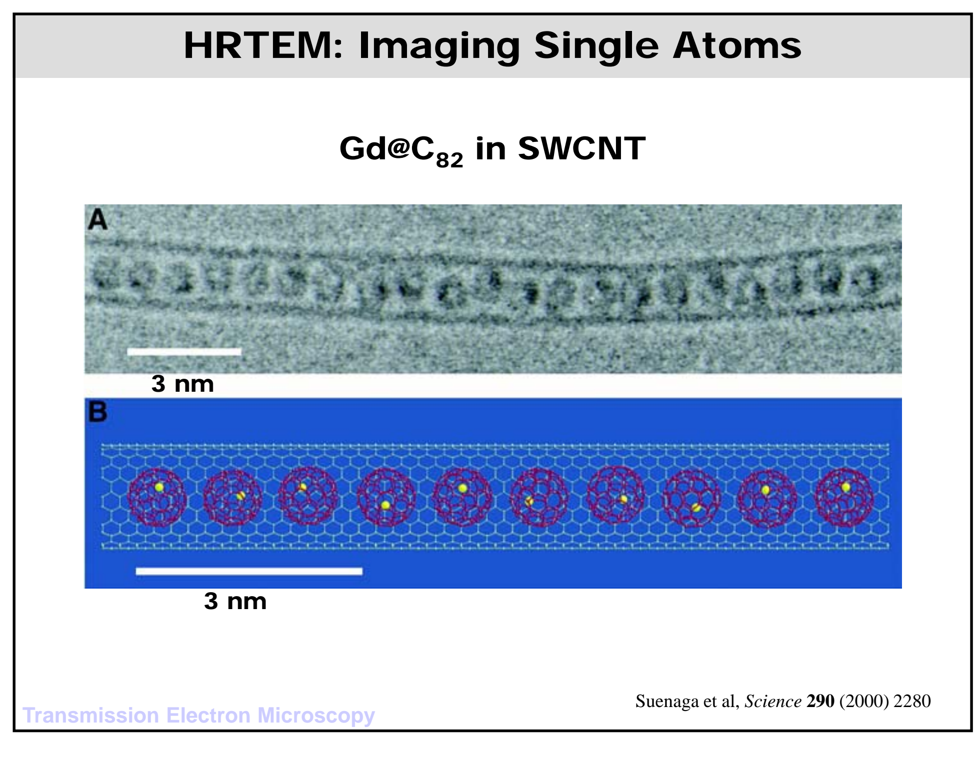

TEM – Imaging and Diffraction
Optic axis
Diffraction pattern
High-resolution image
Interference of several diffracted beams with each other and the direct beam
Image
Transmission Electron Microscopy


TEM – Imaging and Diffraction
Optic axis
Mathematics
Fourier Transform
$F\{f(x)\} = \int_{-\infty}^{+\infty} f(x)\, e^{-2i\pi qx}\, dx$
Fourier analysis
Diffraction pattern
Fourier synthesis
Image
Transmission Electron Microscopy

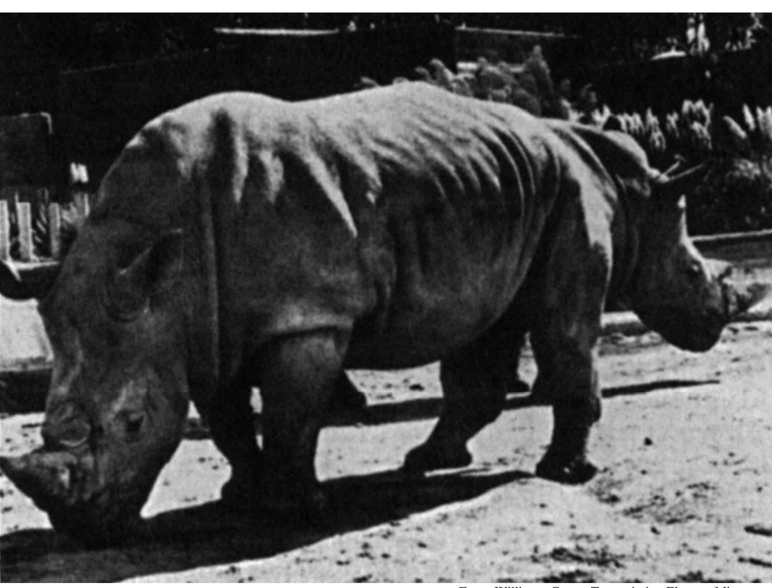

TEM – Imaging and Diffraction
Optic axis
Image Processing
Filtered image
Fourier Transform
Diffraction pattern
Fourier Transform
HRTEM image
Transmission Electron Microscopy


ED + HRTEM
a*
b*
Nb7W10O47 – threefold TTB superstructure
1 nm
Transmission Electron Microscopy


HRTEM: Detection of Defects
Planar defect in ZnNb14O35F2
Transmission Electron Microscopy


HRTEM: Imaging Single Atoms
Gd@C82 in SWCNT
A
3 nm
B
3 nm
Suenaga et al, Science 290 (2000) 2280
Transmission Electron Microscopy

Projection Problem: 3D $\Rightarrow$ 2D



From: Williams, Carter: Transmission Electron Microscopy

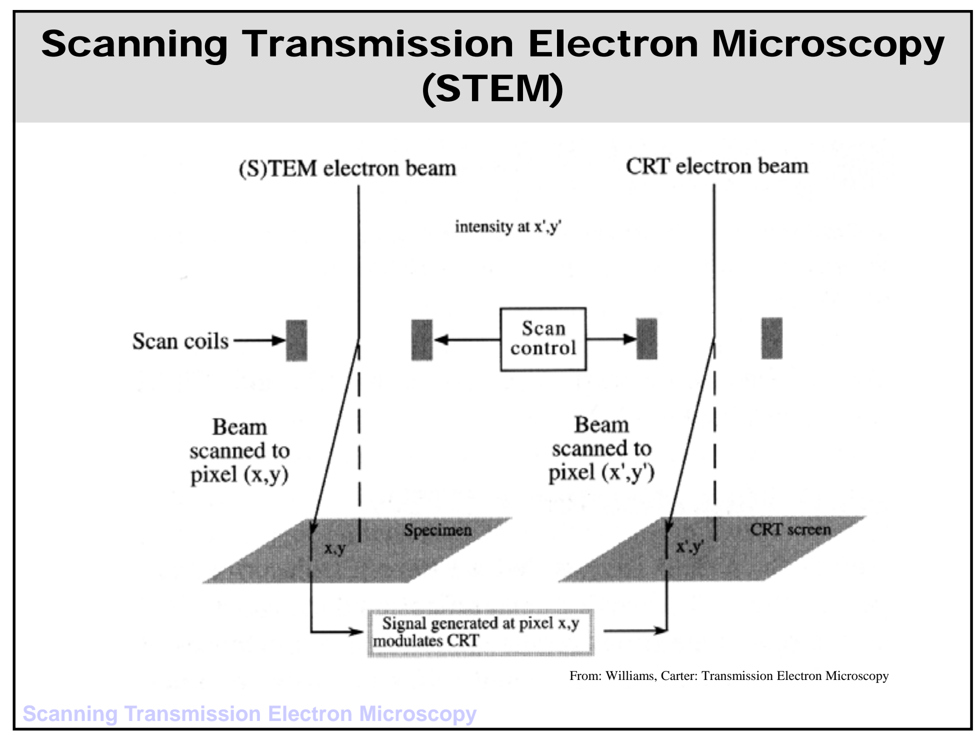
Transmission Electron Microscopy

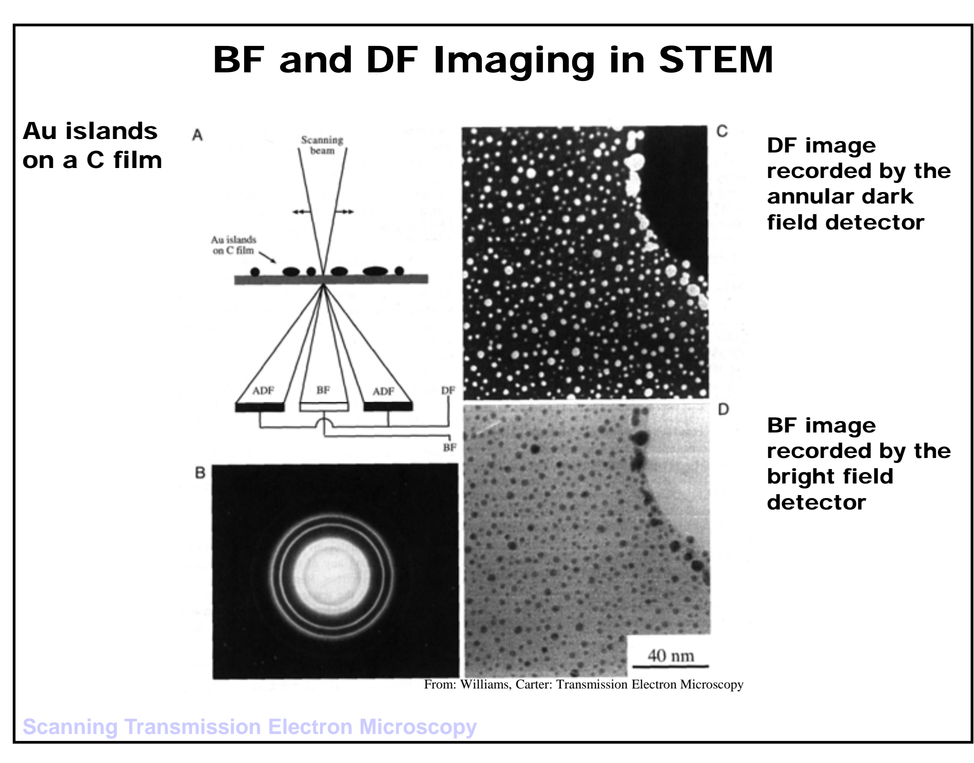
Types of contrast:

