



Scanning Electron Microscopy of Polymer Materials

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The lecture was created for courses on Polymer Morphology.

Great majority of information in this lecture holds for non-polymeric materials as well.

Focus of the lecture:

- (1) the basic methods of SEM, important for polymers (SE, BSE, EDX, STEM)
 - (2) how to interpret/get information from SEM micrographs of polymer systems
- * other methods of SEM not so important for polymer systems are just briefly listed
 - * basic theory of electron microscopy has been explained in the 1st lecture of the course

Background of the slides:

blue = theory; green = examples; yellow = calculations; grey = supplements

Micrographs in this lecture:

(Almost) all micrographs in this lecture come from our laboratory + majority of samples from IMC \Rightarrow we can discuss/collaborate on whatever will be shown in the presentation.

Part 1

Brief Introduction to SEM

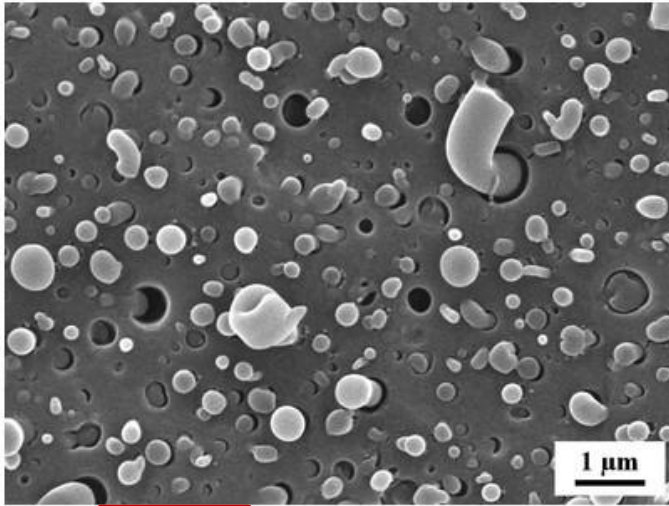
Contents

- ❖ Four basic modes of SEM
- ❖ SEM signal from macro-, microscopic and atomistic point of view

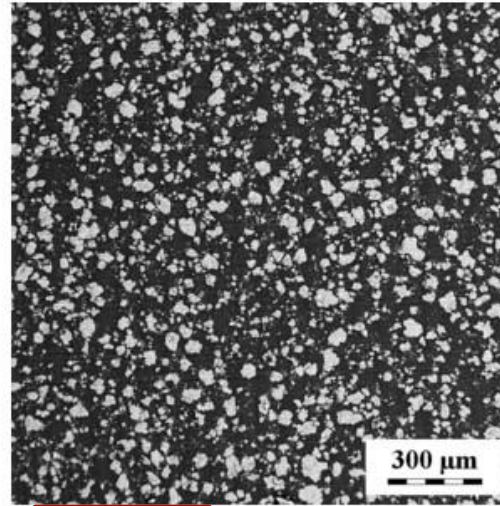
Notes:

- Supplement #1 gives overview of other SEM methods and possibilities
- Supplement #2 gives basic information about SEM hardware components

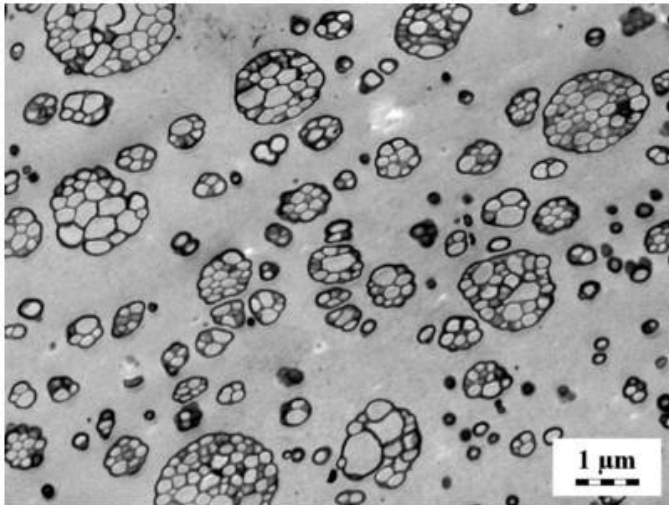
SEM microscopy :: four main modes



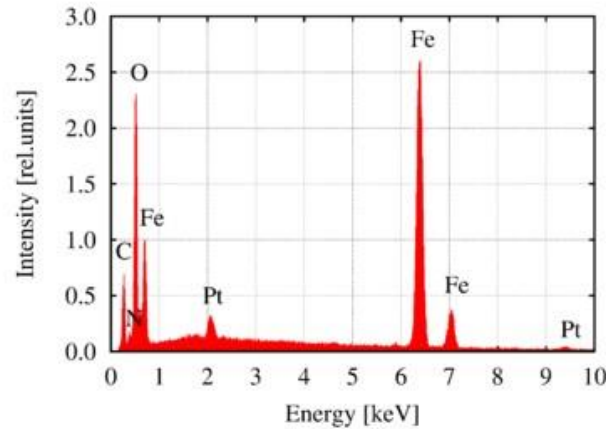
SEM/SE: topographic contrast in PP/COC blend (fracture surface)



SEM/BSE: material contrast in Epoxy/ATH composite (smooth surface)



SEM/TE: transmitted electrons in HIPS copolymer (ultrathin section)



SEM/EDX: elemental analysis of magnetic polymer microspheres

SEM/SE

- secondary electrons
- topographic contrast
- >90% applications

SEM/BSE

- backscattered electrons
- material contrast

SEM/TE

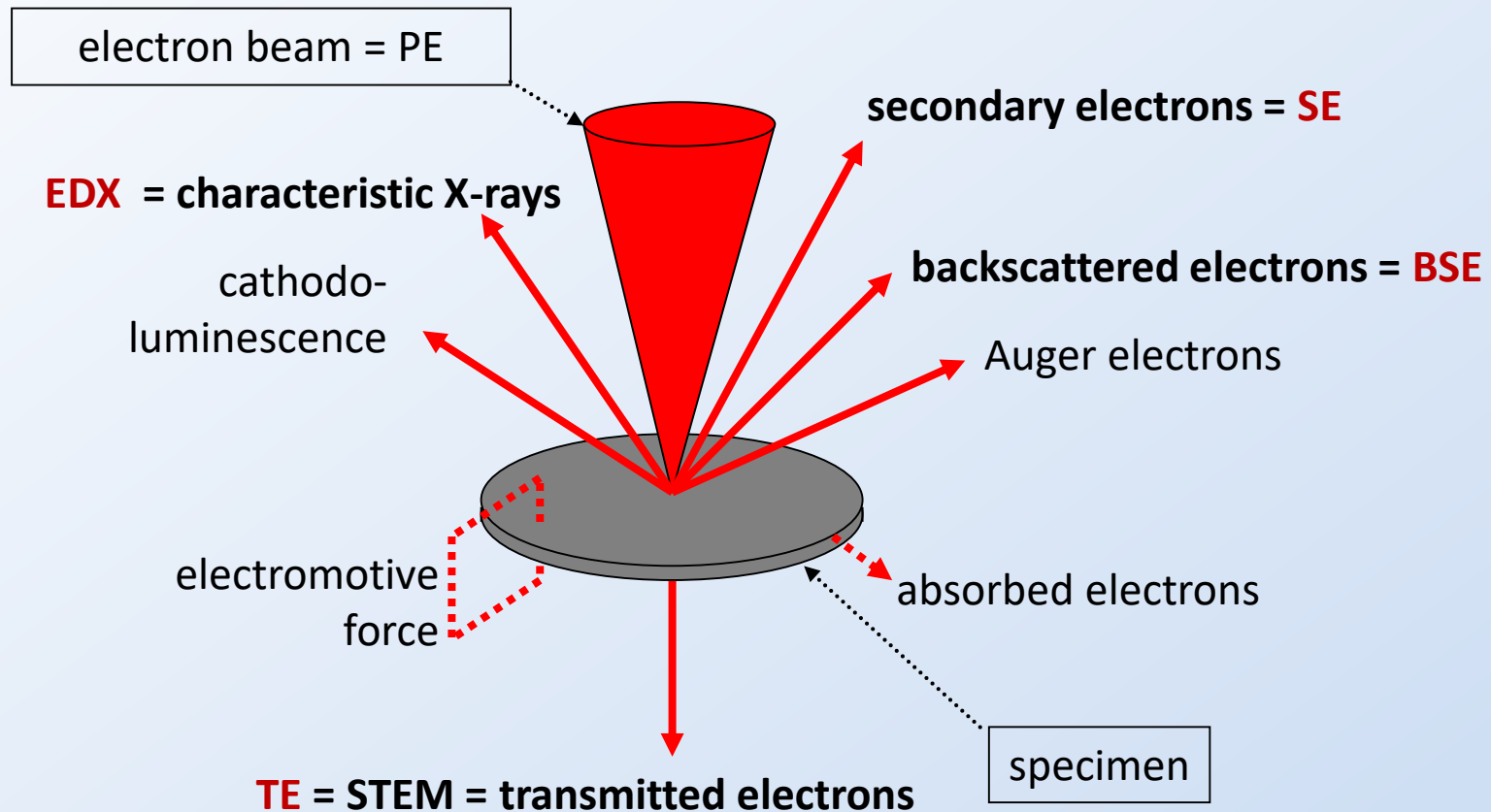
- transmitted electrons
- internal structure

SEM/EDX

- characteristic X-rays
- energy-dispersive analysis of X-rays (EDS, microanalysis)

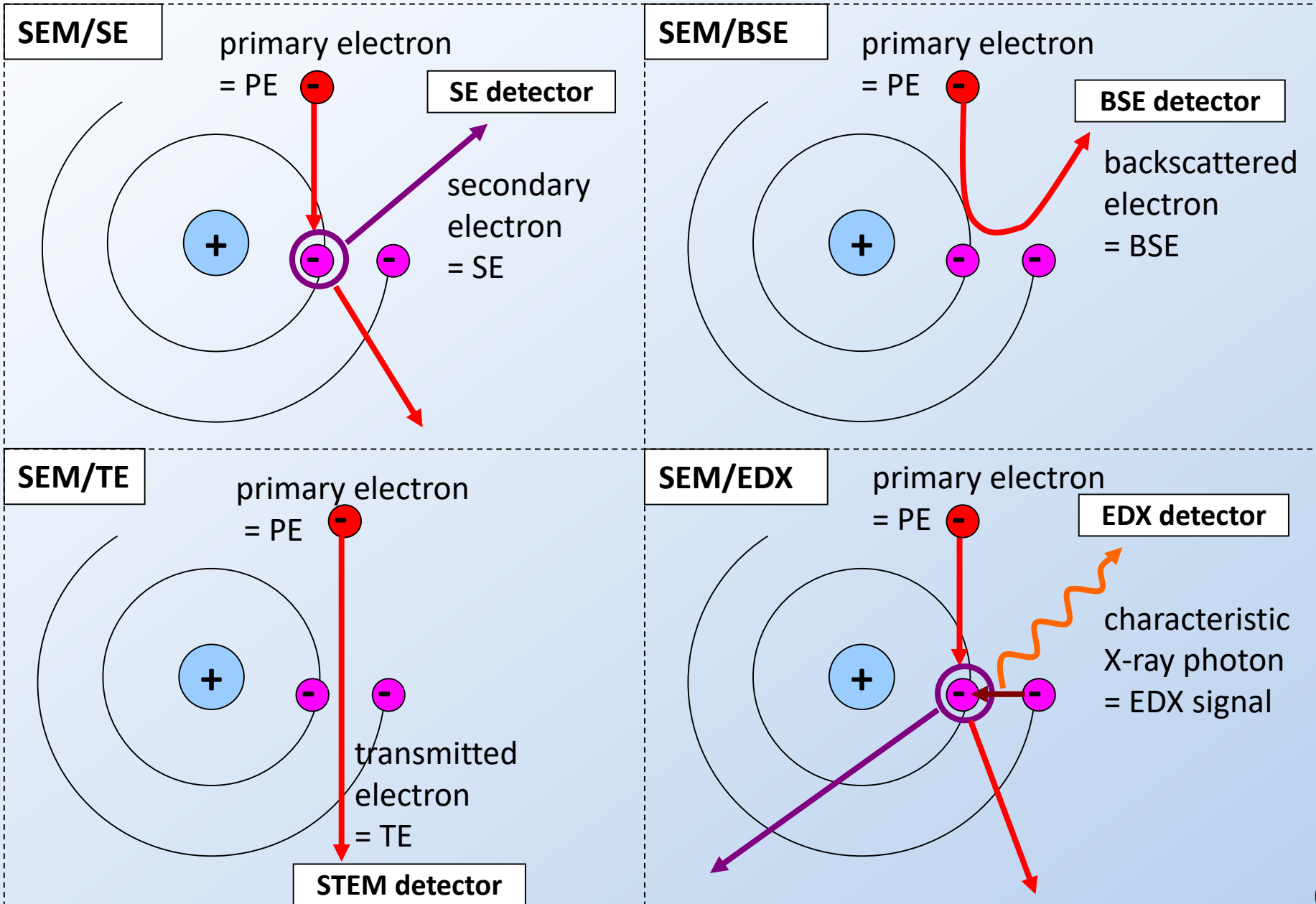
SEM :: microscopic view :: beam-specimen interactions

Interaction of electron beam with specimen
= origin of various signals in SEM



* Note: EDX = energy-dispersive analysis of X-rays = EDS = energy-dispersive spectroscopy.

SEM :: atomistic view :: electron-atom interactions



Supplement #1a :: SEM :: summary of methods

1) Methods according to detected signal:

basic methods (covered in this lecture):

SE, BSE, TE=STEM, EDS=EDX

further methods (very rarely applied to polymers, not in this lecture):

WDS=WDX, EBSD, CL, AES: mostly for inorganic/metal/crystalline materials

Other methods, even less frequently applied to polymers...

These are the main methods used for polymer systems \Rightarrow main part of this lecture

2) Methods according to vacuum in the specimen chamber:

(not discussed in detail, but some results shown in the following slides)

- HVSEM = standard SEM = high-vacuum SEM (conductive/coated specimens)
- LVSEM = low-vacuum SEM (non-conductive / beam-sensitive / frozen specimens)
- ESEM = environmental SEM (wet specimens observed at 'natural' conditions)

3) Other modern methods/trends:

(not discussed in detail, but some results shown in the following slides)

- low-voltage/low-energy SEM = observation at lower landing energies (lower sample damage + higher surface contrast, but lower resolution)
- in-situ SEM = observation at higher pressures/temperatures
- 3D-SEM, FIB-SEM = observation of morphology in three dimensions

* VP-SEM = variable-pressure SEM = a general, more correct term for LVSEM + ESEM

* How to make polymer samples conductive = suitable for the most common (HV)SEM?

Routinely: cover with thin (~ 5nm) metal/carbon layer in a commercial device.

* More information about SEM methods (this brief list is still incomplete!):

[Wikipedia - Scanning electron microscopy]

Sabbatini L: Polymer surface characterization, Chapter 6: Electron microscopy

Supplement #1b :: The common microscopic methods for characterization of polymer morphology

Summary the four most common SEM methods (SEM/SE, BSE, EDX, TE) and the three basic modes of SEM microscopy (high + low-vacuum + environmental SEM):

	(HV)SEM high-vacuum SEM	LVSEM low-vacuum SEM	ESEM environmental SEM
SEM/SE	the most common: ~90% of applications	frequent: SE of non-conductive	rare: SE of wet
SEM/BSE	frequent: composites	frequent: BSE of non-conductive	very rare: BSE of wet
SEM/EDX	frequent: microanalysis	frequent: EDX of non-conductive	very rare: EDX of wet
SEM/TE	rare: polymer blends	exceptional: no application	very rare: NPs in solution

Note1: Each of the 4×3=12 methods may require special detector ⇒ not all methods are available in common SEM

Note2: LVSEM is used also for frozen specimens (hydrogels)

Note3: This course is focused on the most used methods: **HVSEM/SE, BSE, EDX, TE;** the others just very briefly.

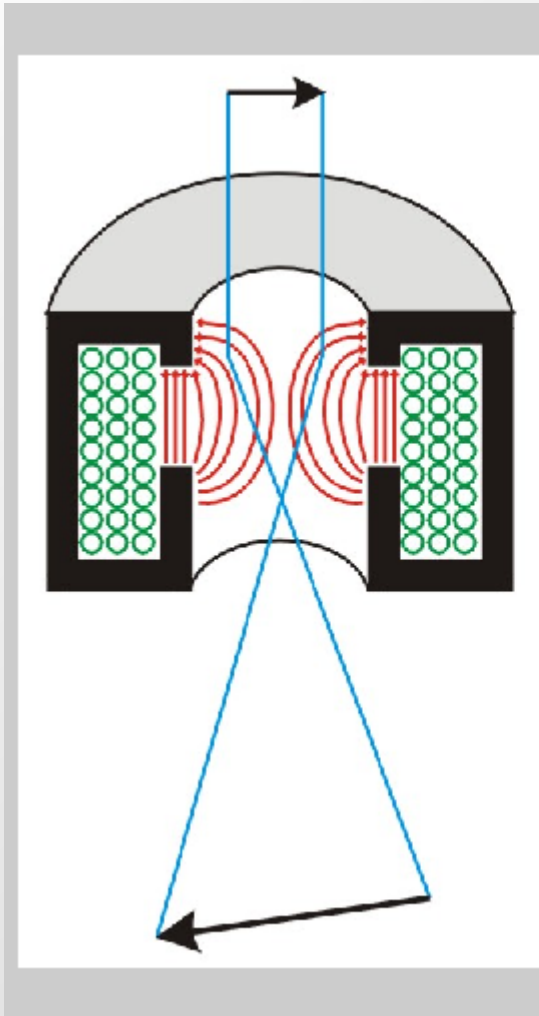
Two specific method for characterization of polymer particles in solution:

- ❖ Wet-STEM microscopy → particles observed *in thin layer of liquid*
- ❖ Cryo-TEM microscopy → particles observed *frozen in thin layer of ice*

Some examples associated with these two methods will be shown during the course.

Supplement #2a :: SEM components

Electromagnetic lenses



A magnetic lens consists of a coil of copper wires inside the iron pole pieces. A current through the coils creates a magnetic field (symbolized by red lines) in the bore of the pole pieces. The rotationally symmetric magnetic field is inhomogeneous in such a way that it is weak in the center of the gap and becomes stronger close to the bore. Electrons close to the center are less strongly deflected than those passing the lens far from the axis. The overall effect is that a beam of parallel electrons is focused into a spot (so-called cross-over).

In a magnetic field, an electron experiences the Lorentz force F :

$$F = -e(E + \mathbf{v} \times \mathbf{B})$$
$$|F| = evB\sin(\mathbf{v}, \mathbf{B}) \quad -eE$$

E : strength of electric field
 B : strength of magnetic field
 e/v : charge/velocity of electrons

The focusing effect of a magnetic lens therefore increases with the magnetic field B , which can be controlled via the current flowing through the coils. As it is described by the vector product, the resulting force F is perpendicular \mathbf{v} and \mathbf{B} . This leads to a helical trajectory of the electrons and to the magnetic rotation (image is rotated in respect of the object).

Particle with charge Q is moving with velocity \mathbf{v} in the electromagnetic field; electric and magnetic forces are acting on the particle:

$$\mathbf{F} = \mathbf{F}_E + \mathbf{F}_M$$

Electric force \mathbf{F}_E is given by the intensity of electric field \mathbf{E} :

$$\mathbf{F}_E = Q \cdot \mathbf{E}$$

Magnetic force \mathbf{F}_M is given by magnetic induction \mathbf{B} :

$$\mathbf{F}_M = Q \cdot (\mathbf{v} \times \mathbf{B})$$

Force acting on electron:

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

Connection with real life: electromagnetic lens deflects electrons due to inhomogeneous magnetic field; strength of the lens can be adjusted by changing current (logically: $B \propto N \times I$).

* Moreover, electron trajectories can be calculated – this is employed in construction of microscopes.

Supplement #2b :: SEM components

Electron guns, Apertures and Detectors

Electron guns

(anything that easily emits electrons)

- W-filament
- LaB₆ crystal
- hot FEG
- cold FEG

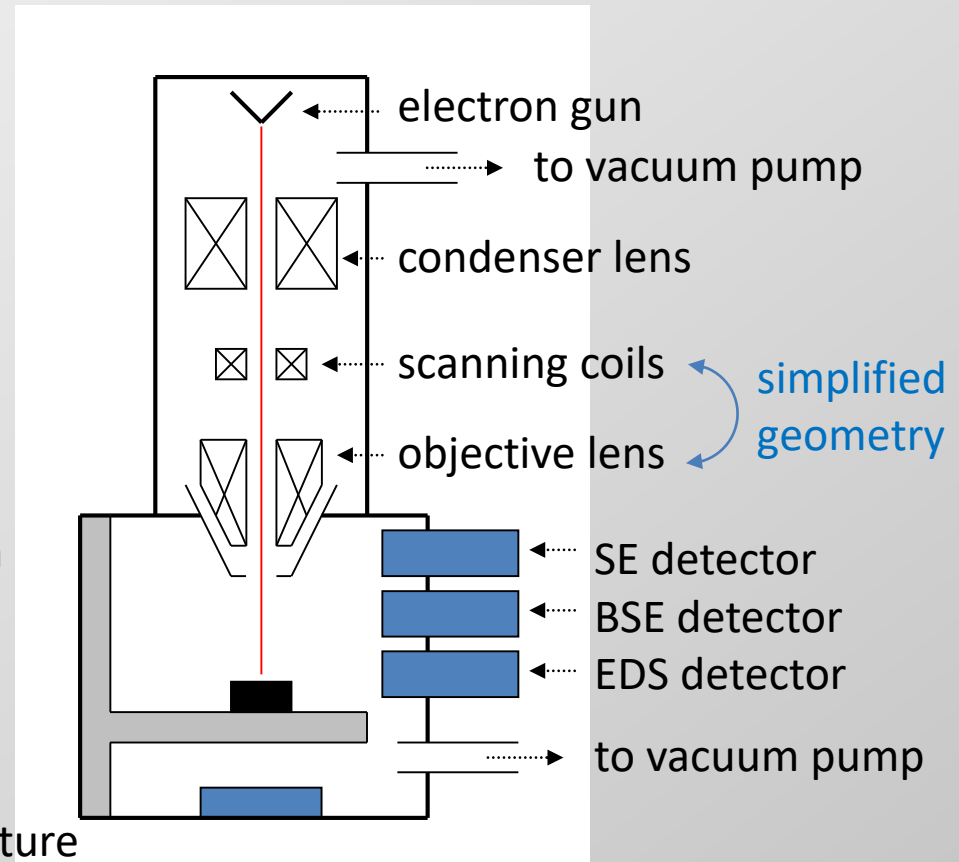
increase in:
quality, lifetime
required vacuum
price

Apertures

- not as important as in TEM
- many users do not even know about them
- require centering: manual, then electrical
- after some time: cleaning or replacement
- experienced users change them:
high resolution SEM/SE → small aperture
faster collection in SEM/EDX → large aperture

Detectors

- (almost) every SEM: SE, BSE + more-and-more common: EDX + sometimes for polymers: TE
- modern SEMs: detectors for various vacuum modes (HVSEM, LVSEM, ESEM – see next)
- modern SEMs: detectors for electrons emitted with specific energies/angles



Part 2

More theory and resolution of SEM

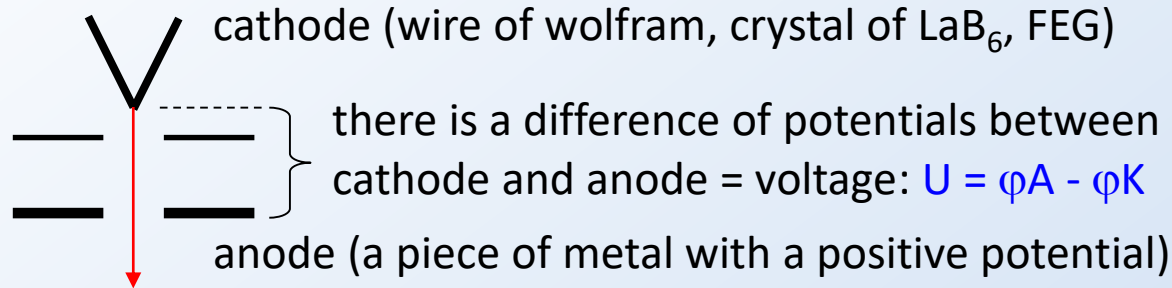
Contents

- ❖ Velocity and wavelength of electrons in SEM
- ❖ Penetration depth of the electrons into a specimen
- ❖ Simulation of the electron trajectories in a specimen
- ❖ Resolution in SEM (in all four basic modes = SE, BSE, TE, EDX)

SEM :: How fast do the electrons fly?

Velocity and wavelength of electrons :: Explanation.

Scheme of electron gun in SEM/TEM.



Note:

φ = electric potential = work required to carry e^+ (unit positive charge) to the given location from infinity
 U = voltage = electric potential difference = work required to carry e^+ between two locations

How it works?

Voltage U extracts the electrons from cathode → according to secondary school physics:

$$E_1 = QU = eU$$

... E_1 = potential energy of an electron at anode = charge * voltage

$$E_2 = 1/2 * m * v^2$$

... E_2 = kinetic energy of an electron at anode = 1/2 * mass * velocity²

$$E_1 = E_2$$

...potential energy E_1 is completely converted to kinetic energy E_2

$$v = \sqrt{(2eU/m)}$$

...combining the above equations we get velocity of the electron v

$$\lambda = h/(m*v)$$

...using Broglie relationship we can calculate also electron wavelength λ

The result can be obtained with a simple calculator...

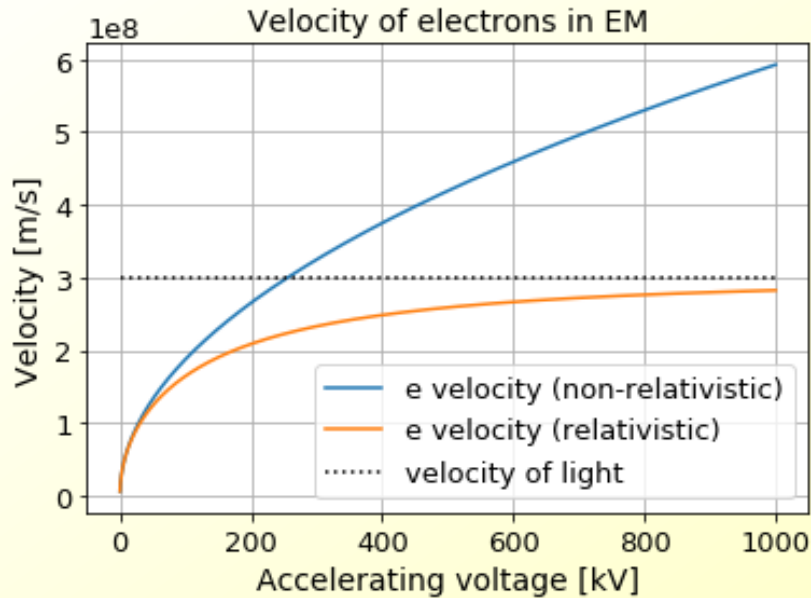
LM: source = a source of light/photons ⇒ $v \sim$ visible light = c , $\lambda \sim$ visible light = 400-800 nm

SEM: source = electron gun ($U = 1-30\text{kV}$) ⇒ $v = \sqrt{(2eU/m)} \approx 0.28c$, $\lambda = h/(m*v) \approx 0.009 \text{ nm}$

TEM: source = electron gun ($U = 20-300\text{kV}$) ⇒ $v = \sqrt{(2eU/m)} \approx 0.89c$, $\lambda = h/(m*v) \approx 0.003 \text{ nm}$

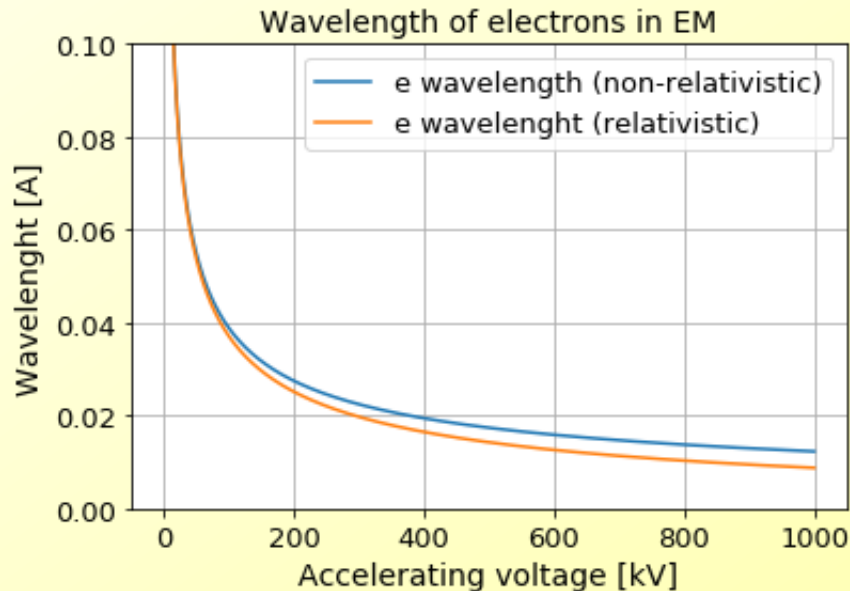
SEM :: How fast do the electrons fly?

Velocity and wavelength of electrons :: Calculation



Velocity of electrons is very high:

- ❖ comparable to velocity of light
 - ❖ relativistic corrections needed for precise calculation
- ⇒ energy of electrons (PE) is sufficient to kick off secondary electrons (SE) and produce numerous other signals, such as BSE, EDX, TE...



Wavelength of electrons is very low:

- ❖ light: $\lambda \approx 6000 \text{ \AA}$
 - ❖ X-rays: $\lambda \approx 1 \text{ \AA}$
 - ❖ electrons: $\lambda \approx 0.03 \text{ \AA}$
- ⇒ high resolution of EM (diffraction limit)
- ⇒ specifics of electron diffraction (TEM lecture)

Complete calculation in Python/Jupyter

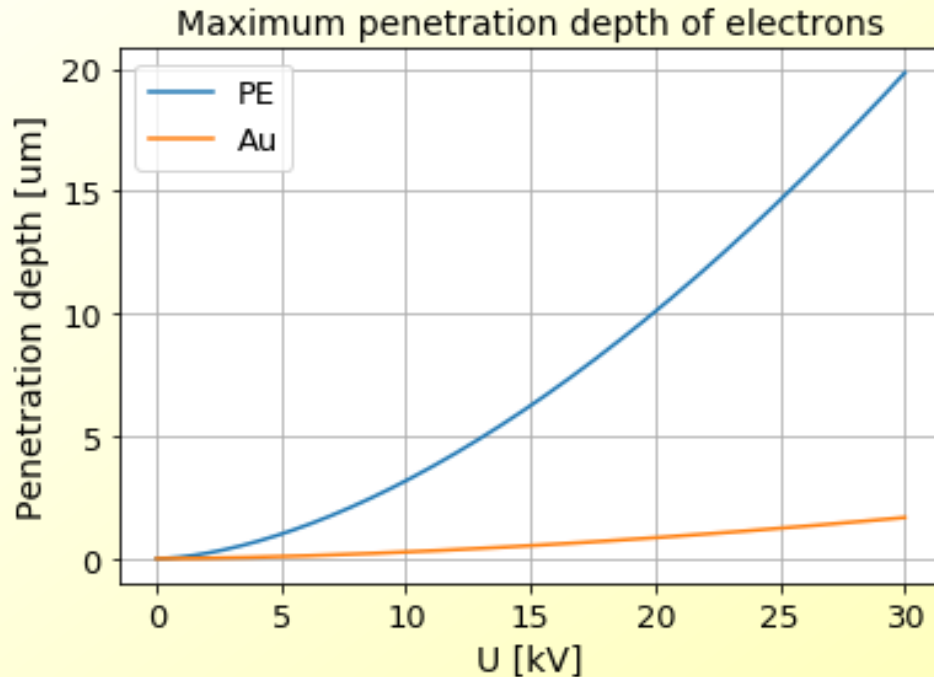
HW #1: create Python/Jupyter functions and calculate velocity and λ of e^- @ 1,10,100kV

SEM :: How deep into a specimen do the electrons penetrate?

Penetration depth of electrons :: Approximate calculation

There is an old, semi-forgotten formula (Kanaya-Okayama) which estimates penetration depth.

$$R[nm] = 27.6 \frac{M[g/mol] \times U[kV]^{5/3}}{\rho[g/cm^3] \times Z[]^{8/9}}$$



Note: The estimate of penetration depth from Kanaya-Okayama formula is surprisingly precise; this is confirmed on the next page, where we employ more precise Monte Carlo simulation.

Typical applications of K-O formula:

- ❖ SEM/EDX: from what depth do we get the signal?
- ❖ SEM/TE: estimate of thickness of thin films
- ❖ ...

Conclusions:

- 1) Penetration depths in SEM are low: <20 μ m
- 2) Penetration depths are very different for light- and heavy-elements materials
- 3) Penetration depth increases with increasing accelerating voltage \approx velocity of electrons

Complete calculation in Jupyter/Python \rightarrow see example + reproduce the graph: HW2

Note :: Motivation and help for HW1 and HW2

HW1:

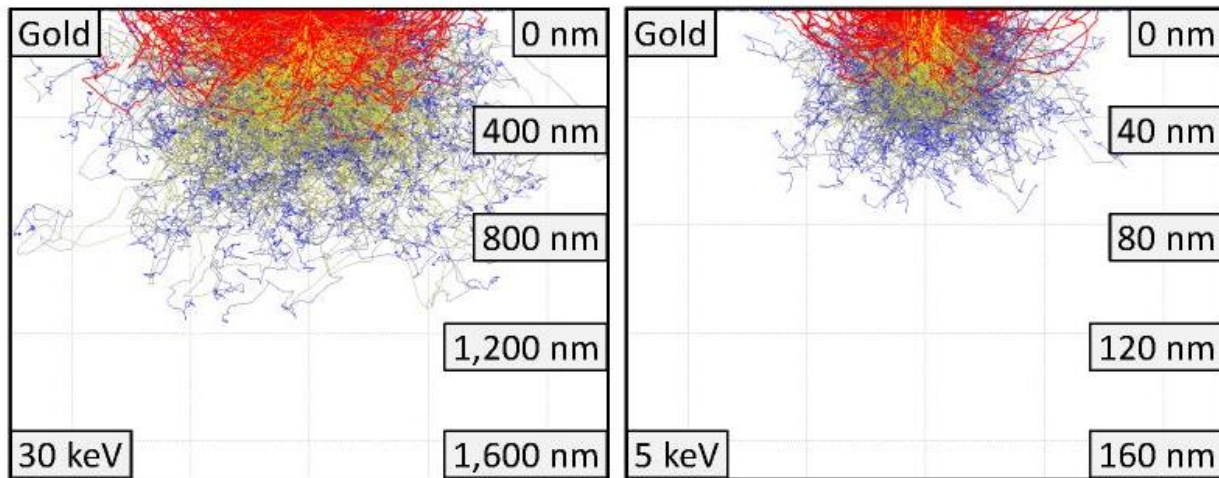
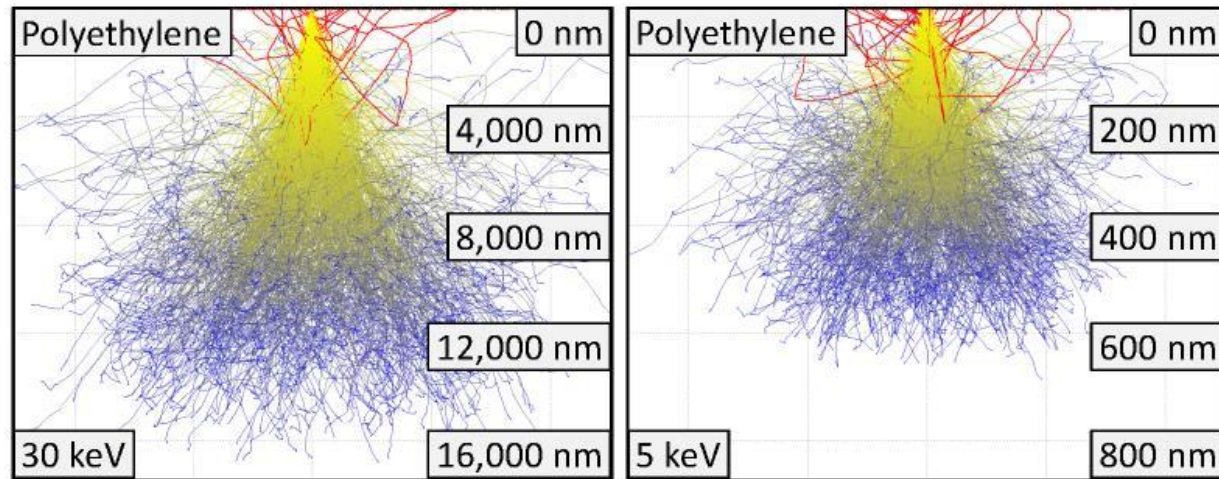
- ❖ motivation = learn how to define functions in Python
- ❖ basic help (sufficient for doing the homework) → Lecture EM0 – Jupyter – Intro
- ❖ detailed information (FMTYEWTK) → Google – Search – Functions in Python

HW2:

- ❖ motivation = learn how to draw graphs in Python
- ❖ basic help (sufficient for doing the homework) → Lecture EM0 – Jupyter – Intro
- ❖ advanced help (for nicer graphs in Python) → Lecture EM0 – Jupyter – More graphs
- ❖ detailed information (FMTYEWTK) → Google – Search – Python matplotlib
- ❖ why graphs in Python (and not in Excel, Origin)? → direct visualization of calculations

SEM :: How deep in the specimen do the electrons penetrate?

Penetration depth of electrons :: Monte Carlo simulation



Electron-specimen interaction for:

- different materials
polyethylene × gold
- different accelerating voltages: 30kV × 5kV

Electron trajectories:

- yellow→blue:
PE with decreasing energy
- red: BSE electrons

Conclusions:

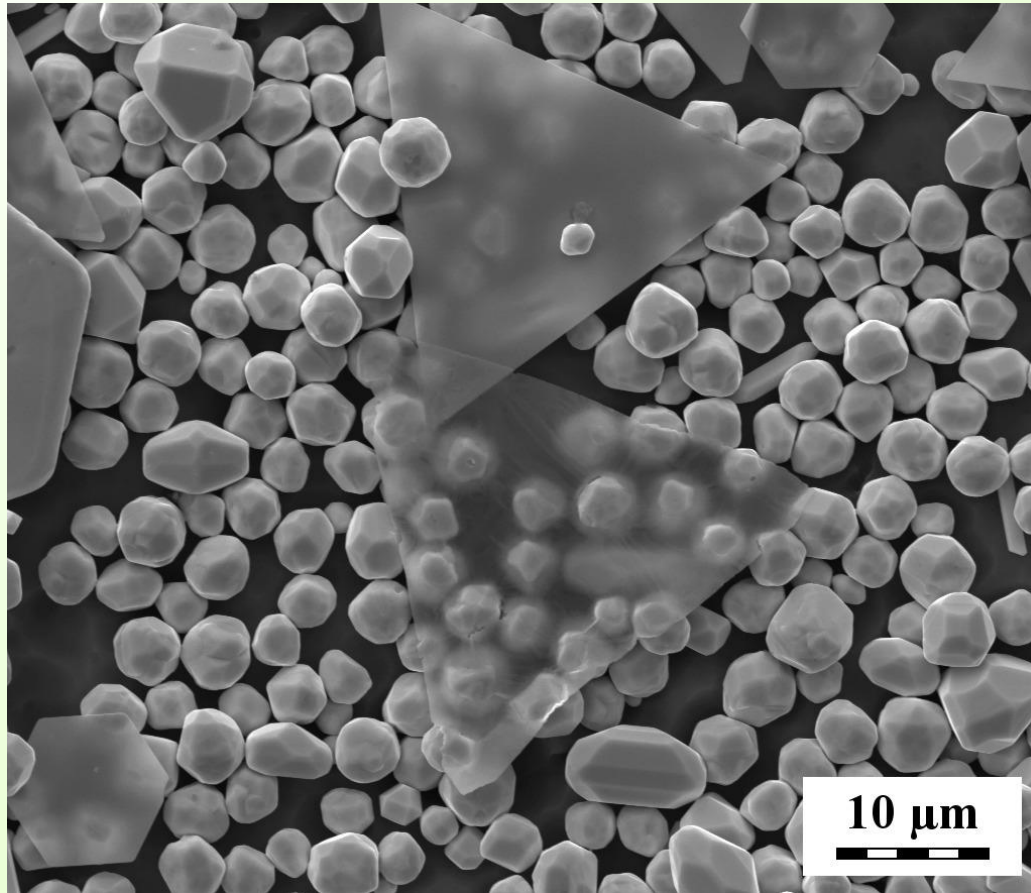
- **shape of interaction volume**
depends on material
- **penetration depth**
depends on material
- **BSE yield**
increases with Z strongly

Program CASINO = Monte Carlo simulation of electron-specimen interactions.