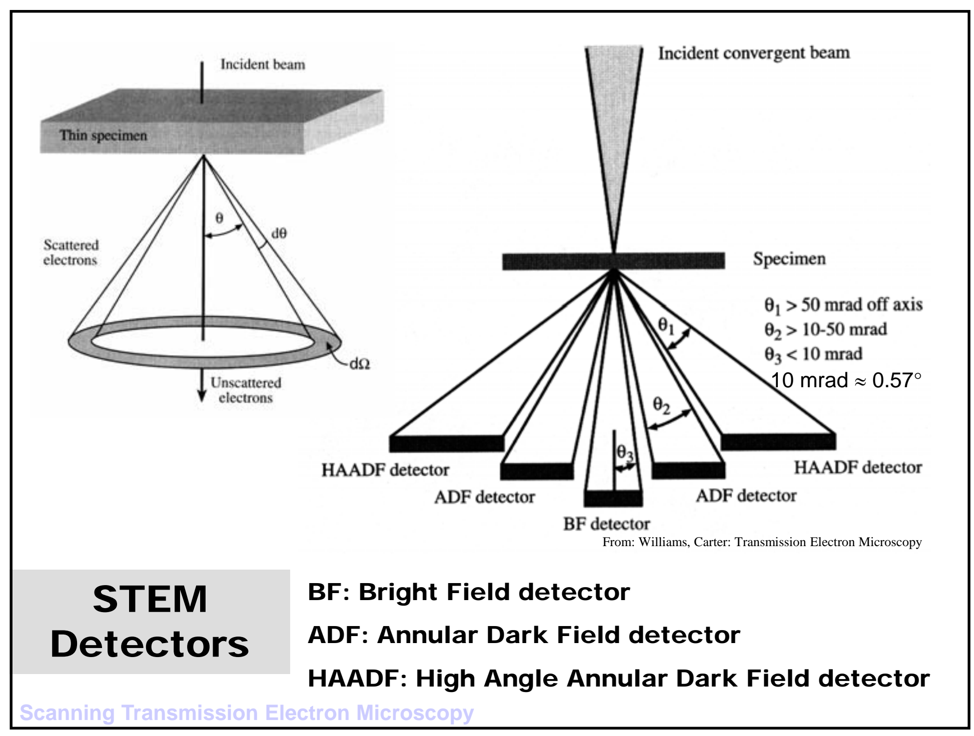
- **Mass-thickness (BF/DF)**
- **Bragg (BF/DF)**
- **Phase (HRTEM; resolution limit < 1Å)**

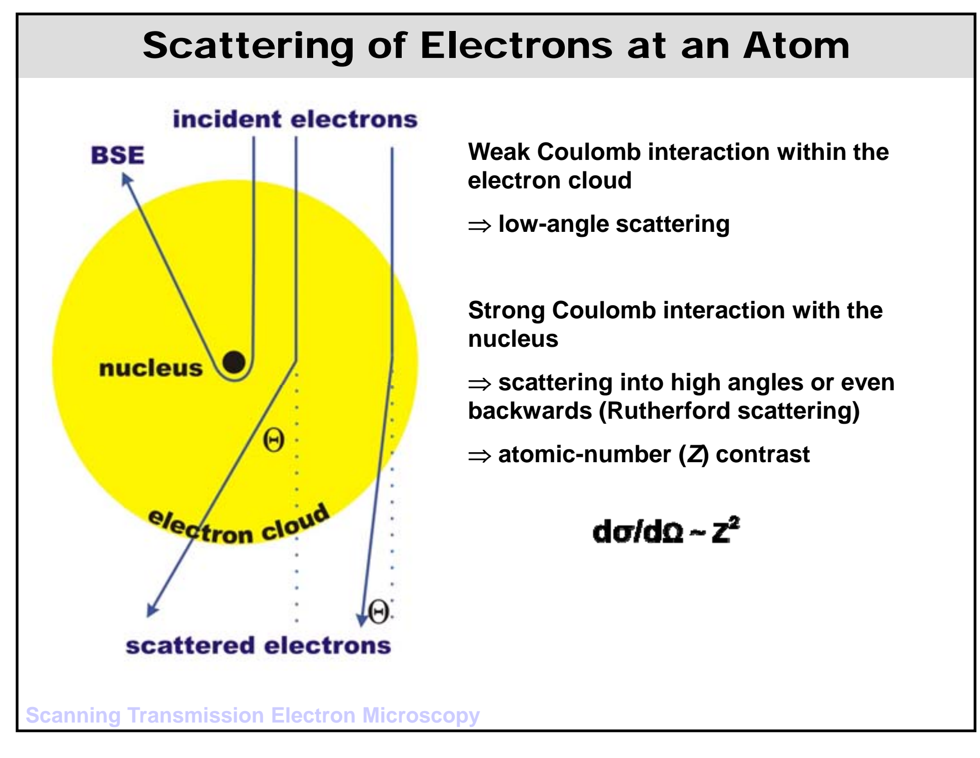
Determination of

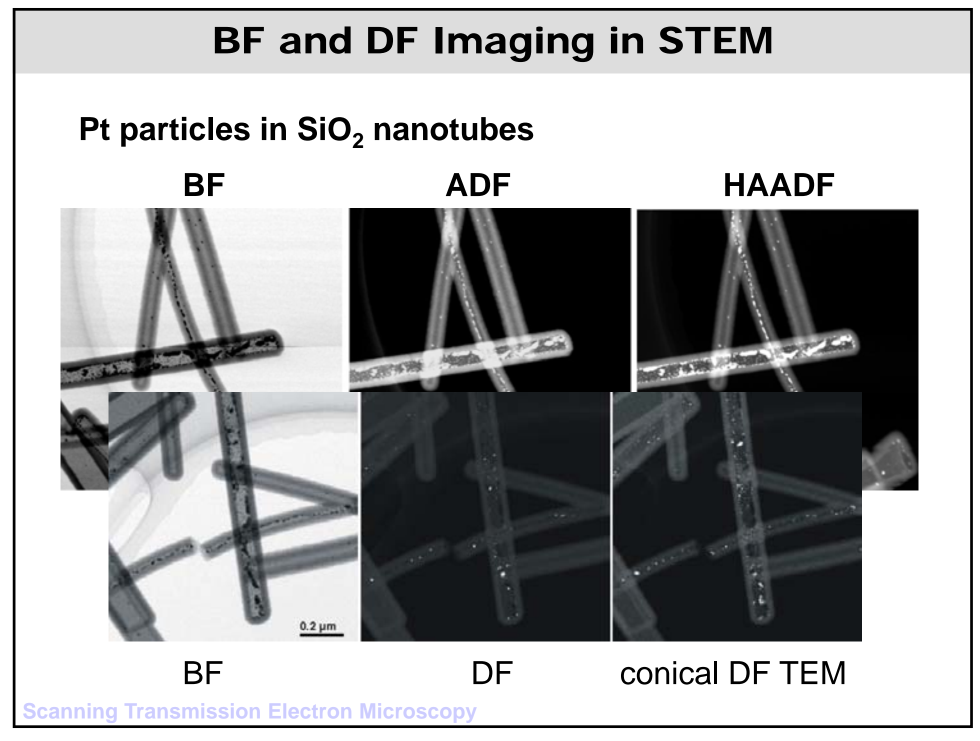
- **Structure: HRTEM**
- **Defects: HRTEM, TEM**
- **Lattice constants and symmetry: ED**
- **Particle size: TEM, HRTEM**