Freeware, easy user interface, 2D/3D - www.gel.usherbrooke.ca/casino/index.html

SEM :: How deep in the specimen do the electrons penetrate?

Penetration depth of electrons :: Real-life example.



Sample:

Au microcrystals on Al support
(collaboration with IIC AS CR, T.Baše)

- big thin microcrystals tend to grow with crystal facets {111}
- small isometric crystals tend to grow with facets {100}+{111}
- the thin microcrystals can be employed as a model surface...

Sample preparation:

Very simple – conductive sample:
just insert in SEM & observe.

Microscopy

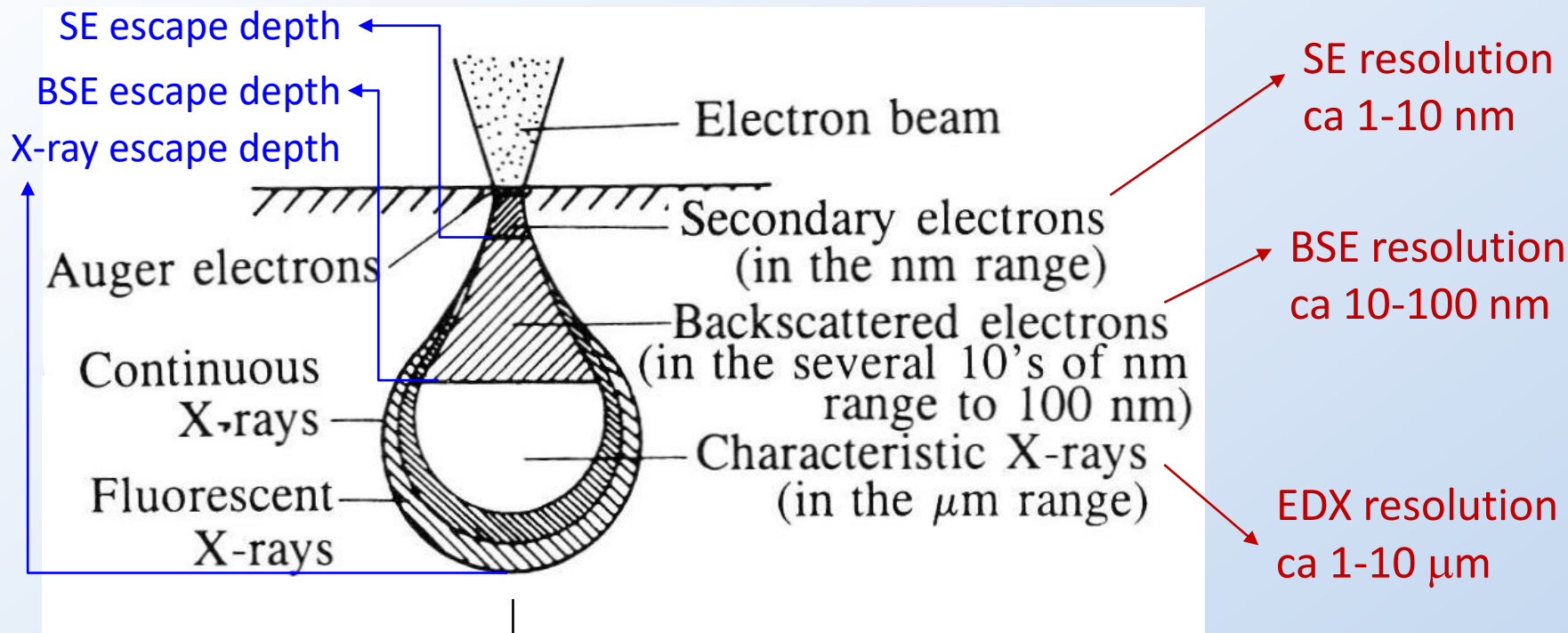
Objective: morphology \Rightarrow SEM/SE.

Conclusion: The previous simulations (CASINO) and calculations (K-O formula) we know that the gold microcrystal must be extremely thin in order to be translucent.

The thickness of the crystals can be even estimated: for Au/30kV the electrons penetrate to max. $\approx 1 \mu\text{m}$ + enough of them must get back to the detector \Rightarrow **thickness $\ll 0.5 \mu\text{m}$.**

SEM :: Resolution of the microscope in various modes

Interaction of electron beam with specimen → resolutions in SEM



STEM resolution depends on sample thickness, usually it is comparable to that of SE, i.e. ca 1-10 nm.

* Note how is the resolution associated with the escape depth.

Interaction of primary electrons (PE) with the sample takes place in the interaction volume. Size and shape of the interaction volume depend on: (1) composition, (2) energy of electrons, which is connected with their penetration/escape depth, and (3) beam size = spot size.

SEM :: Summary of formulas used in this section

Velocity of electrons, v [m/s] in EM as a function of accelerating voltage U [V].
Units and constants: e = electron charge [1.60×10^{-19} C], m_e = electron mass [9.11×10^{-31} kg].

$$v(U) = \sqrt{\frac{2eU}{m_e}}$$

Wavelength of electrons, λ [m], in EM as a function of accelerating voltage U [V].
Units and constants: h = Planck constant [6.63×10^{-34} m² kg s⁻¹], m_e = electron mass [9.11×10^{-31} kg] .

$$\lambda(U) = \frac{h}{\sqrt{2m_e eU}}$$

Penetration depth, R [nm], of the electrons into a specimen (Kanaya-Okayama formula).
Units and constants: M [g/mol], U [kV], ρ [g/cm³], and Z = sum of all Z [dimensionless].

$$R(M, \rho, Z, U) = 27.6 \frac{MU^{5/3}}{\rho Z^{8/9}}$$

Part 3

SEM/SE – interpretation of micrographs

Contents

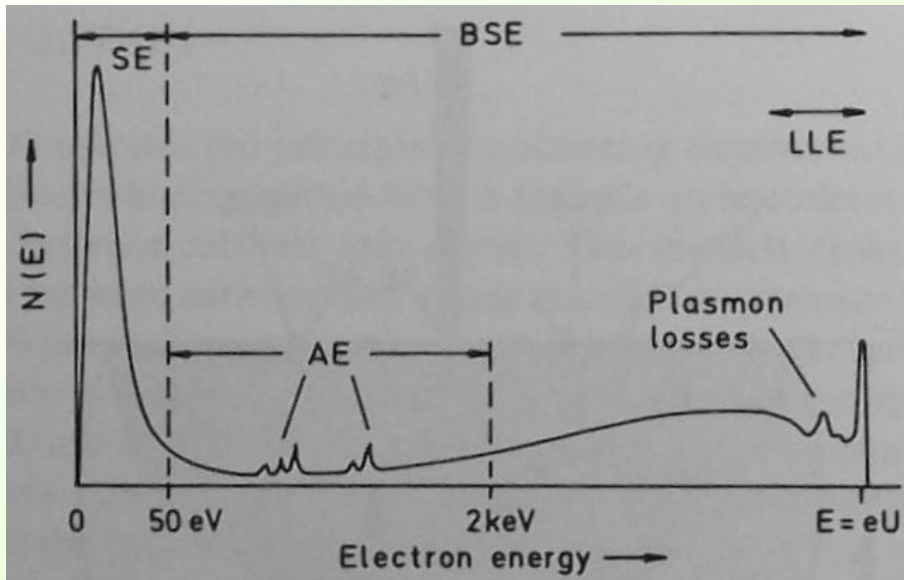
- ❖ General rules for SE & origin of topographic contrast
- ❖ Application of the rules on real micrographs

Notes:

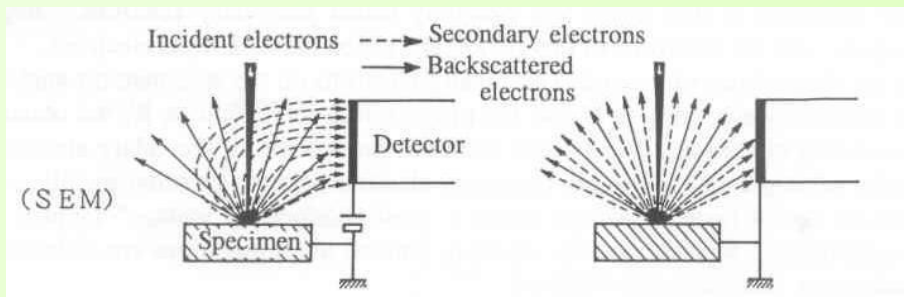
- SE = Secondary Electrons
- SEM/SE imaging = SE imaging = SEI
- SE imaging is a key mode of SEM:
 - ⇒ SEM/SE \approx 90% of SEM applications in Polymer Science
 - ⇒ this is the key part of the whole lecture

SEM/SE :: Interpretation of micrographs

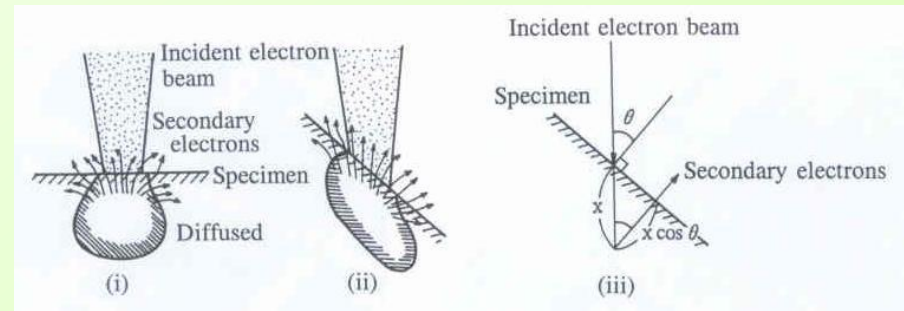
Four simple images that suffice for interpretation of most SEM/SE micrographs.



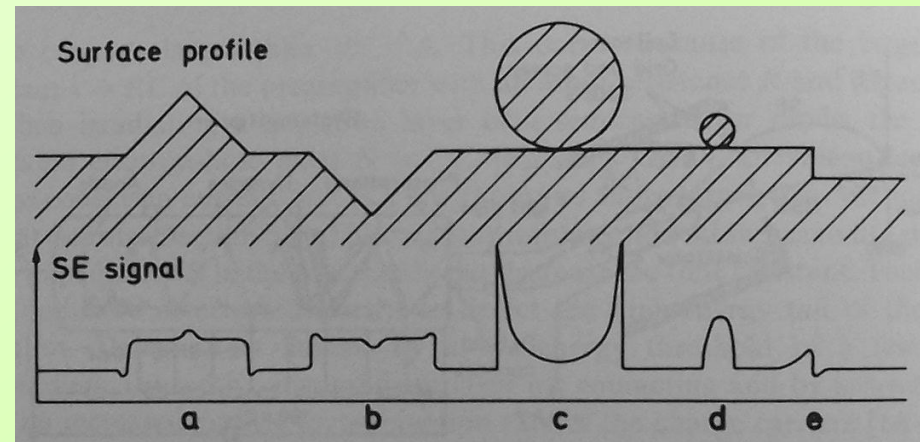
1. SE energy is very low (< 50 eV).
This is much less than that of PE and BSE.



2. (Almost) all SE reach the detector,
due to its positive charge/potential.



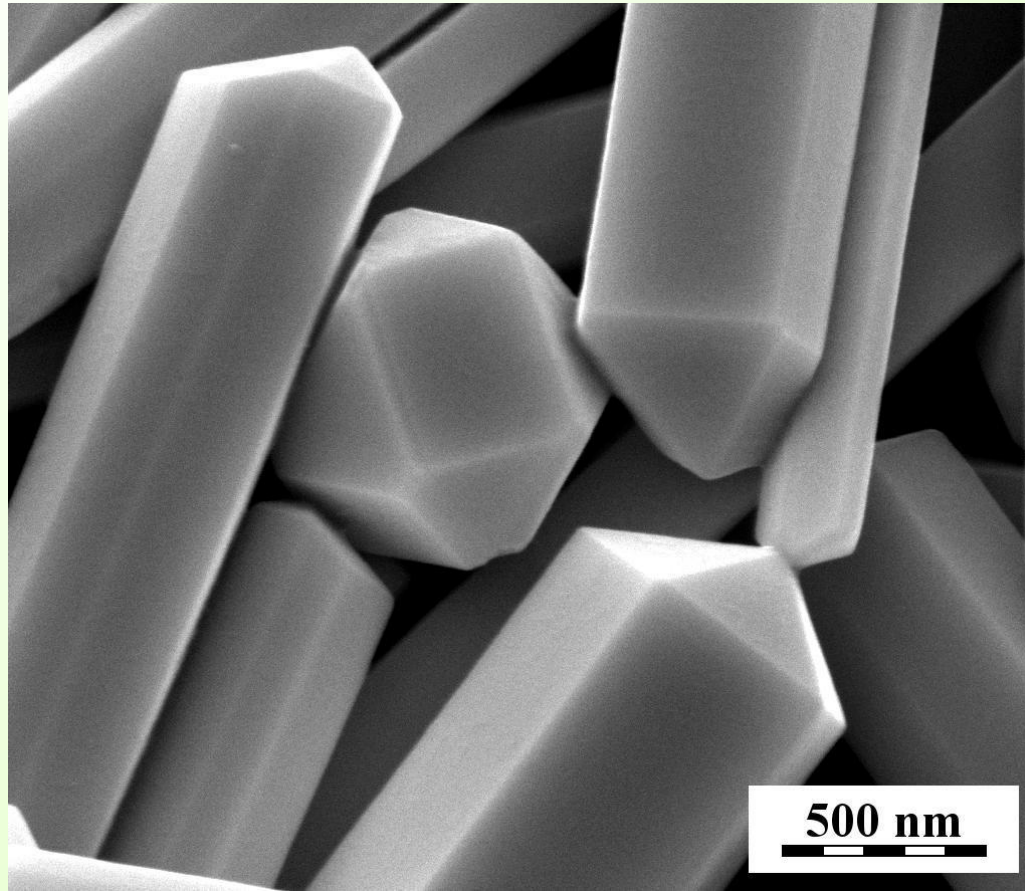
3. SE yield depends on the sample geometry:
low energy \Rightarrow released from thin layer
SE amount depends on inclination/tilt



4. Consequently, SE micrographs exhibit
mostly topographic contrast, as shown
schematically here \uparrow .

SEM/SE :: Interpretation of micrographs

(1) Surface tilt contrast (strong effect).



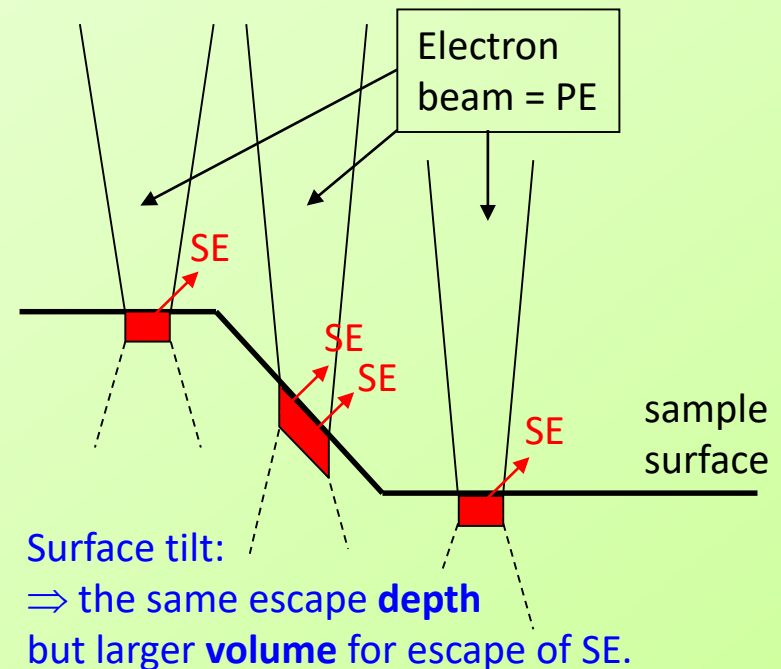
SEM/SE micrograph showing Ag microcrystals on Al support.

Sample preparation and microscopy:

Conductive metal Ag microcrystals deposited on conductive Al support.
⇒ no tricks: just insert in SEM & observe

Explanation of contrast:

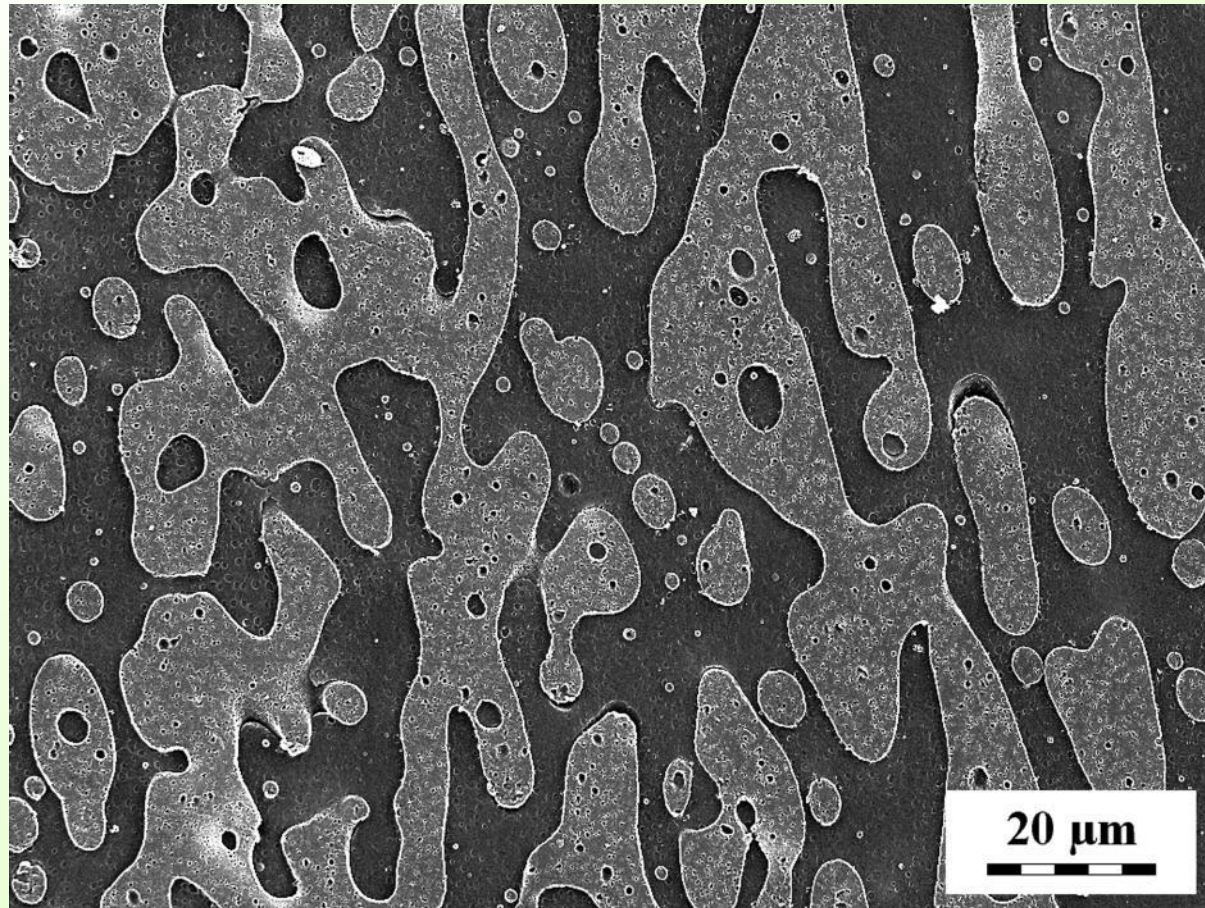
diameter of scanning beam is constant, but inclined planes exhibit higher projection



Conclusion: The amount of SE generated depends on the inclination/tilt of the specimen.

SEM/SE :: Interpretation of micrographs

(2) Edge effect (strong effect).



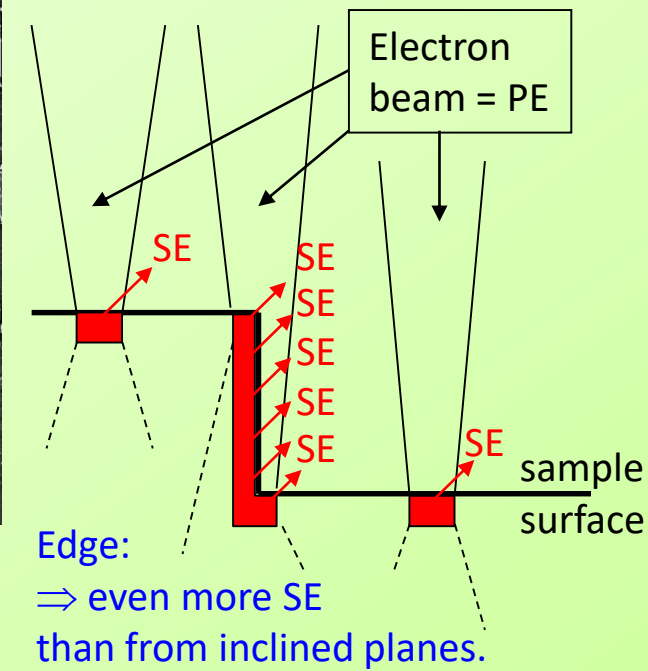
SEM/SE micrograph showing polymer blend RTPP/ABS (50/50), smoothed and etched surface.

Sample preparation & microscopy:

- 1) smoothing in LN₂
- 2) permanganic etching of RTPP *
- 3) Sputtering with Pt (~4nm layer)
- 4) Observation in (HV)SEM/SE

Explanation of contrast:

an extra SE from sharp edges

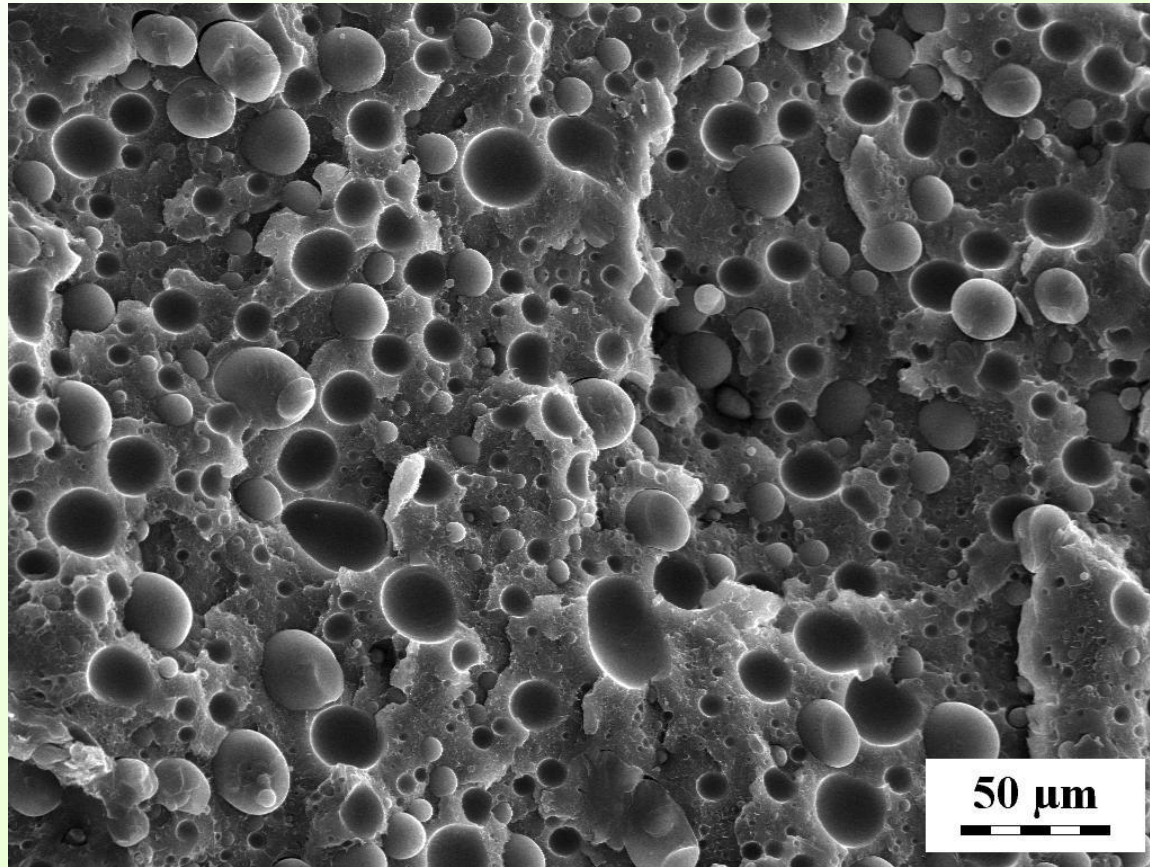


Conclusion: SEM/SE – the strong signal from sharp edges = edge effect.

* Details about smoothing & etching => Slouf M et. al: *Polym. Eng. Sci.*, 47:582–592, 2007.

SEM/SE :: Interpretation of micrographs

(3) Contrast of “hills and holes” (strong effect, combination of several phenomena).



SEM/SE micrograph showing a fracture surface of the polymer blend PP/PS (20/80).

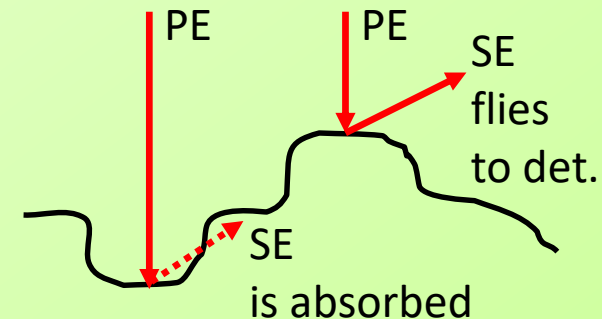
Sample preparation & microscopy:

sample (4 × 1 × 0.2 cm)

fracture in LN₂ | 4nm Pt | SEM/SE

Explanation of contrast:

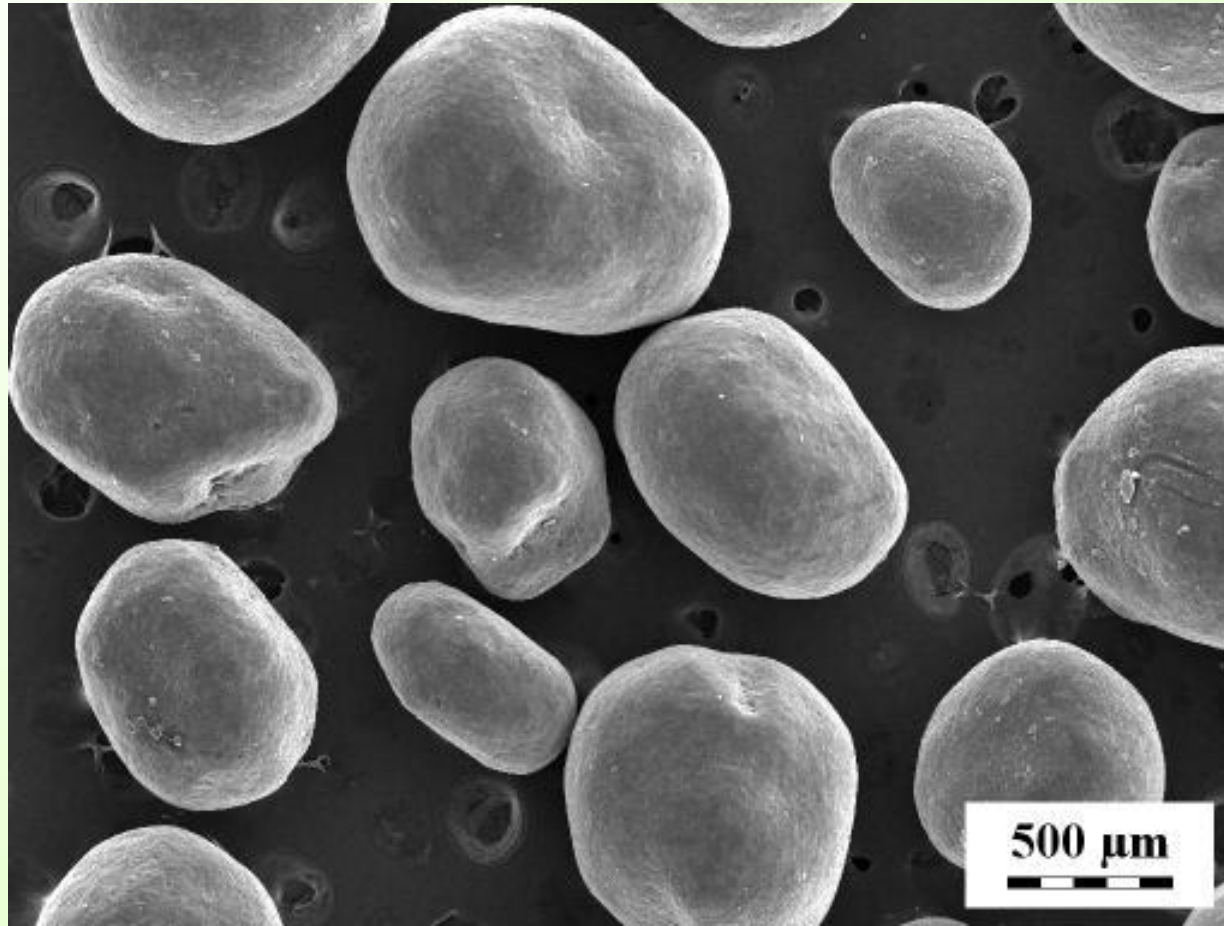
- polymer blend: PS matrix containing spherical PP particles
- fracture surface shows PP particles = “hills” and their imprints = “holes”
- all SE from particles/hills can reach the detector
- some SE from imprints/holes can be absorbed on the walls



Conclusion: In the SE micrographs, “holes” appear darker than “hills” .

SEM/SE :: Interpretation of micrographs

(4) Microparticles (special case of edge effect).

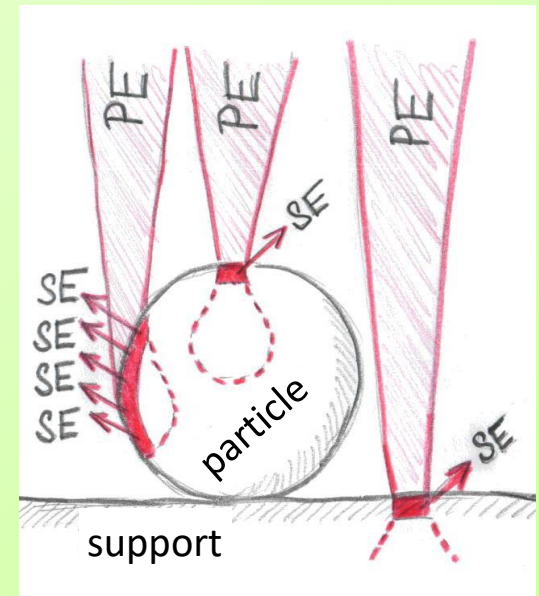


SEM/SE micrographs: polymer microparticles on C-tape.

Sample preparation and microscopy:

- 1) fix the microspheres using conductive adhesive C-tape
- 2) sputter with Pt (~4nm)
- 3) observe in SEM/SE

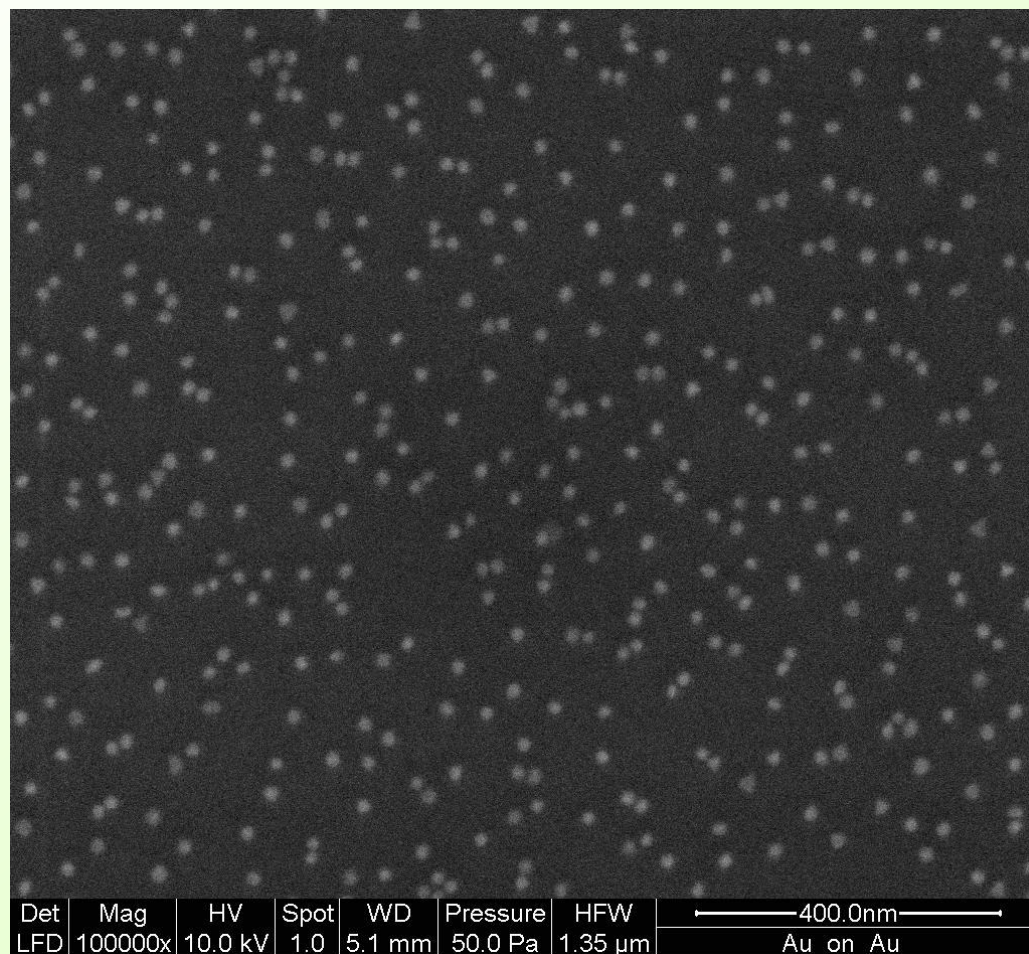
Contrast explanation:



Conclusion: particles \gg spot size \Rightarrow strongest signal at the edges.

SEM/SE :: Interpretation of micrographs

(5) Topographic contrast – nanoparticles (special case of edge effect).



LV-FEG-SEM/SE micrograph of Au nanoparticles on Au microcrystal.

Sample preparation and microscopy:

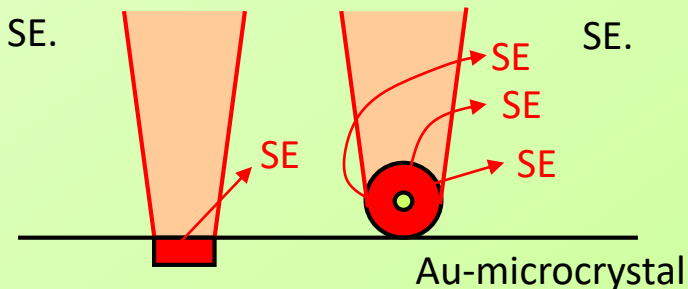
- 1) drop 2 μ L of Au-nanoparticles on Au-microcrystal on a supporting glass
- 2) observation in LVSEM[/SE (low-vacuum SEM; to avoid charging)

Explanation of contrast:

- If the size of the particle is comparable to the size of the electron beam (spot size), the SE can escape from (almost) all volume of the particle.

Flat support:
usual amount
of SE.

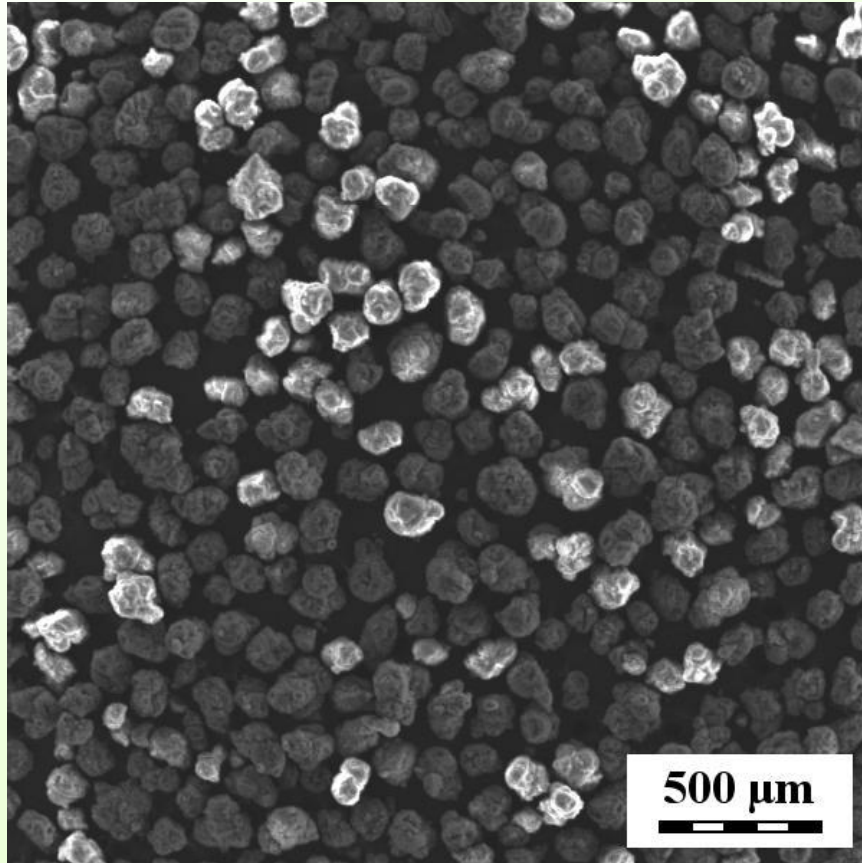
Small particle:
much more
SE.



Conclusion: Particles \approx spot size \Rightarrow as small bright spots.

SEM/SE :: Interpretation of micrographs

(6) Charging of not-so-well-fixed parts of the sample (strong effect – if it occurs).



SEM/SE micrograph:
cross-linked PE filled with ATH.

Sample preparation and microscopy:

- powder of PE filled with ATH (aluminum trihydrate) fixed on double adhesive conductive carbon tape (C-tape)
- sputter coating with Pt (4nm) in order to:
 - avoid charging
 - minimize specimen damage
 - increase surface contrast
- observation of microparticles in SEM/SE

Explanation of contrast:

Theoretically all particles should have the same contrast (the same material, size, preparation...)

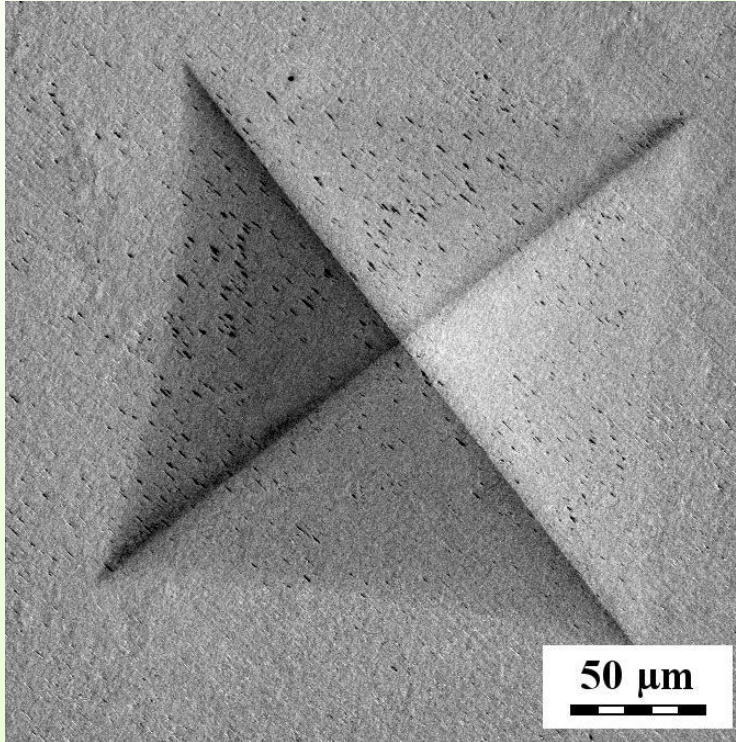
In practice some particles, which are not in such a good contact with conductive support exhibit charging, resulting in higher SE signal.

Conclusion: Charging may occur when some parts of a specimen are not in a good contact with the conductive support. This may lead to: (i) increase in SE signal of the charged parts of the specimen and/or (ii) image artifacts (horizontal lines) and/or (iii) specimen damage.

SEM/SE :: Interpretation of micrographs

(7) Shadowing contrast (medium effect).

SE
detector
position
in our
SEM



SEM/SE micrograph showing the result of microindentation test on UHMWPE: imprint of Vickers pyramid on the cut surface of the polymer.