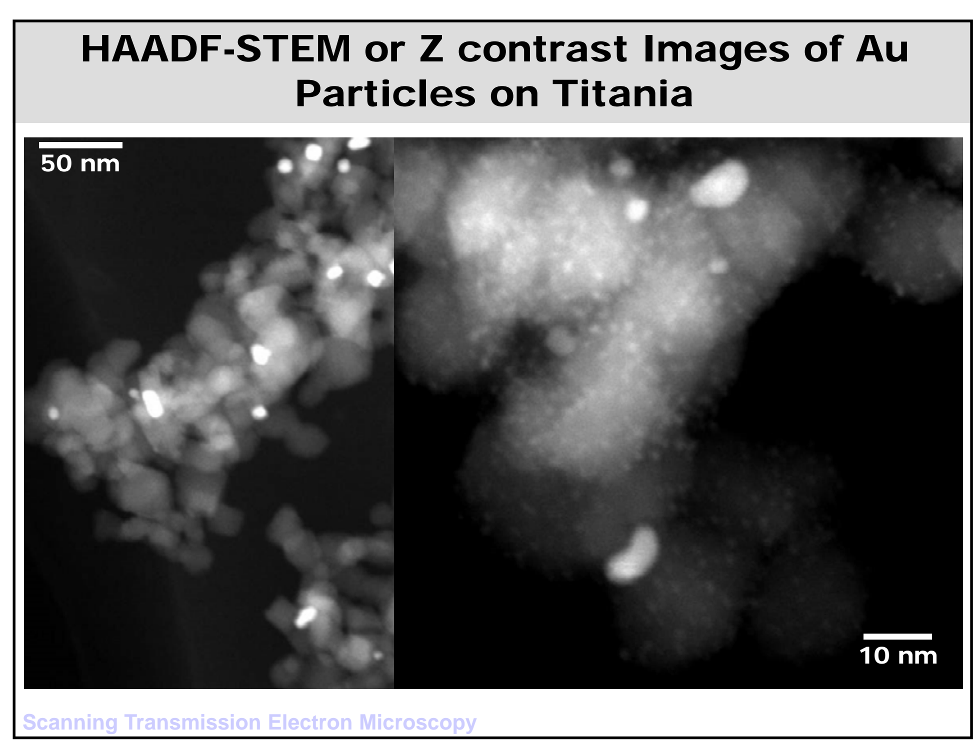

Scanning Transmission Electron Microscopy (STEM)
(S)TEM electron beam
CRT electron beam
intensity at x',y'
Scan coils
Scan control
Beam scanned to pixel (x,y)
Beam scanned to pixel (x',y')
Specimen
x,y
CRT screen
x',y'
Signal generated at pixel x,y modulates CRT
From: Williams, Carter: Transmission Electron Microscopy
Scanning Transmission Electron Microscopy

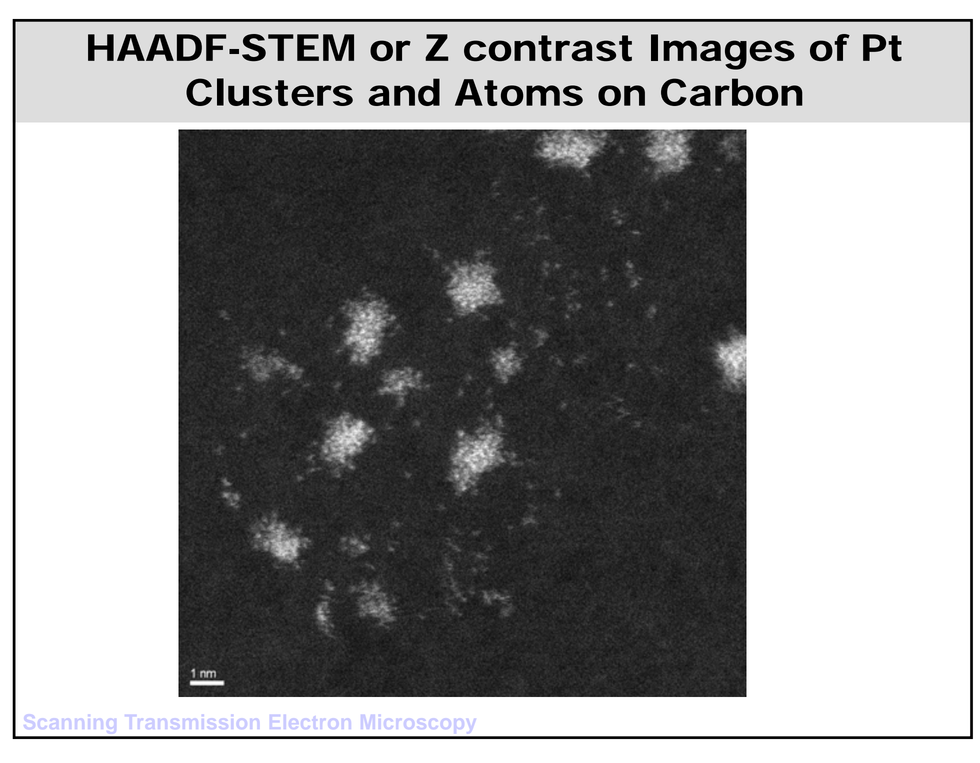

BF and DF Imaging in STEM
Au islands on a C film
A
Scanning beam
Au islands on C film
ADF
BF
ADF
DF
BF
B
C
DF image recorded by the annular dark field detector
D
BF image recorded by the bright field detector
40 nm
From: Williams, Carter: Transmission Electron Microscopy
Scanning Transmission Electron Microscopy

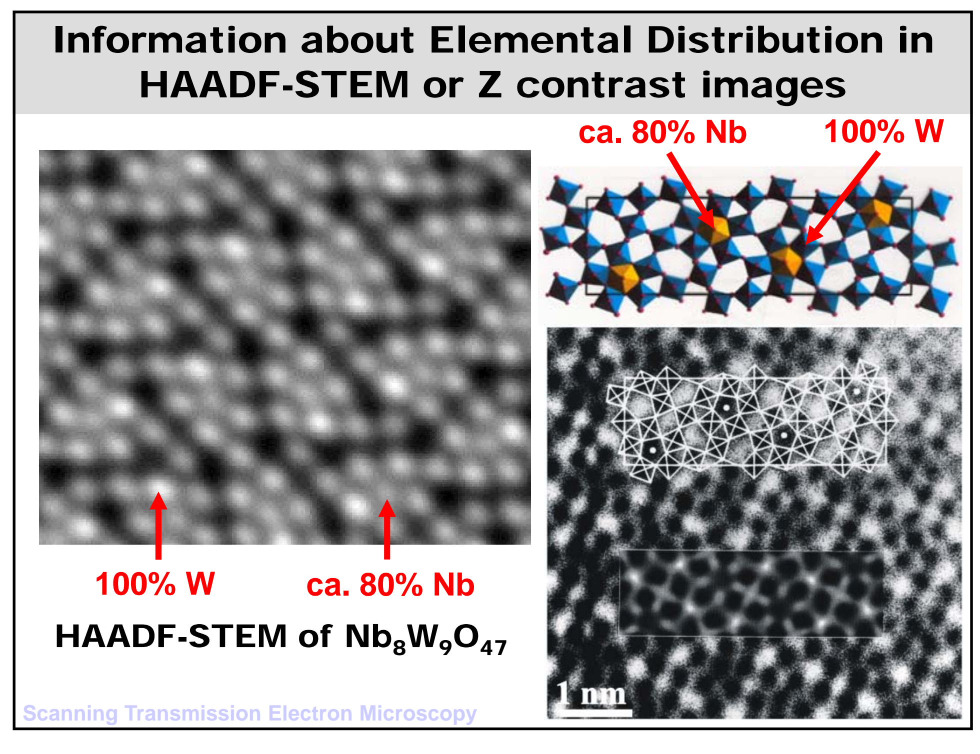

Incident beam
Thin specimen
Scattered electrons
θ
dθ
dΩ
Unscattered electrons
Incident convergent beam
Specimen
θ1 > 50 mrad off axis
θ2 > 10-50 mrad
θ3 < 10 mrad
10 mrad ≈ 0.57°
θ1
θ2
θ3
HAADF detector
ADF detector
BF detector
ADF detector
HAADF detector
From: Williams, Carter: Transmission Electron Microscopy
STEM Detectors
BF: Bright Field detector
ADF: Annular Dark Field detector
HAADF: High Angle Annular Dark Field detector
Scanning Transmission Electron Microscopy