Sample preparation and microscopy:

- smooth cut surface prepared in a rotary microtome with a glass knife
- indentation using a Vickers microhardness tester
 - ⇒ regular square pyramid forced into the specimen; load = 200gf, loadtime = 6s; surface in the horizontal position (tilt \approx 0 deg)
- Pt(4nm), observation in HVSEM/SE

Explanation of contrast:

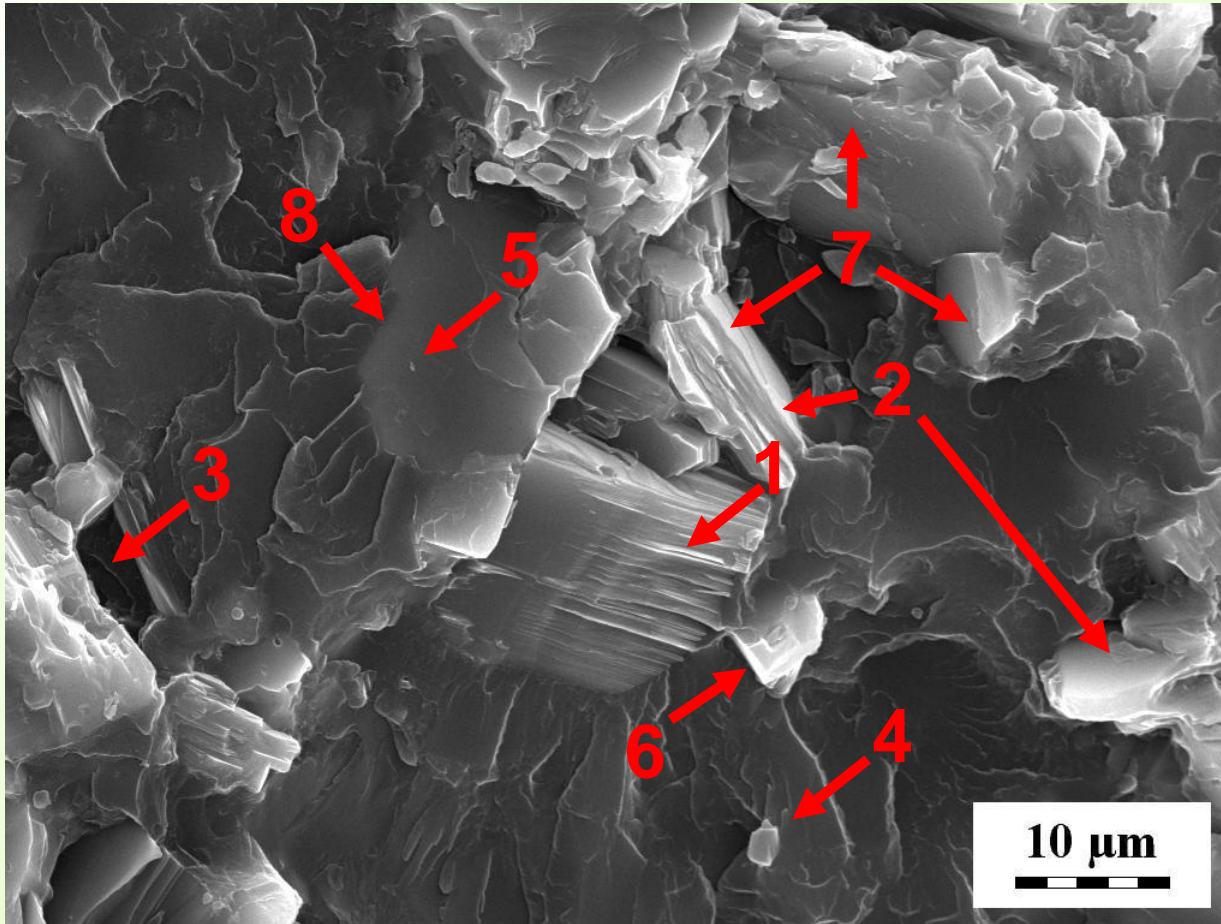
Theoretically all faces of the pyramid should yield the same SE signal (the same inclination relative to PE beam).

In practice the faces inclined towards the detector have slightly higher signal.

Conclusion: The amount of SE *produced* depends on the angle of incidence only, but the amount of SE *detected* depends on the orientation of the inclined/tilted parts of the specimen. Medium effect on signal, being sample/detector/geometry/orientation specific.

SEM/SE :: Interpretation of micrographs

(8) Material contrast (weak effect).



Sample preparation:

bulk sample (1 × 1 × 0,4 cm)
fracture surface in LN₂

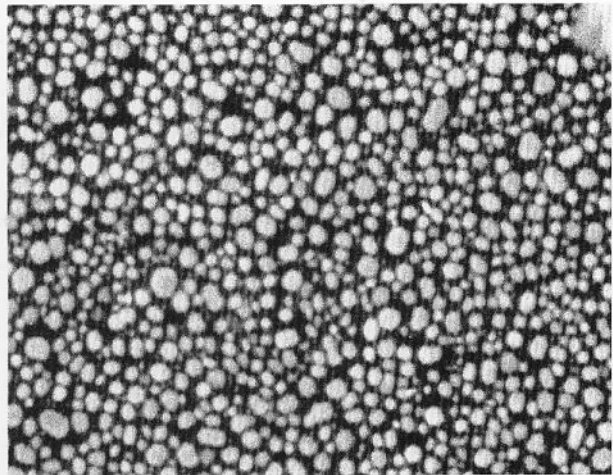
Explanation of contrast:

- SE yield from the polymer matrix is slightly different from SE yield from the ATH microparticles (8).
- This is a *material contrast* in SE imaging, which *tends to quite weak*.
- We note that all other types of topographic contrast, i.e. surface tilt (1), edge effect (2), “hills and holes” (3), contrast of big (4) and small (5) particles, charging (6), and shadowing contrast (7) are stronger than material contrast (8).

SEM/SE showing fracture surface of Epoxy/ATH composite.
(ATH = Aluminum trihydrate = $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$)

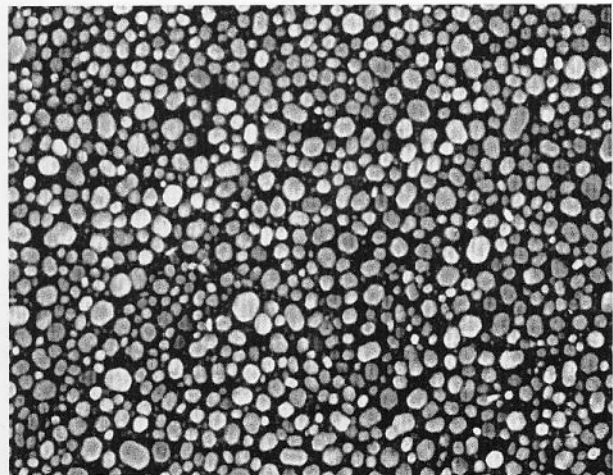
Conclusion: In SEM/SE, the topographic contrast is stronger than the material contrast.
Relative strength of the contrast usually decreases in the sequence: (1-4) > (5-7) >> (8).

Supplement #3 :: Effect of accelerating voltage in SEM/SE



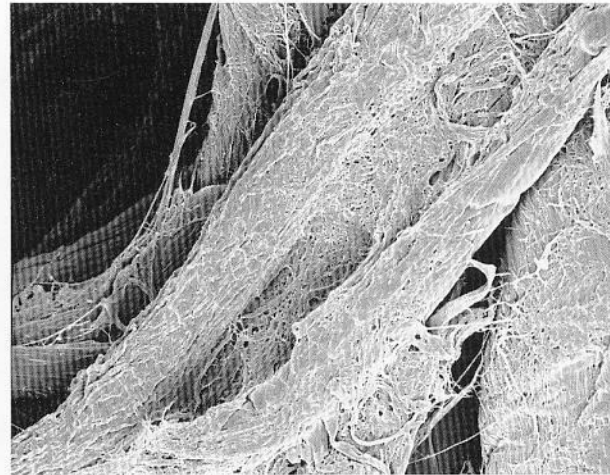
(a) 5 kV

× 36,000



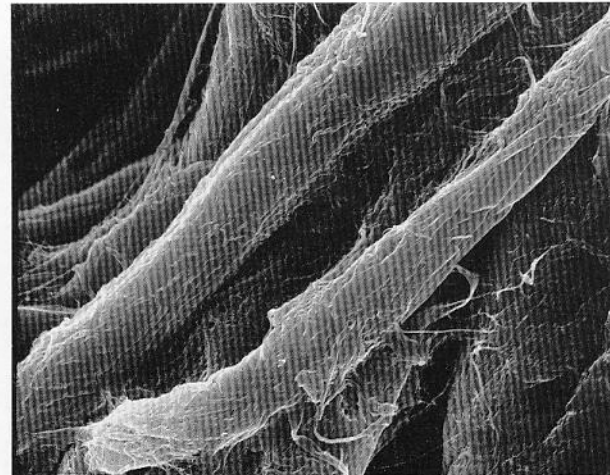
(b) 25 kV

× 36,000



(a) 5 kV

× 1,400



(b) 25 kV

× 1,400

← higher surface detail is linked with lower penetration depth of PE into the sample, i.e. lower accelerating voltage means less signal from sub-surface region

← this micrograph shows shadowing contrast (see slide 26, contrast in SEM/SE #7), i.e. the side of the fiber inclined towards the detector gives higher SE signal

Higher accelerating voltage
⇒ higher resolution.

Lower accelerating voltage
⇒ more information from surface.

Part 4

SEM/BSE – interpretation of micrographs

Contents

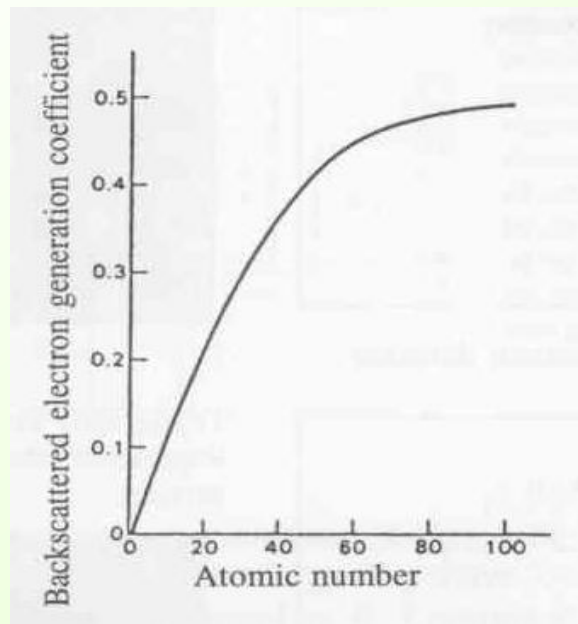
- ❖ General rules for BSE & origin of material contrast
- ❖ Application of the rules on real micrographs

Notes:

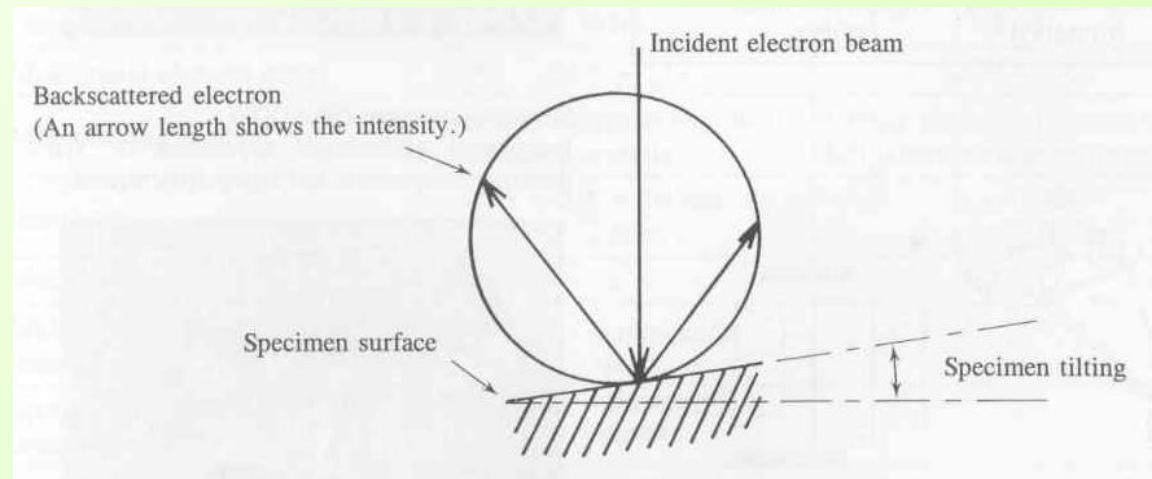
- BSE = Secondary Electrons
- SEM/BSE imaging = BSE imaging = BEI
- Note – SEM/BSE is the second most important mode of SEM:
 - ⇒ SEM/BSE imaging is frequently used for polymer (micro)composites
 - ⇒ Polymer **micro**composites usually contain materials with different Z
 - ⇒ Polymer **nano**composites usually require higher magnifications → TEM

SEM/BSE :: Interpretation of micrographs

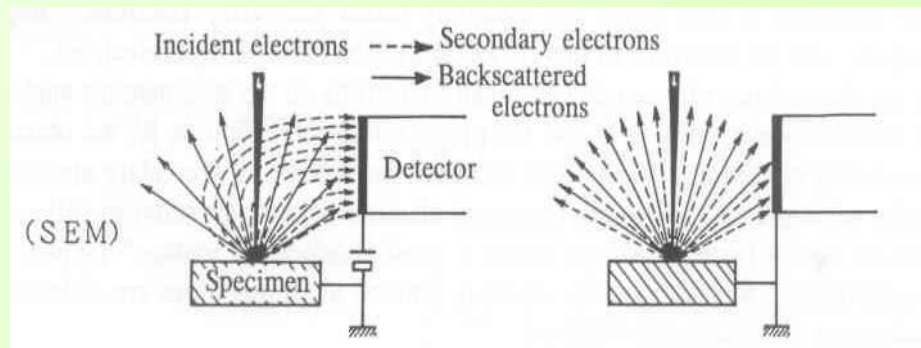
Four simple images that suffice for interpretation of most SEM/BSE micrographs.



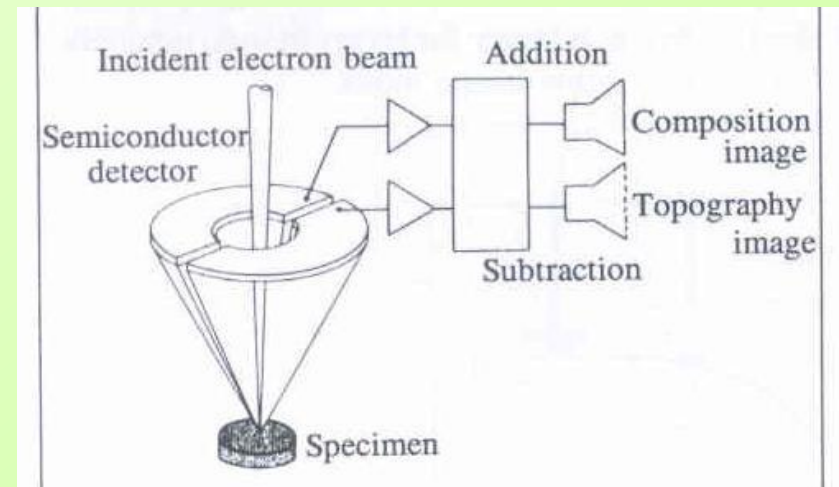
1. BSE signal is proportional to atom number Z.



2. BSE signal is connected with the tilt of the specimen.



3. BSE have higher energies than SE \Rightarrow they cannot be deflected towards the detector.



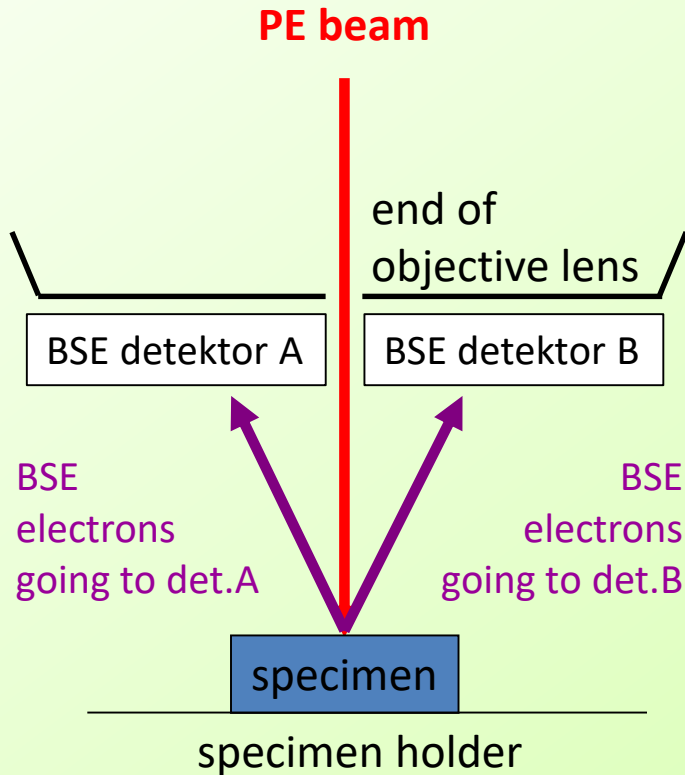
4. BSE detector is usually above the sample and consists of several parts/sectors.

SEM/BSE :: Material (and topographic) contrast.

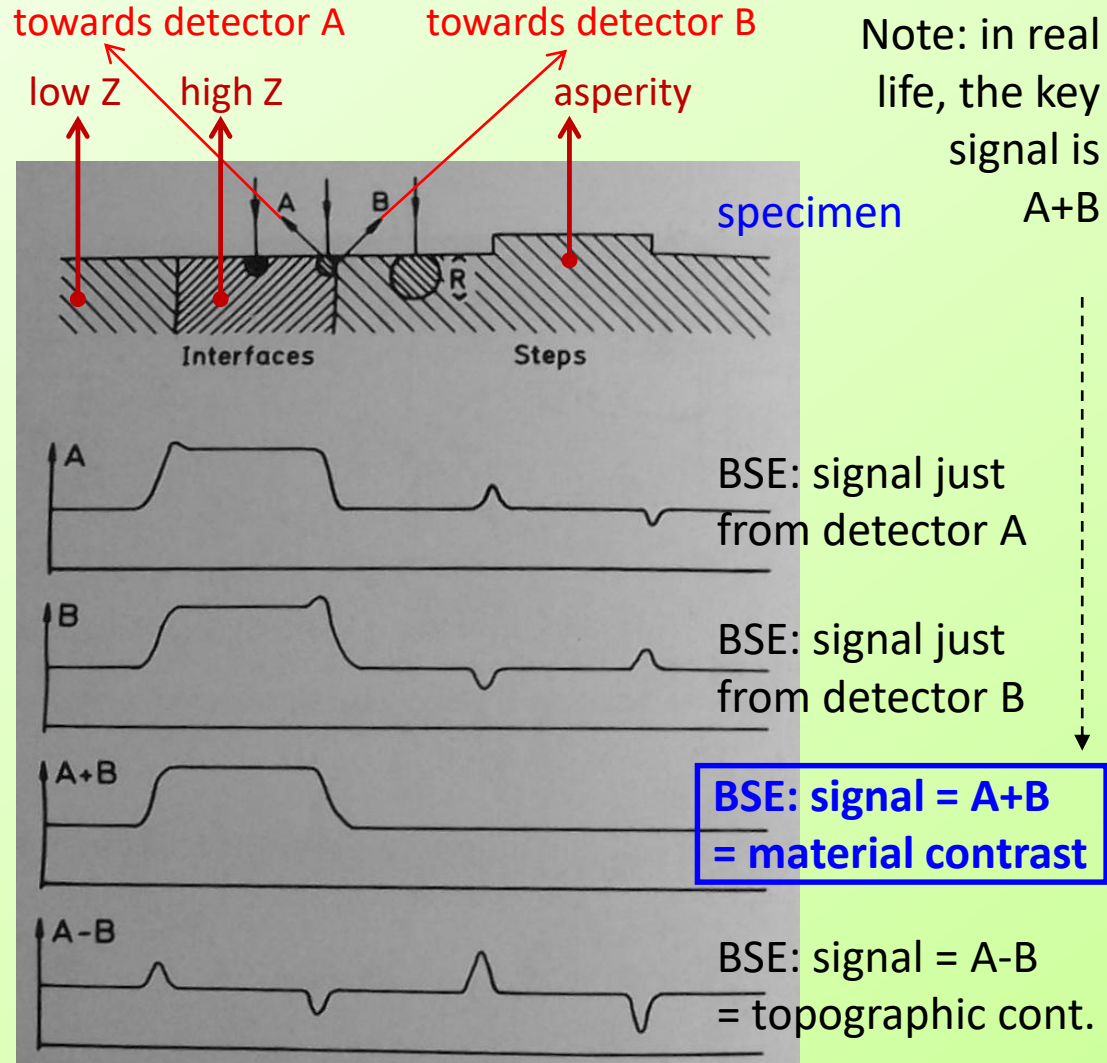
COMPOsition imaging in BSE = used almost exclusively = material contrast.

TOPOgraphic imaging in BSE = used rarely = topographic contrast (resolution < SE).

Typical arrangement of BSE detectors in the chamber of a SEM microscope.



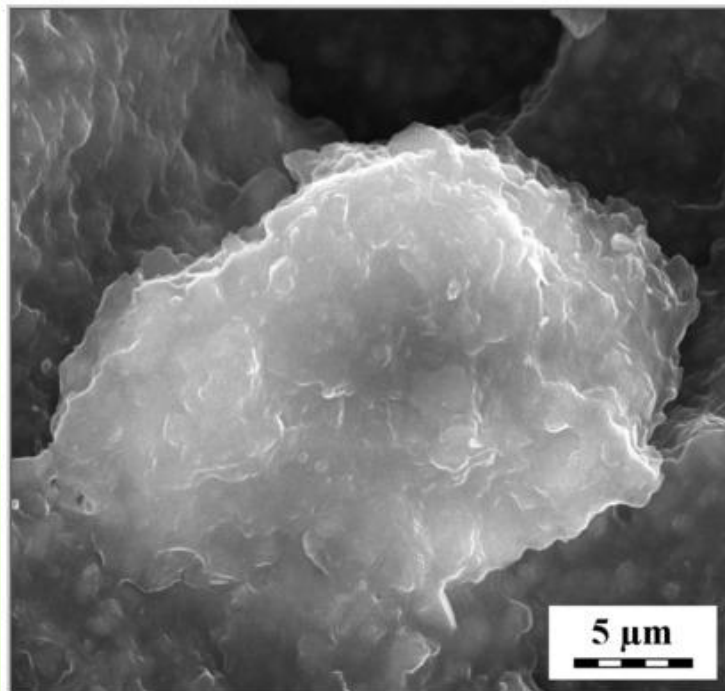
Geometry in the SEM chamber.



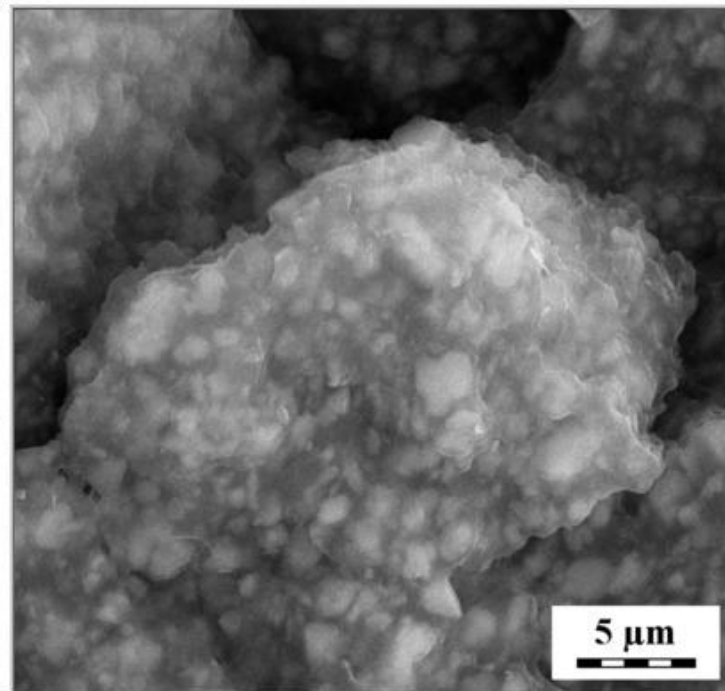
COMPO (A+B) and TOPO (A-B) signals in BSE.

SEM/BSE :: Interpretation of micrographs

(1) **Combination SE-BSE**: useful differentiation of topographic and material contrast.



(a) PE/AlOH SEM/SE



(b) PE/AlOH SEM/BSE

Technical note:
Why we see the particles below the surface?

- ❖ Electrons penetrate below the surface
- ❖ And we can estimate or simulate this:
⇒ **Section 3**

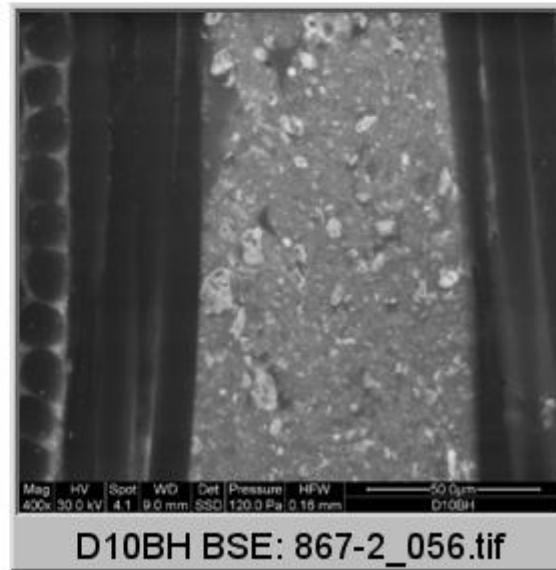
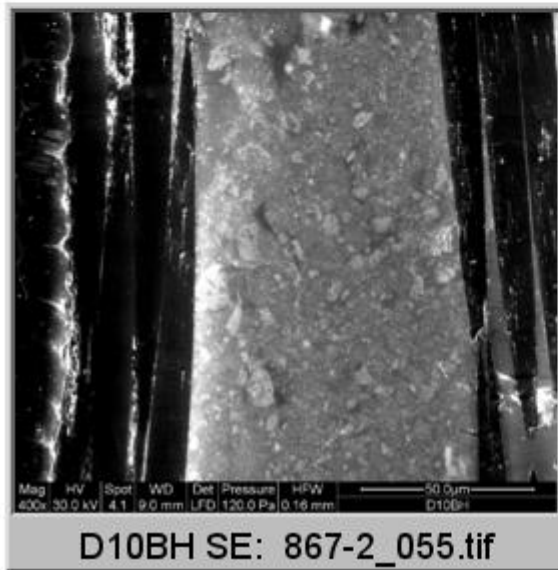
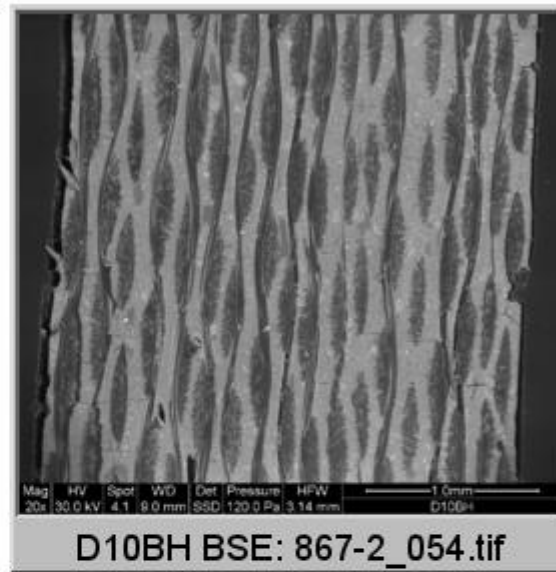
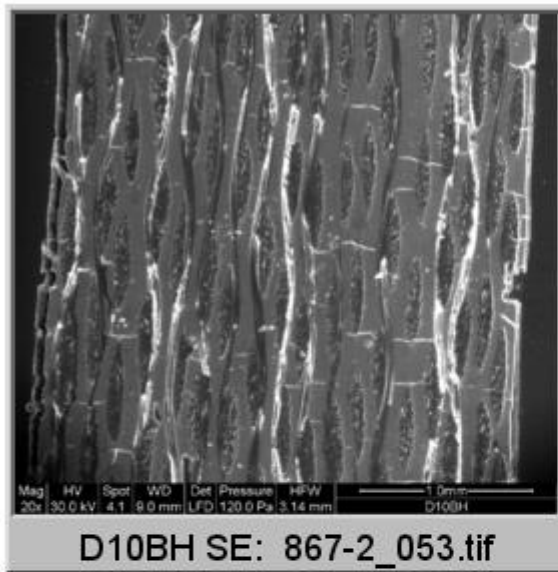
Sample: polyethylene (PE) filled with microparticles of ATH (aluminium trihydrate) fracture surface in liquid nitrogen, covered with thin carbon layer, imaging at 30kV.

SEM/SE: material contrast in SE is weak (2nd order effect), topographic contrast in SE strong: we see edges and fracture lines...

SEM/BSE: material contrast in BSE strong: we see the particles in the polymer matrix ← topographic contrast in BSE weak: but the surface is visible as well

SEM/BSE :: Interpretation of micrographs

(2) Smooth/flat composite specimens: material contrast dominates (BSE >> SE).



Sample: polysiloxane matrix reinforced with aramid fibers and filled with hydroxylapatite nanoparticles (HAP).

Sample preparation: cutting + smoothing → flat surface

Microscopy: low-vacuum mode (LVSEM) LVSEM/SE and LVSEM/BSE

Contrast:

LVSEM/BSE:

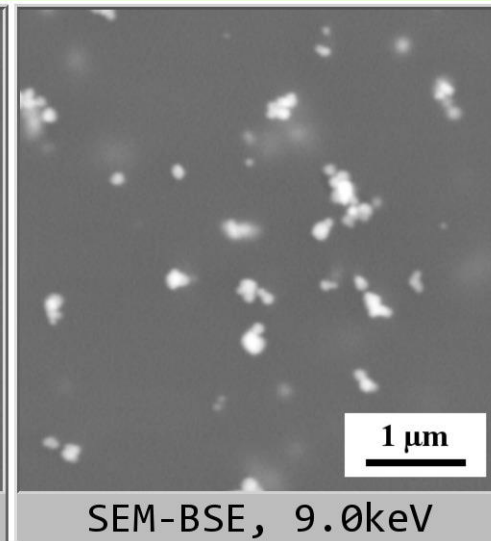
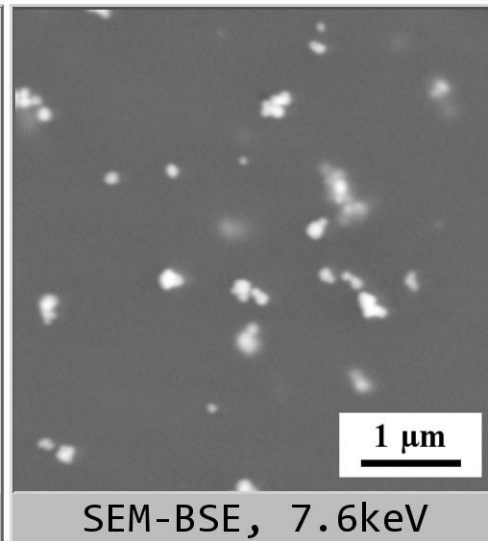
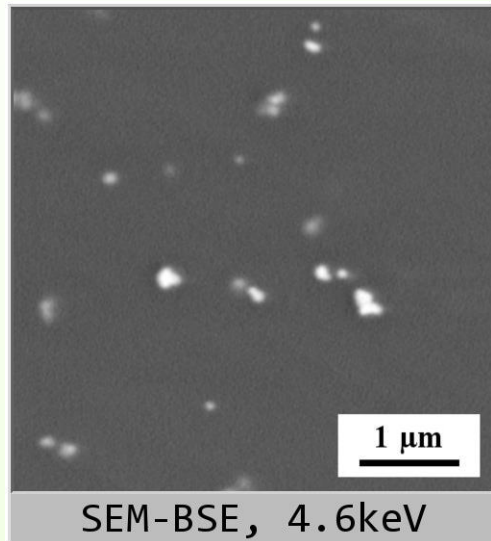
1. strong signal: HAP (Ca,P,O)
2. medium: polysiloxan (Si,O,C)
3. low: aramid (C,N,O).

LVSEM/SE:

1. topographic contrast: microfractures (smoothing artifact, invisible in BSE)
2. material contrast: very weak, as expected

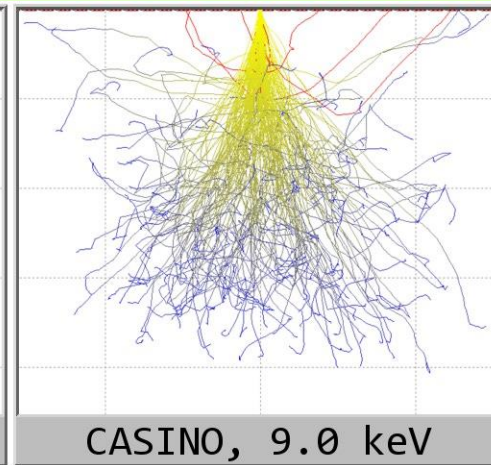
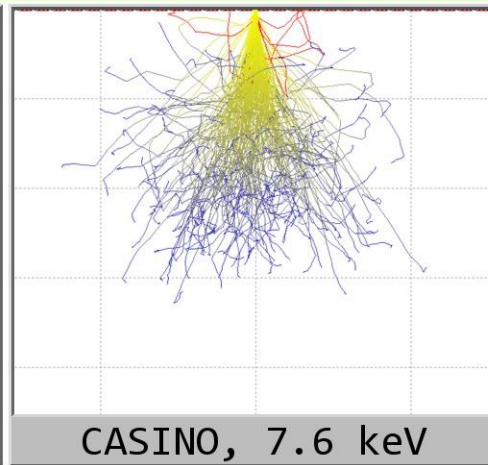
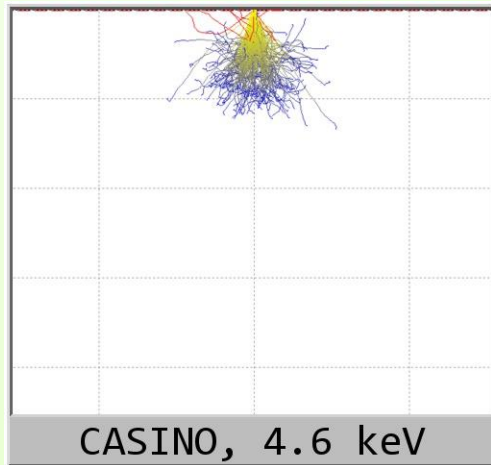
SEM/BSE :: Interpretation of micrographs

(3) BSE at multiple energies = special case = signal as a function of electron energy.



Specimen
PCL/TiO₂(2,5%)
smooth surface
from UMT

←
SEM/BSE
the same place,
only the e-beam
energy is varies



←
**Monte Carlo
simulation:
program CASINO**
penetration of e⁻
into PCL
(z-grid = 400nm
(z-size = 1800nm

Note: this ↑ is basis of MED = Multiple-Energy Deconvolution = a kind of 3D microscopy.
Series of micrographs with various energies of electrons can be combined into 3D-model.
The method has been developed in FEI company.

Part 5

SEM/EDX – interpretation of micrographs

Contents

- ❖ Rules for labeling of EDX transitions
- ❖ Qualitative analysis of EDX spectra + additional theory
- ❖ Quantitative analysis of EDX spectra + additional theory
- ❖ EDX mapping

Notes:

- EDX = Energy dispersive Analysis of X-rays
- EDS = Energy-Dispersive Spectroscopy = EDX
- Note - usage of SEM/EDX in Polymer Science is limited (light elements), but...
 - ⇒ 1st application area: polymer composites
 - ⇒ 2nd application area: analysis of unknown samples and/or impurities
 - ⇒ 3rd application area: reverse engineering ~ industrial espionage

SEM/EDX :: Rules for labelling of EDX transitions

Labeling of EDX transitions (Siegbahn notation) → each transition = one peak in EDX.

Rules for the labeling of the transitions:

(1) Transition **to** the orbital...

K (n=1) → K-transitions

L (n=2) → L-transitions

M (n=3) → M-transitions

*n = principal
quantum number
n=1,2,3... ~K,L,M...*

(2) Transitions **from** the orbital...

1st above ($\Delta n=1$) → α -transitions

2nd above ($\Delta n=2$) → β -transitions

3rd above ($\Delta n=3$) → γ -transitions

...also other transitions, less frequent

Rules for the energy of transitions :

Energy of electron orbital acc.to QM

(1-electron approximation):

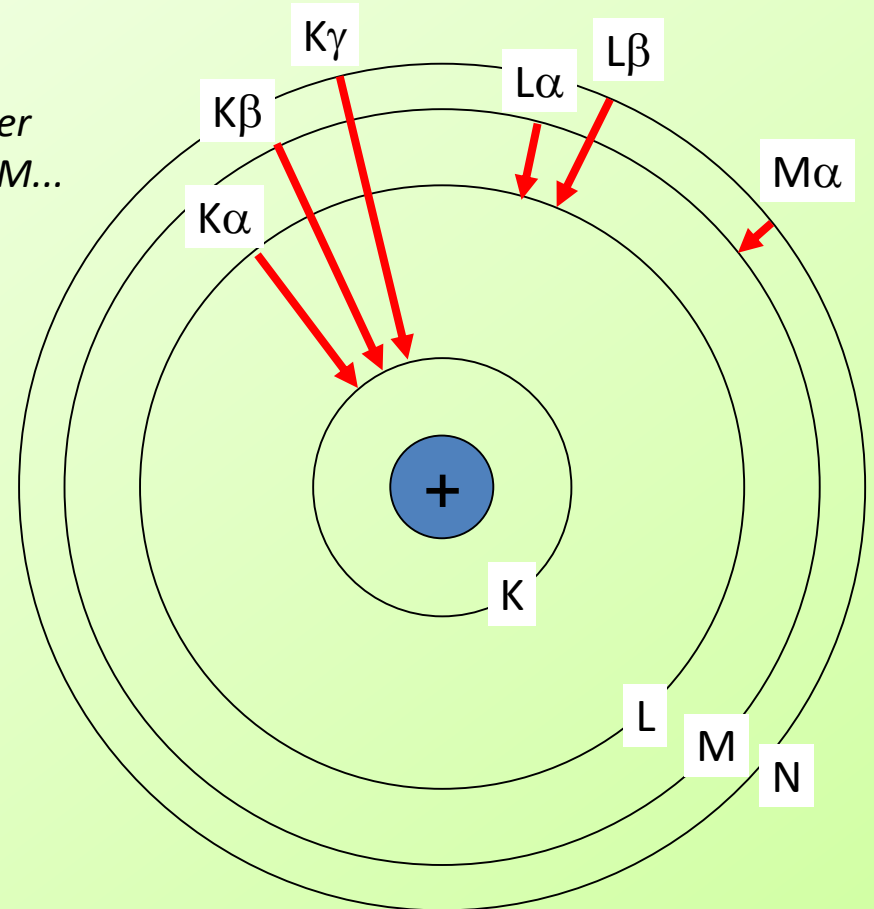
$$E(n) = - \text{constant} * Z^2 / n^2 \quad Z = \text{atomic number}$$

...which implies that:

(3) For all elements: E increases with Z

(4) For given element: $E(M) < E(L) < E(K)$

(5) For given transition: $E(\alpha) < E(\beta) < E(\gamma)$



(6) There are some additional rules/exceptions in the notation. Nevertheless, the most important and also the most intensive peaks in EDX spectra are: **Kα, Kβ, Lα, Lβ, Lγ, and Mα.**

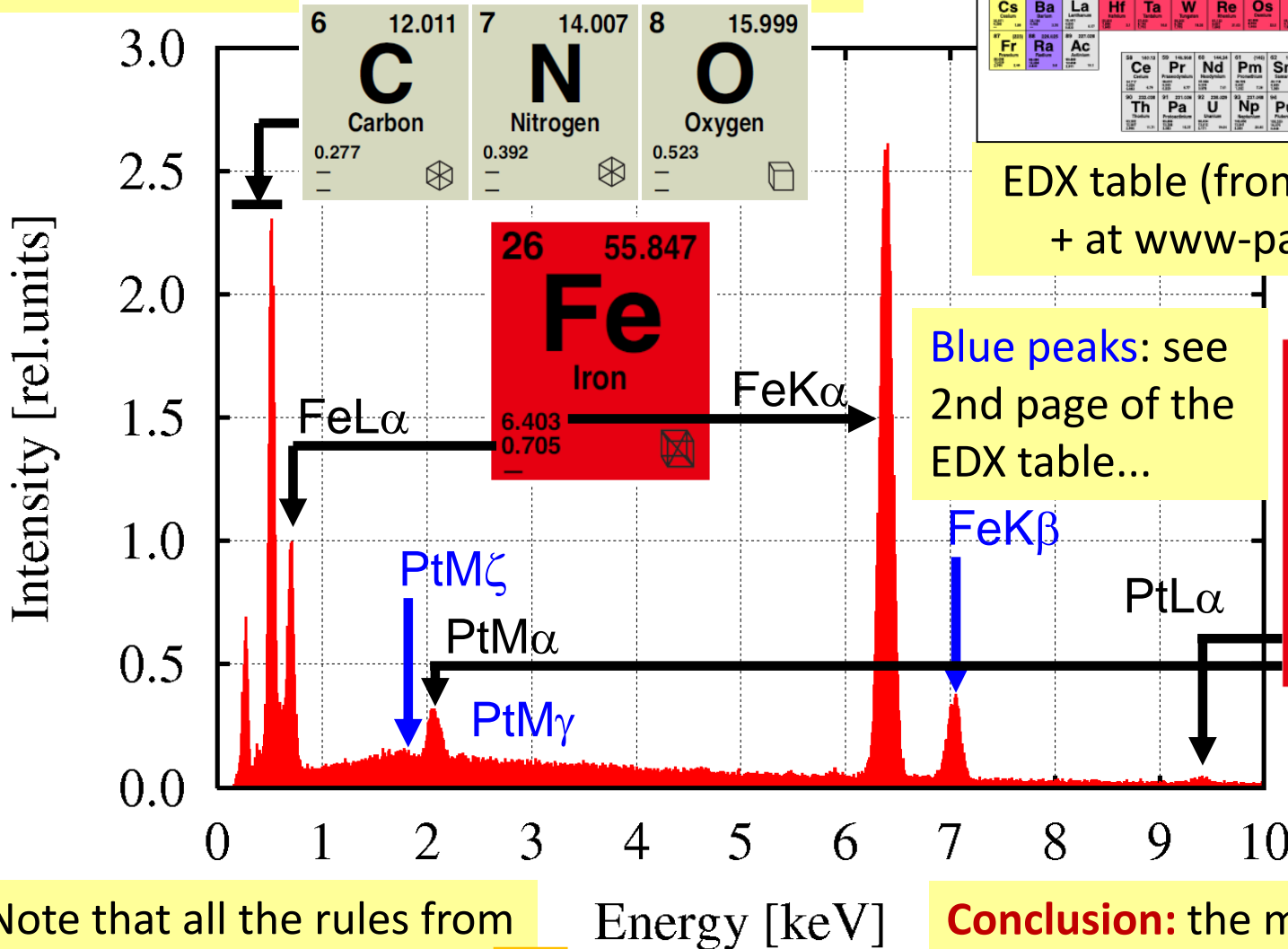
SEM/EDX :: Qualitative analysis (1)

Example: manual qualitative analysis.