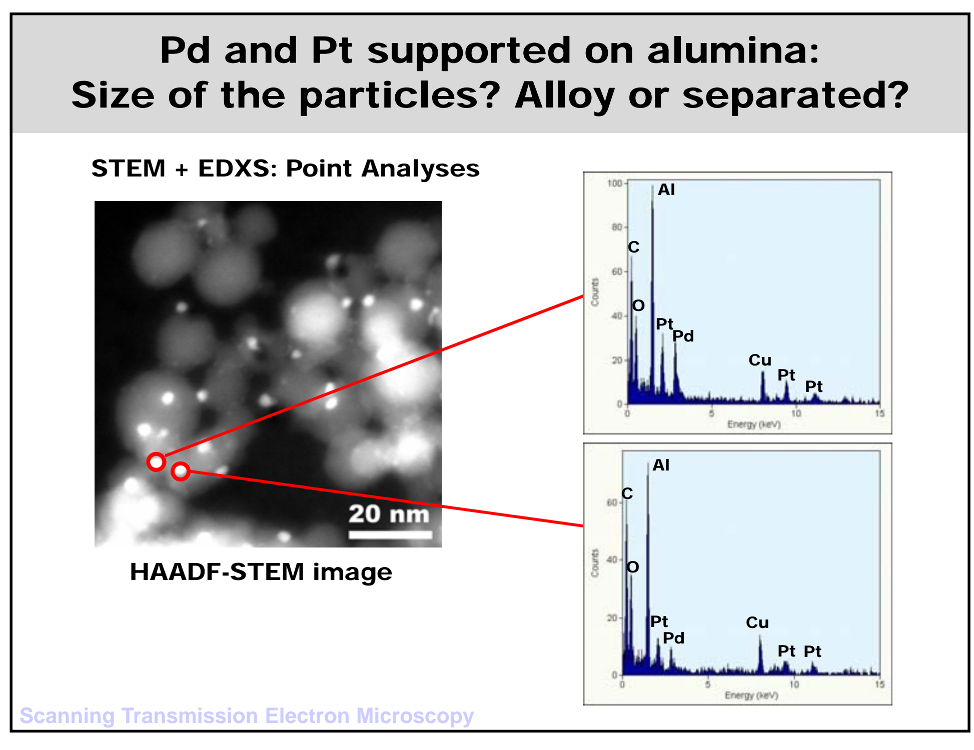

Scattering of Electrons at an Atom
incident electrons
BSE
nucleus
Θ
electron cloud
Θ
scattered electrons
Weak Coulomb interaction within the electron cloud
⇒ low-angle scattering
Strong Coulomb interaction with the nucleus
⇒ scattering into high angles or even backwards (Rutherford scattering)
⇒ atomic-number (Z) contrast
dσ/dΩ ~ Z²
Scanning Transmission Electron Microscopy

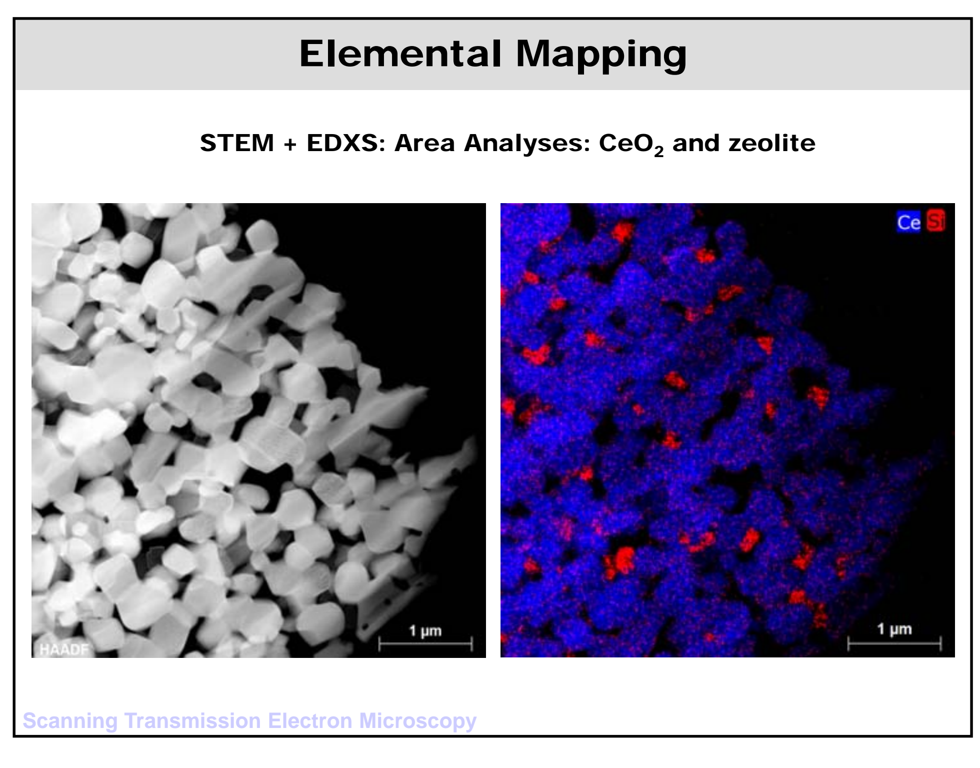

BF and DF Imaging in STEM
Pt particles in SiO2 nanotubes
BF
ADF
HAADF
0.2 µm
BF
DF
conical DF TEM
Scanning Transmission Electron Microscopy

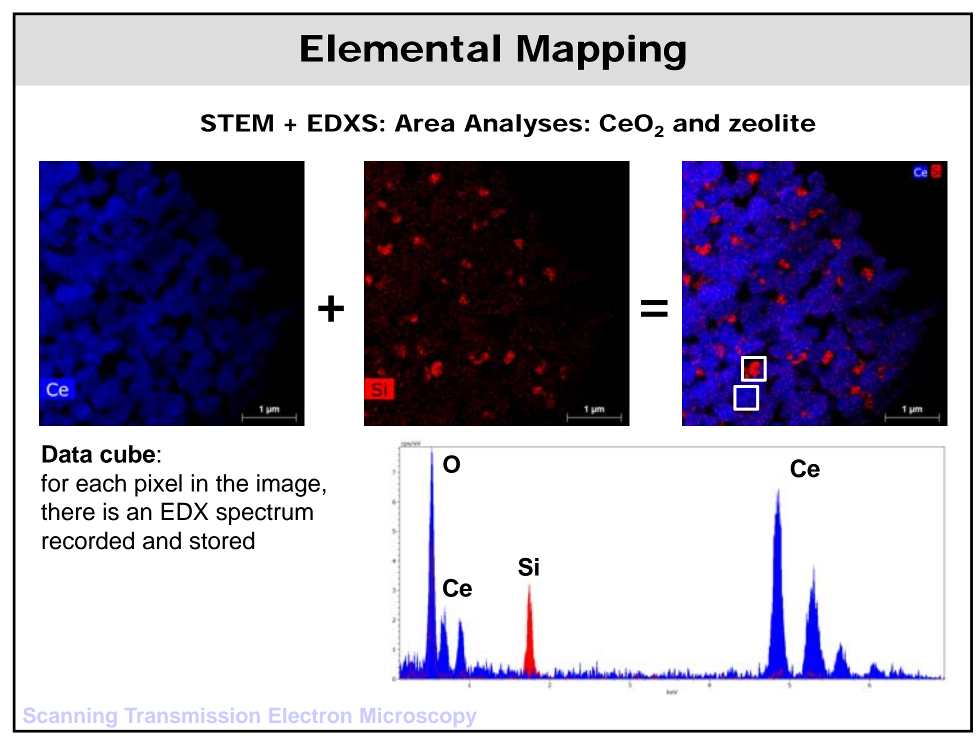

HAADF-STEM or Z contrast Images of Au Particles on Titania
50 nm
10 nm
Scanning Transmission Electron Microscopy