Specimen: magnetic polymer microspheres.

Task: verify, if they contain iron oxide.

EDAX
Periodic Table of the Elements



EDX table (from www.edax.com) + at [www-pages of our course](#)

Blue peaks: see 2nd page of the EDX table...

78	195.08
Pt	Platinum
66.834	9.441
2.048	

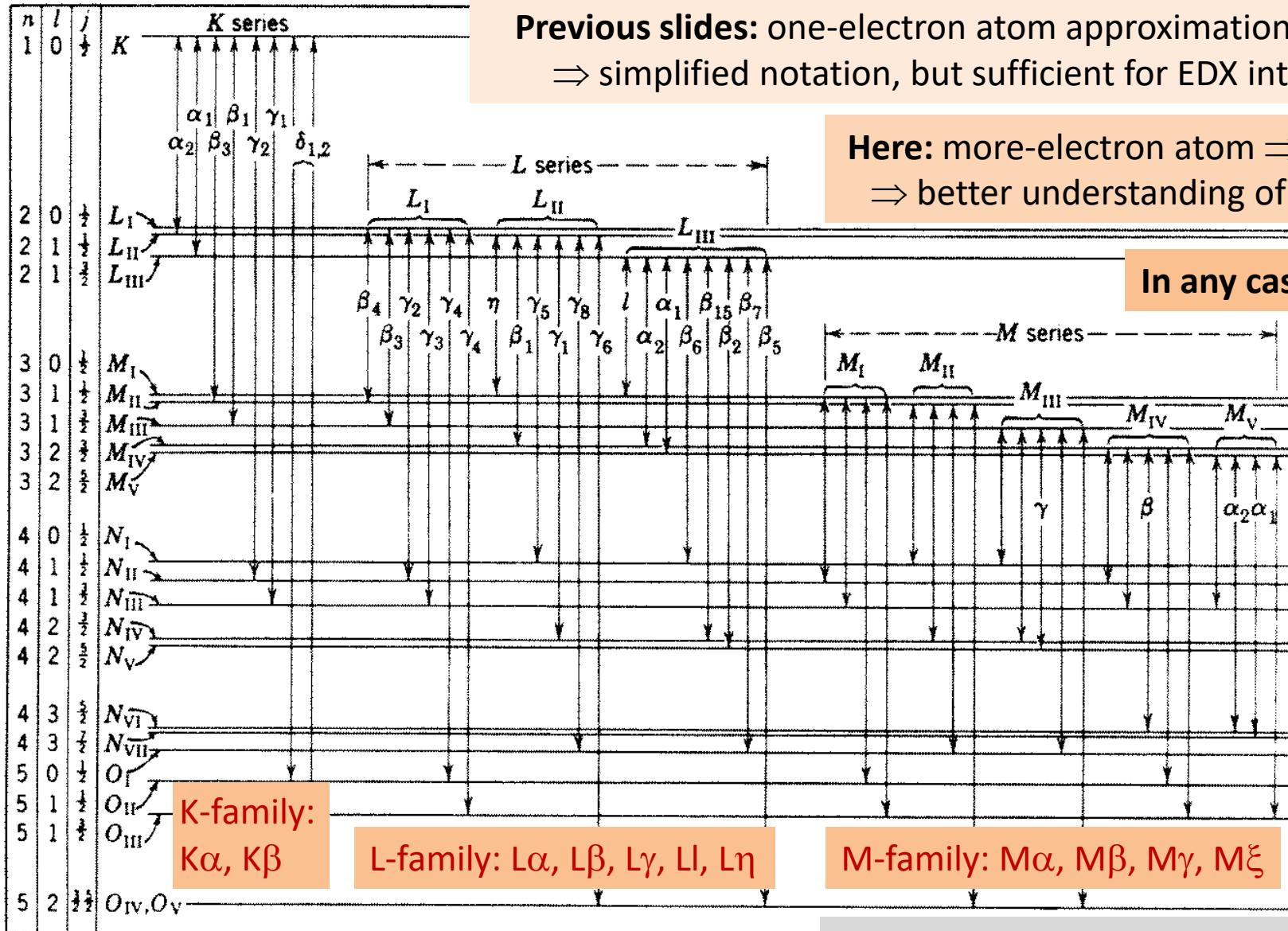
Note that all the rules from the previous page hold!

Conclusion: the microspheres contain iron oxide (peaks Fe,O).

SEM/EDX :: Qualitative analysis (2)

Additional theory: more precise notation of the EDX peaks.

Further info & resources:
<https://en.wikipedia.org/>



Previous slides: one-electron atom approximation $\Rightarrow E = E(n)$
 \Rightarrow simplified notation, but sufficient for EDX interpretation

Here: more-electron atom $\Rightarrow E = E(n, l, j)$
 \Rightarrow better understanding of EDX peaks

In any case, it holds:

splitting: $K(\alpha, \beta)$ $L(\alpha, \beta, \gamma, I)$ $M(\alpha, \beta, \gamma, \xi)$

the strongest peaks: $K\alpha, L\alpha, M\alpha$

K-family:
 $K\alpha, K\beta$

L-family: $L\alpha, L\beta, L\gamma, L_I, L_\eta$

M-family: $M\alpha, M\beta, M\gamma, M\xi$

Fig. 1.13. Some electron states and x-ray notation

SEM/EDX :: Qualitative analysis (3)

Additional theory: calculation of energies of EDX peaks/transitions.

Electron energy (one-electron atom approximation) is given by Eq. 1, where Z = atomic number, n = principal quantum number and $k = R_y = \text{Rydberg unit of energy} = 13.6 \text{ eV}$:

$$E = -k \frac{Z^2}{n^2} = -kZ^2 \frac{1}{n^2} \quad (1)$$

Ab initio calculation/verification of this formula in Jupyter/Python using quantum mechanics

Eq. 1 can be used for straightforward calculation of the energy difference between two orbitals ($n_2 > n_1$). This energy difference (Eq. 2) corresponds to a characteristic X-ray emitted from the atom, as follows from the *law of conservation of energy*.

$$\Delta E = E_2 - E_1 = -kZ^2 \left[\frac{1}{n_2^2} - \frac{1}{n_1^2} \right] = kZ^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad (2)$$

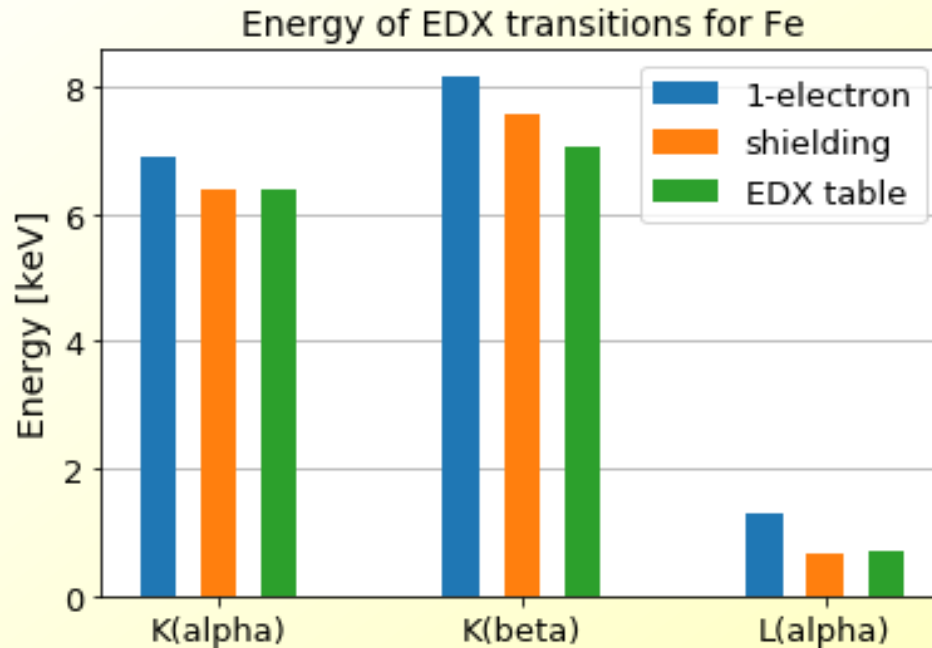
Eq. 2 can be further improved, if we replace the charge of the atom (Z) by an effective charge (Z_{ef}), which is calculated as $Z_{ef} = Z - \sigma$, where σ is the shielding/screening constant introduced by Henry Moseley (see wikipedia – Moseley's law).

$$\Delta E = E_2 - E_1 = kZ_{ef}^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] = k(Z - \sigma)^2 \left[\frac{1}{n_1^2} - \frac{1}{n_2^2} \right] \quad (3)$$

The constant σ represents the shielding of positive charge of nucleus due to electrons in inner shells. The σ values are 1 and 7.4 for K- and L-lines, respectively. The estimates of EDX energies with simple Eq. 2 and Eq. 3 are surprisingly precise – see next page.

SEM/EDX :: Qualitative analysis (4)

Additional theory: comparison of calculated and tabulated energies of EDX peaks.



The output from the calculation in Jupyter/Python.

Note that the calculated values of EDX-peak energies are quite close to the tabulated ones.

This implies that one-electron approximation is quite acceptable in the case EDX.

Calculated (blue, red) and tabulated (green) energies of $\text{FeK}\alpha$, $\text{FeK}\beta$ and $\text{FeL}\alpha$ transitions. The blue and red values are based on the Eq. 2 and 3 from the previous page, respectively.

Complete calculation in Jupyter/Python

HW #3

- 1) Download EDX table from www-pages of our course (or from www.edax.com).
- 2) Calculate energy of transitions $\text{FeK}\alpha$, $\text{FeK}\beta$ and $\text{FeL}\alpha$ and compare with table.
- 3) Output of HW: list or table of values (graph in Jupyter → extra points).

Suppl. #4a :: Extended rules for EDX interpretation

Additional rules that can help during manual interpretation of EDX spectra.

R1: Basic rules directly from the basic relationship $E = -k \cdot Z^2/n^2$:

- For the same transition in different elements: energy increases with Z^2 .
- For transitions within given element: $E(K) > E(L) > E(M)$
- For given transition: $E(\alpha) < E(\beta) < E(\gamma)$

R2: Energy of PE has to be 3× higher than the energy of the last observed transition.

- Logical – to observe the peak: $E(PE) > E(\text{peak})$
- To use the peak for quantitative analysis: $E(PE) > 3 \times E(\text{peak})$

R3: For given element, we have to observe ALL possible transitions.

- Logical: PE → K-vacancy → K-peak → L-vacancy → L-peak → M-vacancy → M-peak
- Note: most detectors 0.15keV – 15...20keV → here we should see all peaks of an element

R4: The main peaks (K,L,M) can be split (this results from QM; intensity ratios are \approx constant):

K family: $K\alpha$ (1) : $K\beta$ (0.1)

L family: $L\alpha$ (1) : $L\beta_1$ (0.7) : $L\beta_2$ (0.2) : $L\beta_3$ (0.08) : $L\beta_4$ (0.05) : $L\gamma_1$ (0.08) : $L\gamma_3$ (0.03) : $L\delta$ (0.04)

M family: $M\alpha$ (1) : $M\beta$ (0.6) : $M\gamma$ (0.05) : $M\xi$ (0.06)

R5: Not all peaks within the family can be resolved for all elements.

- Energy resolution of common EDX detectors $\approx 130\text{eV} \approx 0.13\text{keV}$
- Energy difference between two peaks $> 0.13\text{keV} \Rightarrow$ they can be observed separately:

$K\alpha$ and $K\beta$ separated from $Z \sim 16, 17... \Rightarrow$ S, Cl... $\Rightarrow E(K) > 2.0 \text{ keV}$

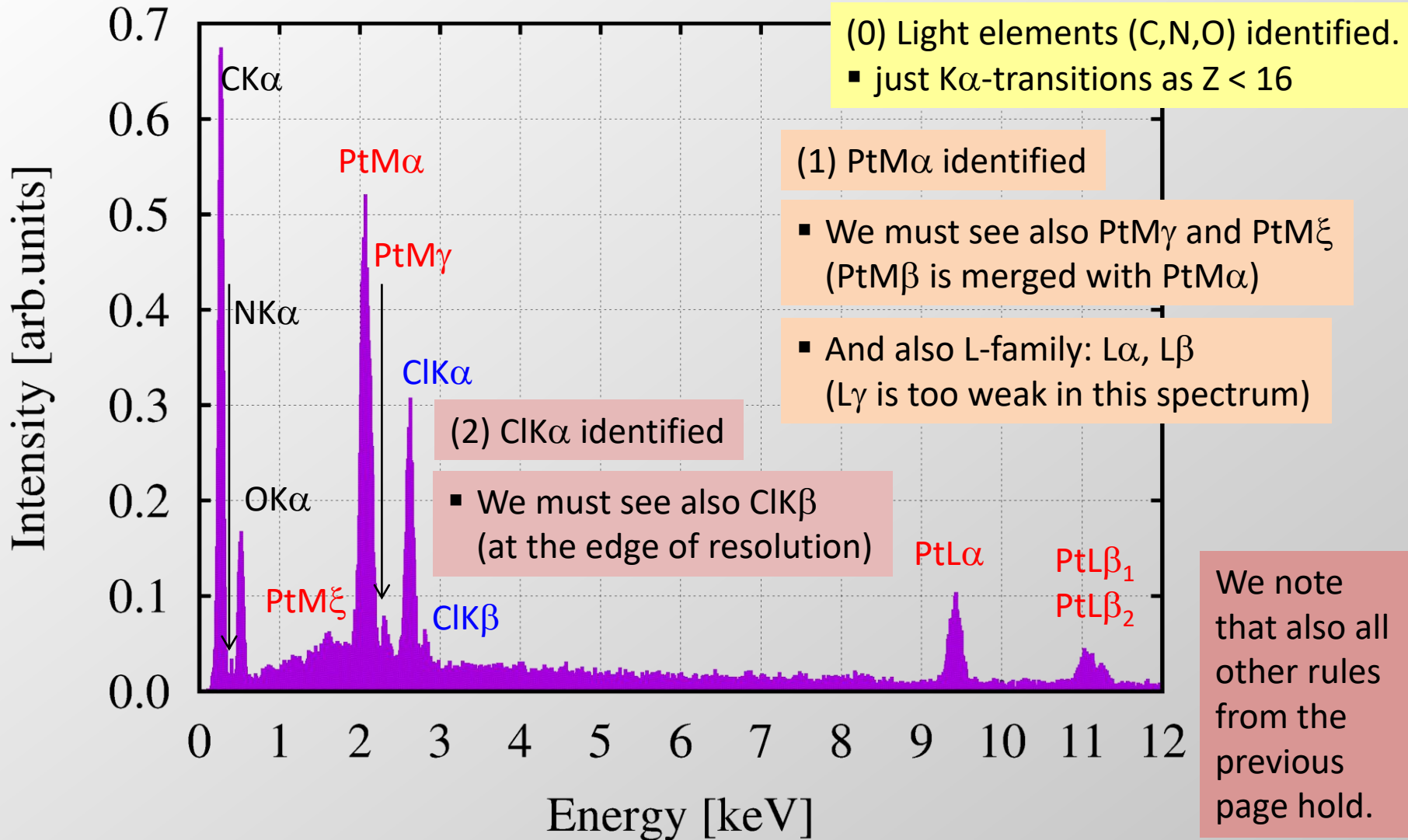
$L\alpha$ - $L\beta$ - $L\gamma$ separated from $Z \sim 45, 46... \Rightarrow$ Rh, Pd... $\Rightarrow E(L) > 2.5 \text{ keV}$

$M\alpha, \beta$ and $M\gamma$ separated from $Z \sim 57, 58... \Rightarrow$ La, Ce... $\Rightarrow E(M) > 0.8 \text{ keV}$

See EDAX
tables for
details.

Suppl. #4b :: Extended rules for EDX interpretation

Sample spectrum illustrating the rules R1-R5 from previous page.



Sample description:

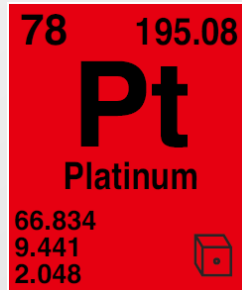
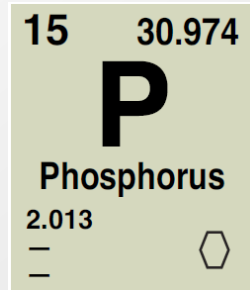
MWCNT (multi-wall carbon nanotubes) covered with a film of PANI (polyaniline).

Problem: is **platinum** (deposited as $K_2[PtCl_6]$ solution) reduced on the surface of MWCNT?

Suppl. #4c :: Extended rules for EDX interpretation

Pitfalls: overlaps, zero peaks, sum peaks, escape peaks...

- ❖ **Overlaps:**
explanation is quite simple
→ see EDX table
→ $PK\alpha \approx PtM\alpha$



- Other possible overlaps:**
TiK β VK α
MnK β FeK α
SK α MoL α Pb M α
....

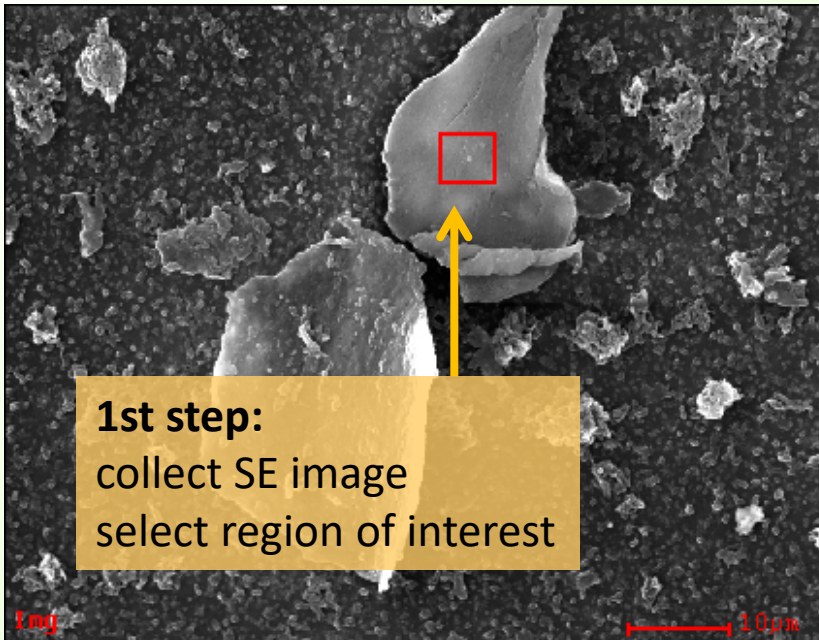
Reminder:
EDX
resolution
 $\approx 0.13\text{keV}$

Solution: none; use another method or reconcile yourself with lower precision...