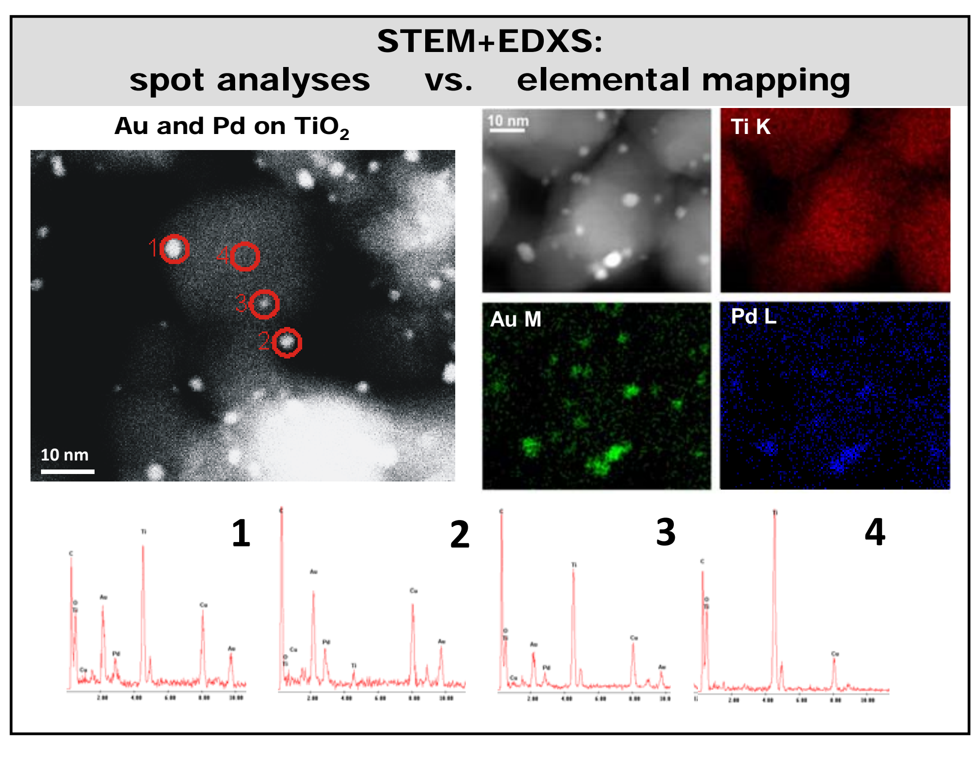

HAADF-STEM or Z contrast Images of Pt Clusters and Atoms on Carbon
1 nm
Scanning Transmission Electron Microscopy


Information about Elemental Distribution in HAADF-STEM or Z contrast images
ca. 80% Nb
100% W
100% W
ca. 80% Nb
HAADF-STEM of $Nb_8W_9O_{47}$
1 nm
Scanning Transmission Electron Microscopy

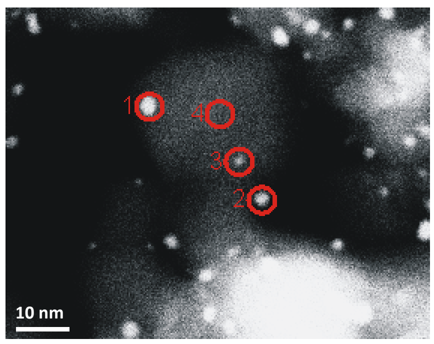

Pd and Pt supported on alumina:
Size of the particles? Alloy or separated?
STEM + EDXS: Point Analyses
20 nm
HAADF-STEM image
Al
C
O
Pt
Pd
Cu
Pt
Pt
Counts
Energy (keV)
Scanning Transmission Electron Microscopy

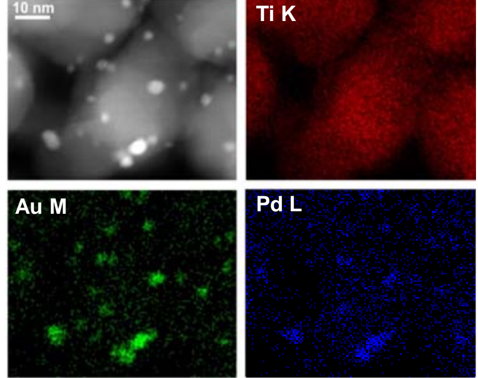

Elemental Mapping
STEM + EDXS: Area Analyses: CeO_2 and zeolite
HAADF
1 µm
Ce Si
1 µm
Scanning Transmission Electron Microscopy


Elemental Mapping
STEM + EDXS: Area Analyses: CeO_2 and zeolite
Ce
Si
+
=
Data cube:
for each pixel in the image, there is an EDX spectrum recorded and stored
O
Ce
Si
Ce
Scanning Transmission Electron Microscopy


STEM+EDXS:
spot analyses vs. elemental mapping
Au and Pd on TiO_2
10 nm
Ti K
Au M
Pd L
1
2
3
4

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

Scanning Transmission Electron Microscopy

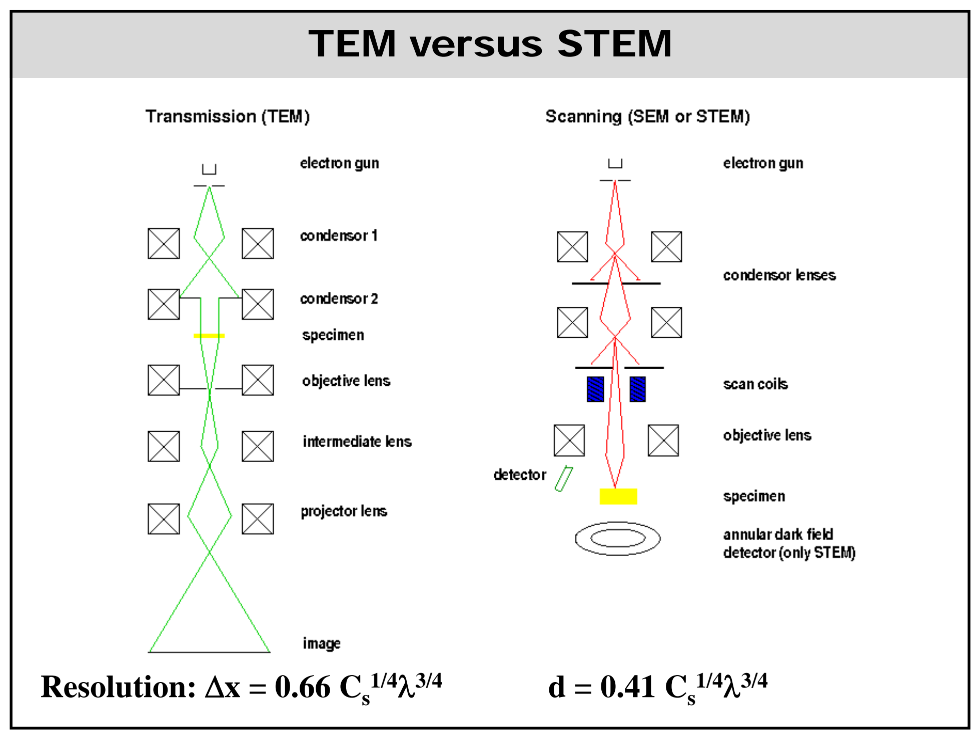
Contrast:

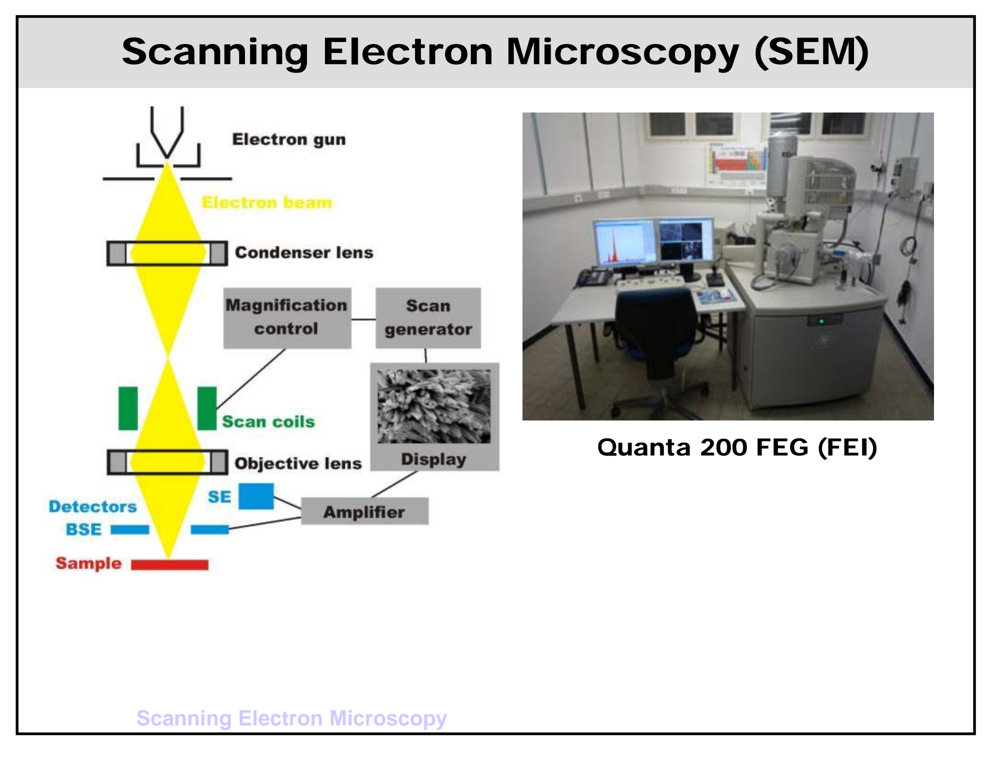
- **Mass-thickness (BF/DF)**
- **Bragg (BF/DF)**
- **Z^2 (HAADF)**

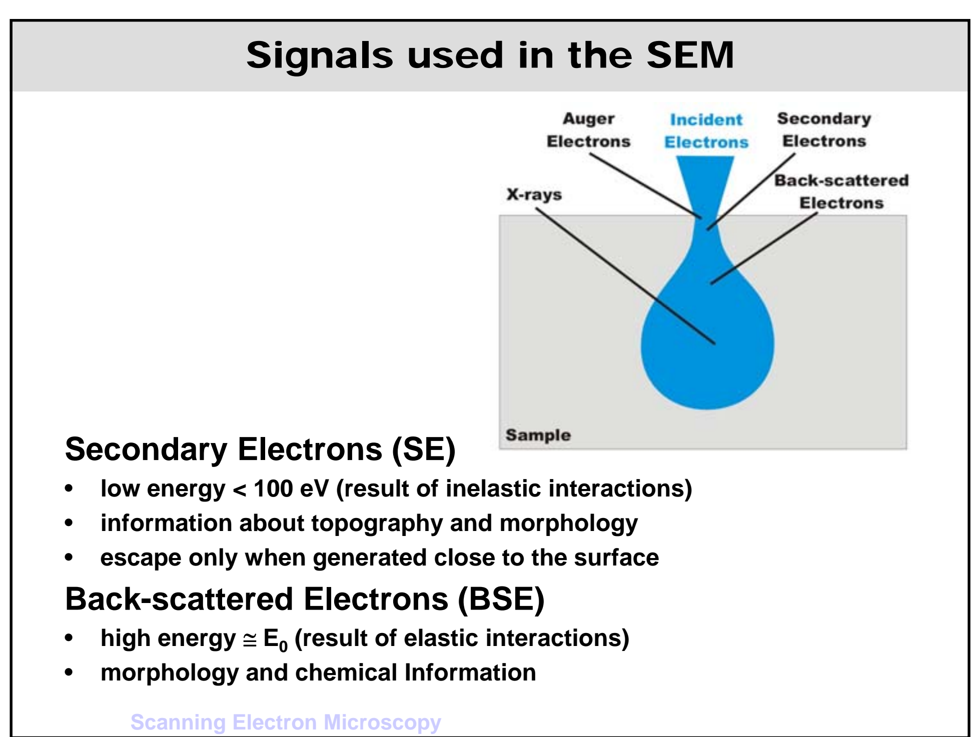
Determination of

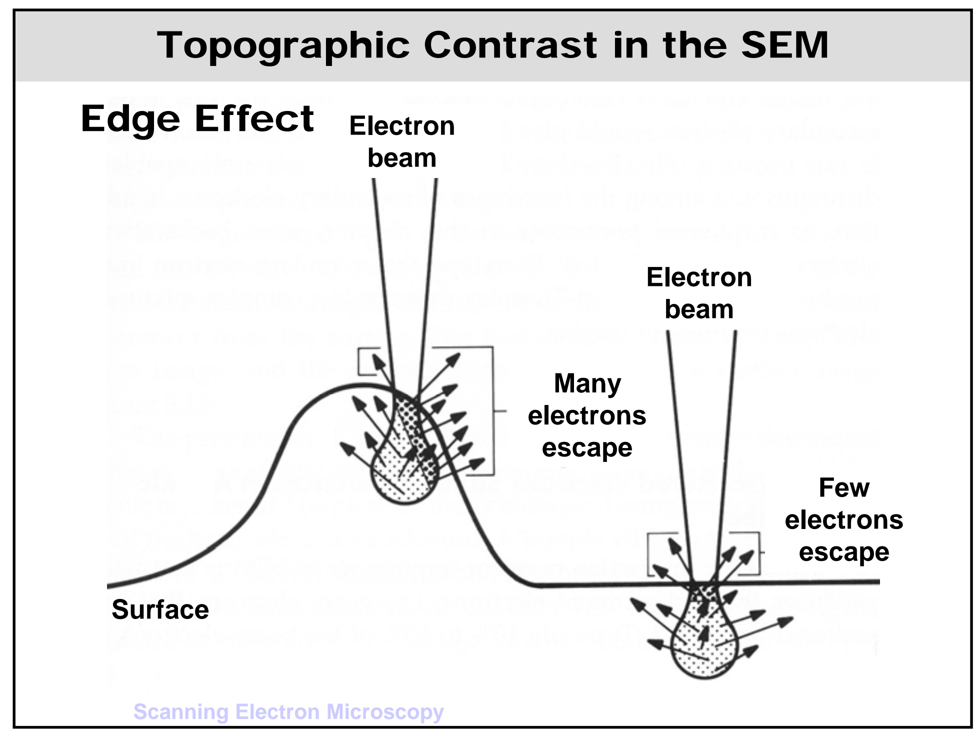
- **Particles on support : HAADF**
- **Structure and defects : HR**
- **Chemical information : HAADF**

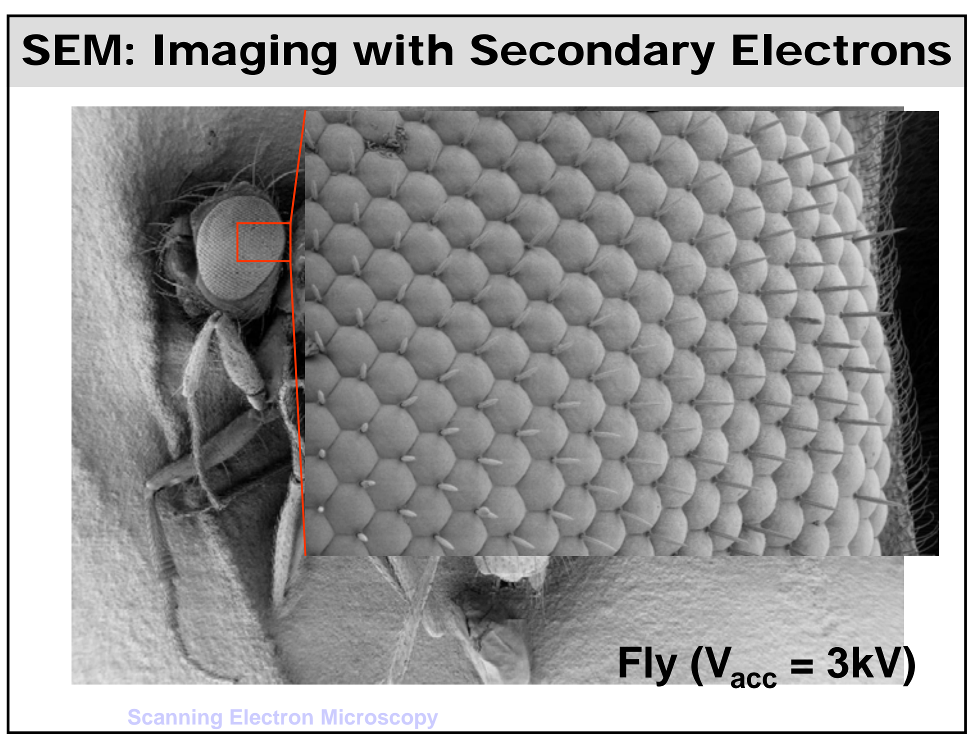
Important: Combination with EDXS or EELS

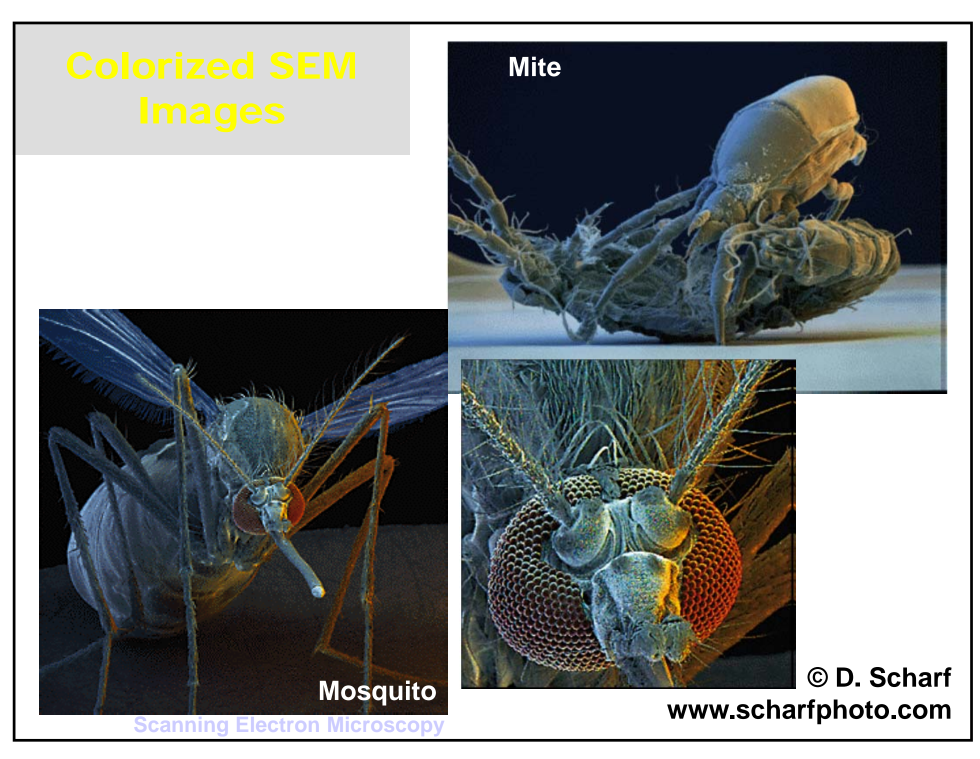

TEM versus STEM
Transmission (TEM)
electron gun
condensor 1
condensor 2
specimen
objective lens
intermediate lens
projector lens
image
Scanning (SEM or STEM)
electron gun
condensor lenses
scan coils
objective lens
detector
specimen
annular dark field
detector (only STEM)
Resolution: Δx = 0.66 Cs1/4λ3/4
d = 0.41 Cs1/4λ3/4


Scanning Electron Microscopy (SEM)
Electron gun
Electron beam
Condenser lens
Magnification control
Scan generator
Scan coils
Objective lens
Display
Detectors
SE
BSE
Amplifier
Sample
Quanta 200 FEG (FEI)
Scanning Electron Microscopy

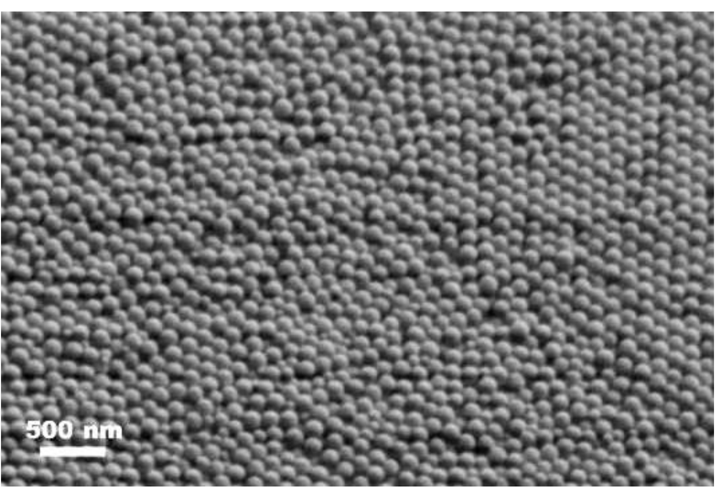

Signals used in the SEM
Auger Electrons
Incident Electrons
Secondary Electrons
X-rays
Back-scattered Electrons
Sample
Secondary Electrons (SE)
low energy < 100 eV (result of inelastic interactions)
information about topography and morphology
escape only when generated close to the surface
Back-scattered Electrons (BSE)
high energy ≅ E0 (result of elastic interactions)
morphology and chemical Information
Scanning Electron Microscopy


Topographic Contrast in the SEM
Edge Effect
Electron beam
Electron beam
Many electrons escape
Few electrons escape
Surface
Scanning Electron Microscopy


SEM: Imaging with Secondary Electrons
Fly (V_{acc} = 3kV)
Scanning Electron Microscopy

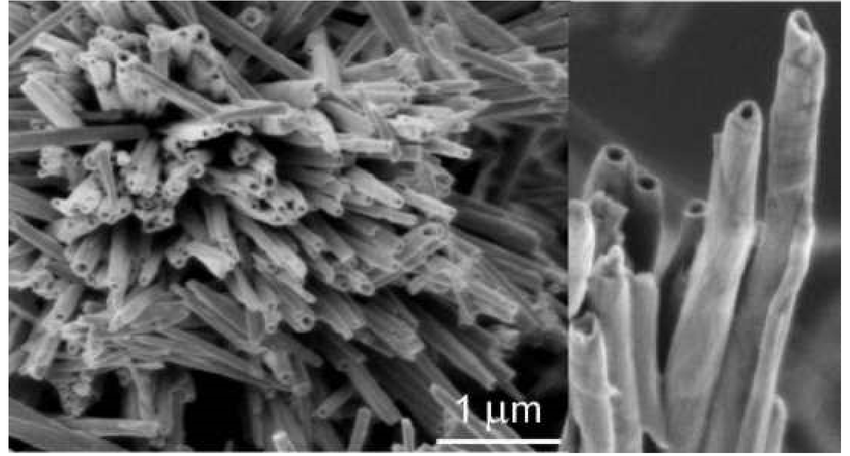

Colorized SEM Images
Mite
Mosquito
© D. Scharf
www.scharfphoto.com
Scanning Electron Microscopy

SEM: Imaging with Secondary Electrons

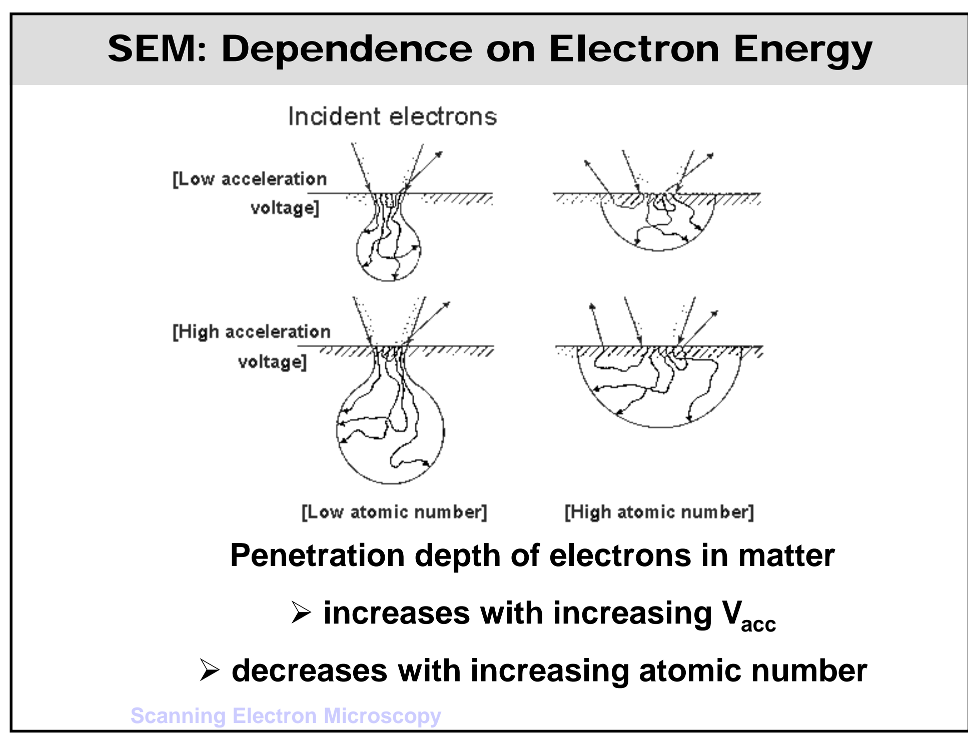


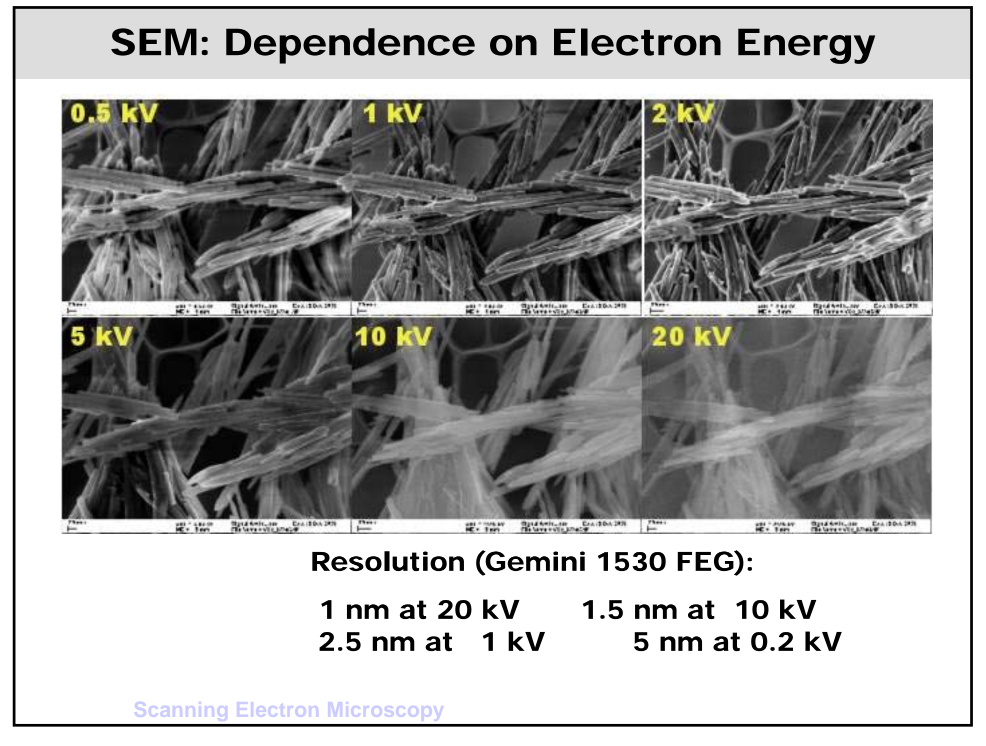
Latex balls (V_{acc} = 1kV)

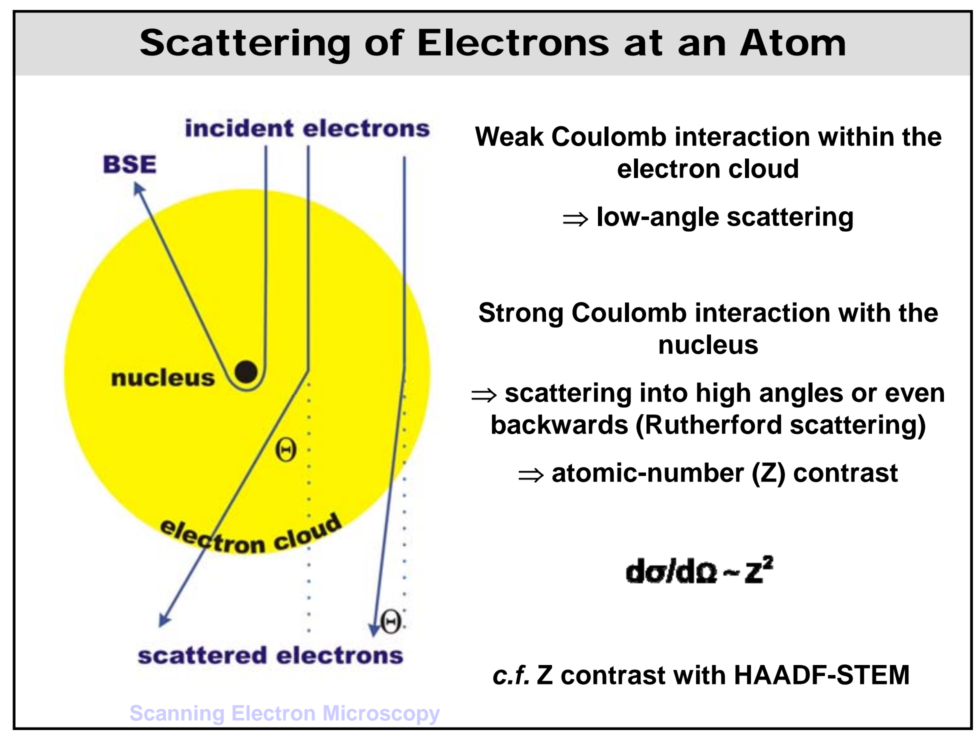
SEM: Imaging with Secondary Electrons

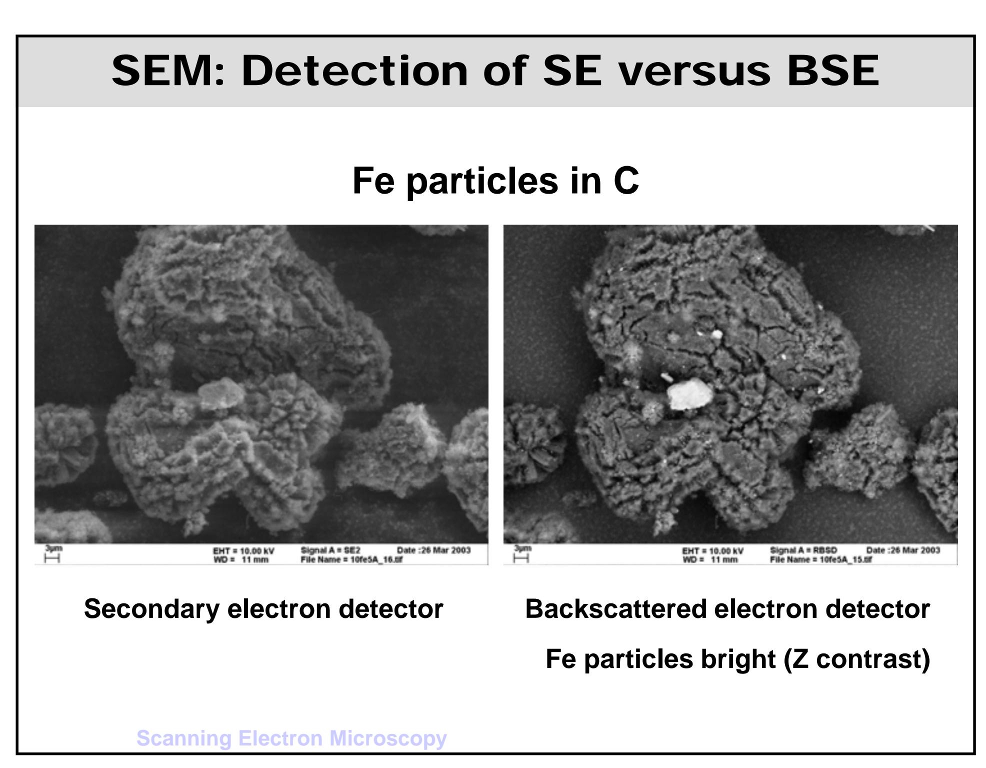


Vanadium oxide nanotubes (V_{acc} = 1kV)


SEM: Dependence on Electron Energy
Incident electrons
[Low acceleration voltage]
[High acceleration voltage]
[Low atomic number]
[High atomic number]
Penetration depth of electrons in matter
➢ increases with increasing V_{acc}
➢ decreases with increasing atomic number
Scanning Electron Microscopy

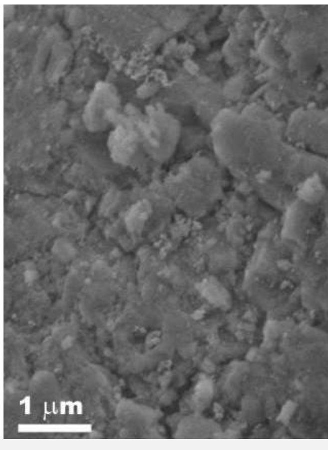

SEM: Dependence on Electron Energy
0.5 kV
1 kV
2 kV
5 kV
10 kV
20 kV
Resolution (Gemini 1530 FEG):
1 nm at 20 kV
1.5 nm at 10 kV
2.5 nm at 1 kV
5 nm at 0.2 kV
Scanning Electron Microscopy


Scattering of Electrons at an Atom
incident electrons
BSE
nucleus
Θ
electron cloud
Θ
scattered electrons
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
Scanning Electron Microscopy

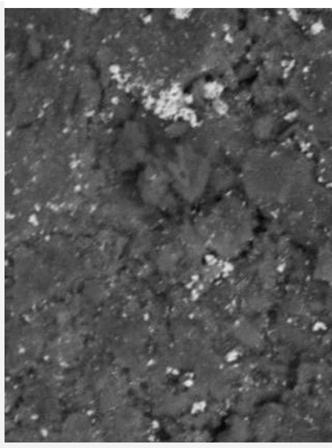

SEM: Detection of SE versus BSE
Fe particles in C
Secondary electron detector
Backscattered electron detector
Fe particles bright (Z contrast)
Scanning Electron Microscopy

SEM: Detection of SE versus BSE

Pt particles on alumina



Secondary electron detector



Backscattered electron detector

Pt particles bright (Z contrast)

Scanning Electron Microscopy (SEM)

Detection of:

- Secondary electrons
- Back-scattered electrons

Determination of

- Morphology
- Surface topology
- Particles of heavy elements

Combination with EDXS

Script: ***Interactions.pdf*** **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)**