- ❖ **Zero peak = Stroke peak:** it may occur due to low SNR, in spectrum at $E \rightarrow 0\text{keV}$.
Solution: increase signal if possible, remove by means of SW and if these fails \Rightarrow ignore it.
Note: Intensive stroke peak indicates high noise \Rightarrow increase signal (beam current, spot size).
- ❖ **Sum peaks:** detector calculates two X-rays as one.
Example: Sulphur ($SK\alpha = 2.31\text{ keV}$) can exhibit sum peak at $2 * 2.31 = 4.62\text{ keV}$.
Solution: change data collection conditions or instruct SW to ignore the sum peaks.
Note: Summing is more common at high count rates and fast processing times where the spectrum is dominated by a single peak. When a spectrum is dominated by two nearly equal peaks it is possible to create a sum peak that is the energy of peak A and peak B.
- ❖ **Escape peaks:** energy of X-ray is decreased by the energy of Si (from the detector).
Example: Iron ($FeK\alpha = 6.40\text{ keV}$) can exhibit escape peak at $6.40 - 1.74(\text{SiK}\alpha) = 4.66\text{ keV}$.
Solution: change data collection conditions and/or instruct SW to ignore the sum peaks.
Note: Escape peaks are always just a small percentage of the parent peak..

SEM/EDX :: Quantitative analysis (1).

Quantitative analysis: ONLY with a computer – too complex for manual analysis.



1st step:
collect SE image
select region of interest

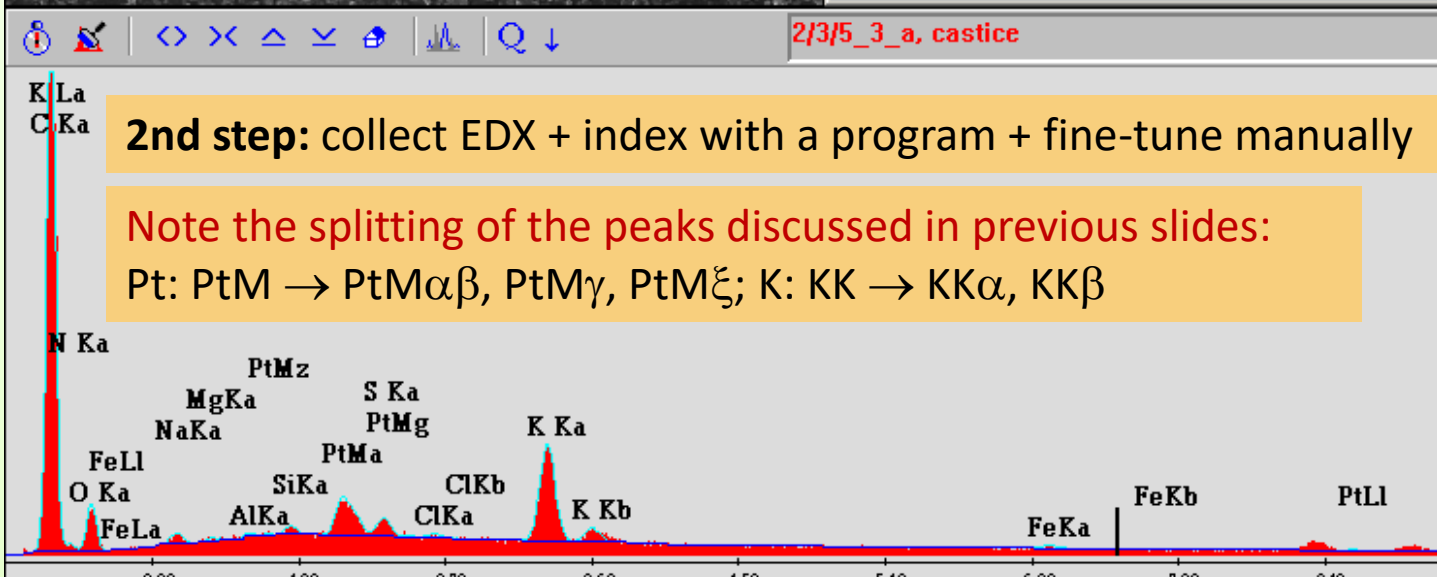
Standardless Quantitative Data

Element	Wt%	At%
C K	75.72	83.26
N K	5.84	5.51
O K	11.43	9.44
NaK	0.55	0.31
MgK	0.11	0.06
AlK	0.08	0.04
SiK	0.19	0.09
S K	0.37	0.15
ClK	0	0
K K	2.81	0.88
FeK	0	0
PtL	2	0

3rd step:
quantify elements
using standardless
ZAF method

Sample:
UHMWPE wear
particles on PC filter;
analysis of impu-
rities from isolation.

Problem:
Step-by-step
optimization of
isolation protocols
so that the final
sample was pure =
showing only C and
O peaks.



Source:
our own project:
*Monitoring and
minimization of
UHMWPE wear.*

SEM/EDX :: Theory :: Quantitative analysis (2).

Quantitative analysis: Why it is so difficult = why do we need a computer program?

Intensities of EDX peaks are proportional to:

- ❖ concentration of the element (not known in advance)
- ❖ relative intensity of given transition for given elements (known, tabulated)

Moreover, the intensities have to be corrected for phenomena that appear in the sample/matrix through which the PE and X-ray travel \Rightarrow we need **matrix corrections:**

- ❖ **Z-correction = atomic number effect** – includes two sub-effects:
 - ❖ backscatter power: electron backscattered prior to ionization & X-ray production
 - ❖ stopping power: electron loses all energy due to inelastic collisions
- ❖ **A-correction = absorption effect** – usually the biggest correction factor
 - ❖ X-ray is absorbed when traveling through the sample
 - probability of absorption depends on: the X-ray energy + atoms in the matrix
 - probability of absorption increases if $E(\text{X-ray}) \approx E(\text{atom-orbital}) \rightarrow$ absorption edges
- ❖ **F = fluorescence effect** – usually the least important of the three factors:
 - ❖ X-ray generates secondary X-ray when traveling through the sample
 - principle: electron \rightarrow (primary) X-ray \rightarrow absorption \rightarrow absorbing atom in excited state relaxes and emits secondary X-ray = secondary fluorescence (lower energy X-ray)

Conclusion:

- ❖ height of an EDX-peak is **NOT** proportional to the element concentration in simple way
- ❖ numerous complex corrections required to quantify elements \Rightarrow task for a computer

SEM/EDX :: Theory :: Quantitative analysis (3).

Quantitative analysis with/without standards – accuracy of standardless analyses.

Two basic types of EDX quantitative analysis:

1. **Standard-based**: precise (used in industry) BUT standards rarely available (in research)
2. **Standardless**: less precise (see below), rather **semi-quantitative** BUT fast and efficient

* **Note: samples for standard-based EDX must be: flat, smooth & homogeneous** ⇒ rare case

Two basic methods/algorithms for SEM/EDX matrix corrections :

1. **ZAF**: traditional, all corrections (Z,A,F) calculated from fundamental equations
2. **Phi-Rho-Z**: semiempirical; ZA corrections from $\varphi\rho$ -z curves, F from fundamental equations

* **Note: the results from the two methods are frequently the same within standard deviations**

How accurate is the standardless EDX analysis?

- ❖ Precision depends on sample... 😊
- ❖ For light elements the accuracy decreases.
- ❖ There are many treatments on the subject, but they usually deal with model samples (flat, smooth, homogeneous).
- ❖ Let us take a real sample with a known composition - microcrystalline powder:
 - Sample: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ microcrystals
 - Microscope: Quanta 200 FEG
 - Matrix correction: standardless ZAF

EDX	Cu %	S %	O %	Cu:S	Error
Exp. #1	20.5	16.1	63.4	1.27	27%
Exp. #2	10.3	11.5	78.2	0.90	-10%
Theory	9.1	9.1	81.8	1.00	0%

* Theory = stoichiometry.

Standardless EDX is semi-quantitative!



$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, bluestone, copper sulfate pentahydrate
ratio Cu:S (atom %)
exactly 1:1 = 1

Suppl. #4 :: SEM/EDX standardless analysis of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

EDAX ZAF Quantification (Standardless)
 Element Normalized
 SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
O K	35.76	63.36	0.0992	1.0763	0.2574	1.0012
S K	18.22	16.11	0.1029	1.0312	0.5478	1.0000
CuK	46.02	20.53	0.4215	0.9102	1.0062	1.0000
Total	100.00	100.00				

Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
O K	215.83	1.92	0.69	112.33
S K	435.61	14.50	0.49	30.05
CuK	585.50	10.07	0.42	58.17

Output from our EDX software showing more detail concerning the results in the previous slide = **standardless EDX analysis of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.**

Note #1: the results seem to be precise (high Peak-to-Background ratio), but they suffer from limited accuracy (incorrect Cu:S ratio).

EDAX ZAF Quantification (Standardless)
 Element Normalized
 SEC Table : Default

Element	Wt %	At %	K-Ratio	Z	A	F
O K	54.96	78.18	0.1787	1.0474	0.3102	1.0007
S K	16.18	11.49	0.1022	1.0040	0.6289	1.0000
CuK	28.85	10.33	0.2584	0.8830	1.0142	1.0000
Total	100.00	100.00				

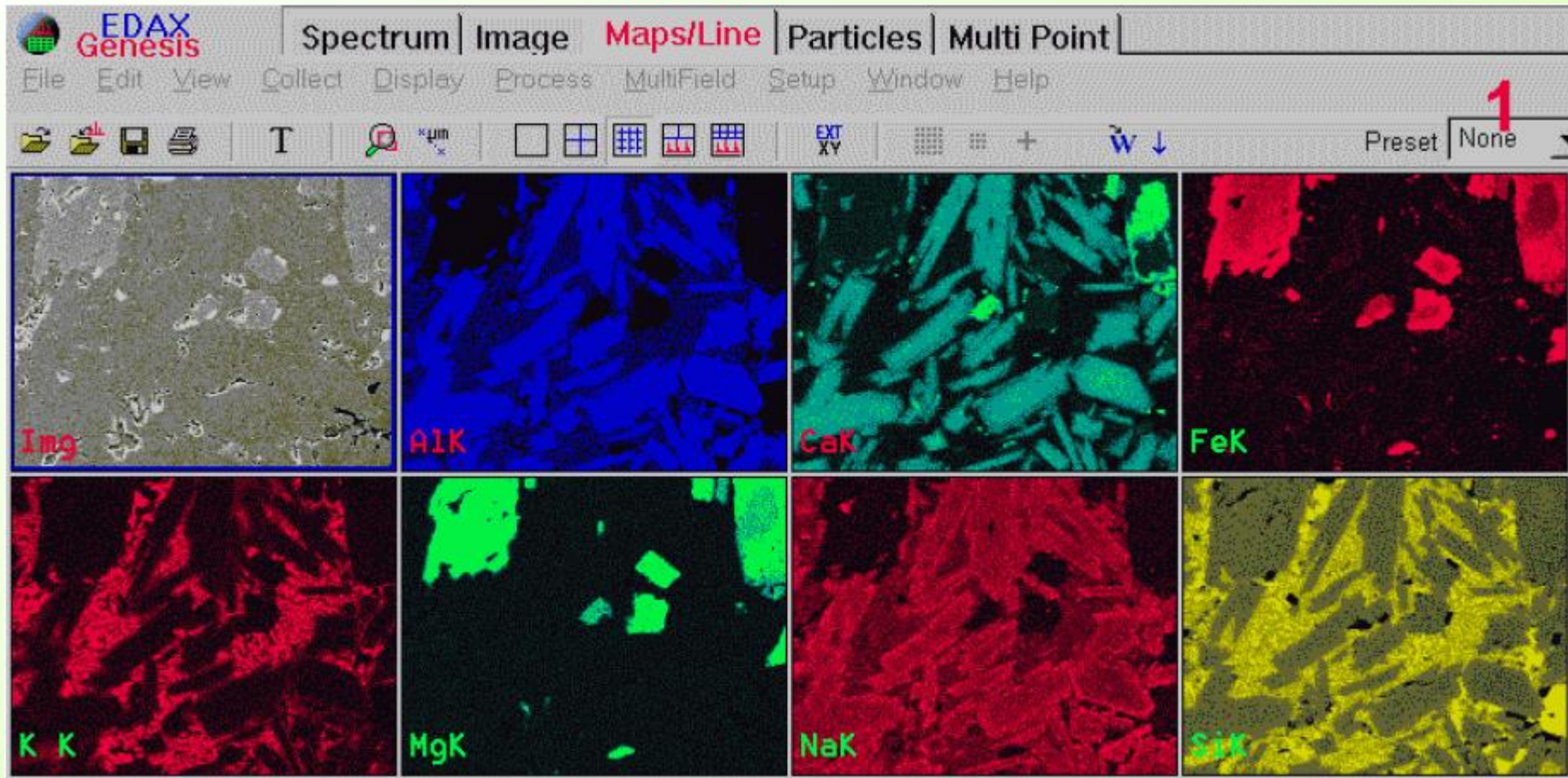
Element	Net Inte.	Bkgd Inte.	Inte. Error	P/B
O K	418.44	1.97	0.48	212.68
S K	465.05	17.84	0.47	26.07
CuK	385.77	10.71	0.51	36.03

Note #2: the results vary from place to place within single specimen. This is probably due to the fact the micropowder is not smooth.

Note #3: the accuracy for the light element (O) is even lower (should be 9× Cu,S).

SEM/EDX :: EDX mapping

EDX mapping: visualization of elemental composition in a sample.



- ❖ **Sample:** inorganic coposite
- ❖ **Source:** EDX manual from our microscope Quanta 200 FEG
- ❖ **Note:** EDX maps are elegant, but their use in the field of polymers is rather exceptional.
⇒ each point = spectrum → very long data collection → polymers damaged by e-beam

Part 6

SEM/TE = STEM – interpretation of micrographs

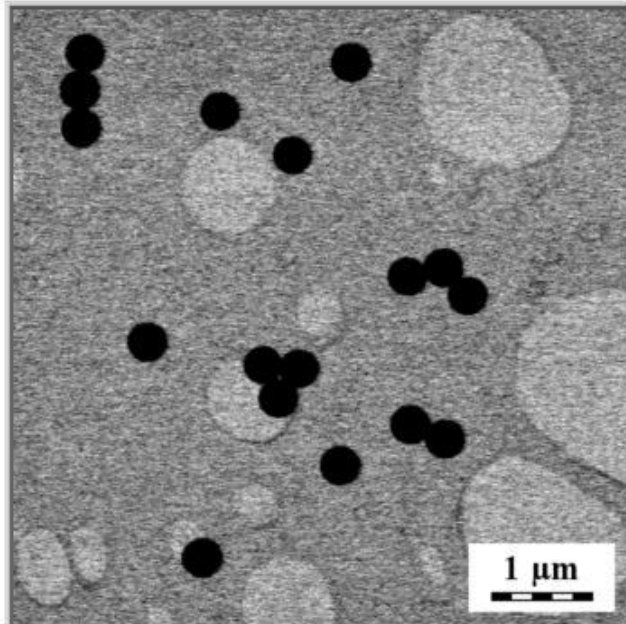
- ❖ STEM - origin of contrast micrographs
- ❖ STEM – typical applications

Notes:

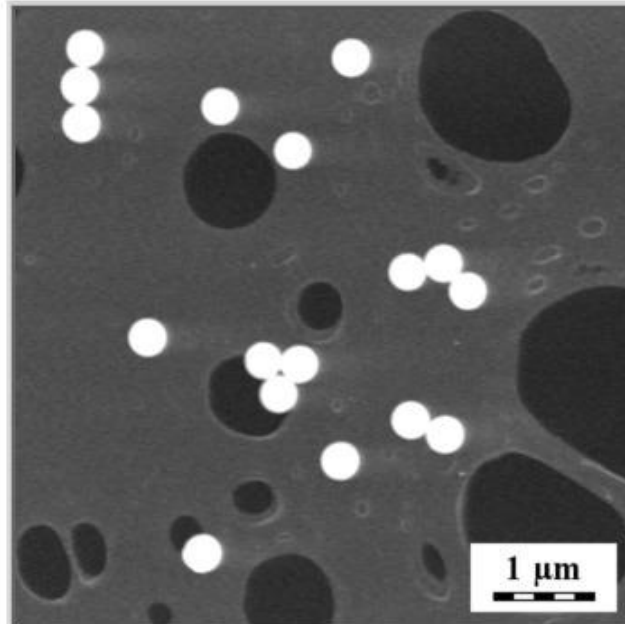
- TE = Transmitted Electrons
SEM/TE imaging = STEM = Scanning Transmission EM
Two sub-modes of STEM: bright-field (BF) and dark-field (DF) see next slides
- Usage of SEM/TE in various fields:
Polymer Science – not so frequent, but useful method (blends)
Biology – rarely used, biologists prefer TEM (higher magnifications)
Inorganics, metals – rarely used, TEM with diffraction mode is preferred

STEM :: Origin of contrast :: Bright Field × Dark Field

Comparison of modes of STEM = SEM/TE → imaging by STEM/BF and STEM/DF.



(a) PS-mspheres : STEM/BF



(b) PS-mspheres : STEM/DF

STEM micrographs of polystyrene particles on holey carbon film.

STEM/BF: detector below the sample

electrons going through detected ⇒ bright background ⇒ BF

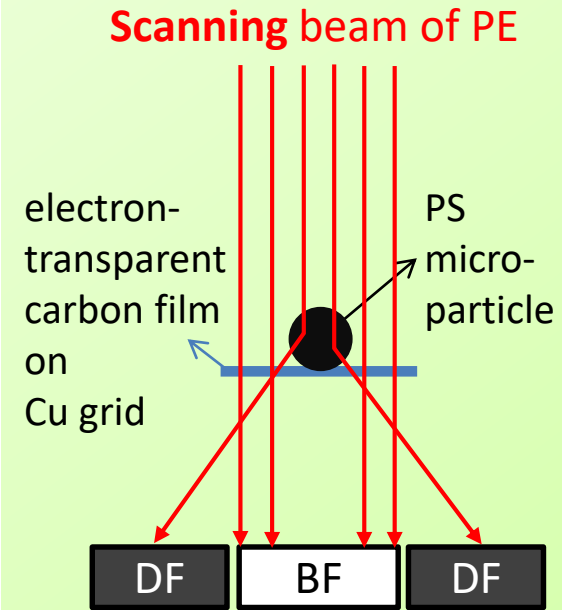
electrons scattered by particles not detected ⇒ dark spots

STEM/DF: detector out of the area scanned by the beam of PE

electrons going through not detected ⇒ dark background ⇒ DF

electrons scattered/absorbed by particles detected ⇒ bright spots

STEM/ED does not exist ⇒ scanning beam ⇒ no (classical) interference ⇒ no (classical) diffraction



Detector for BF

(just below the sample)

and detector for DF

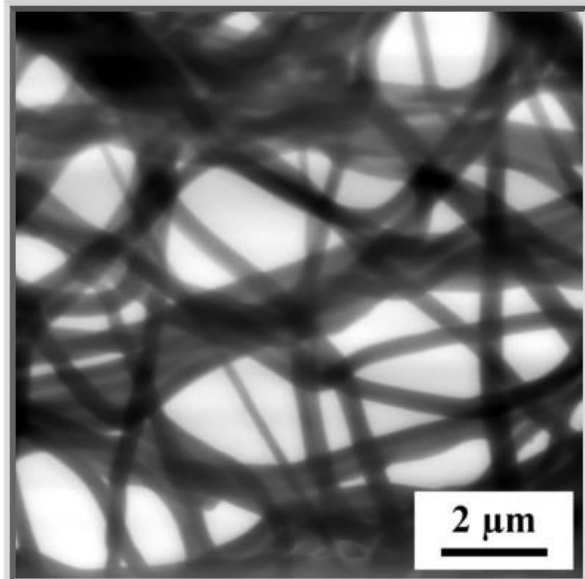
(out of area scanned by PE)

* Note: DF usually exhibits lower signal, but higher contrast than BF.

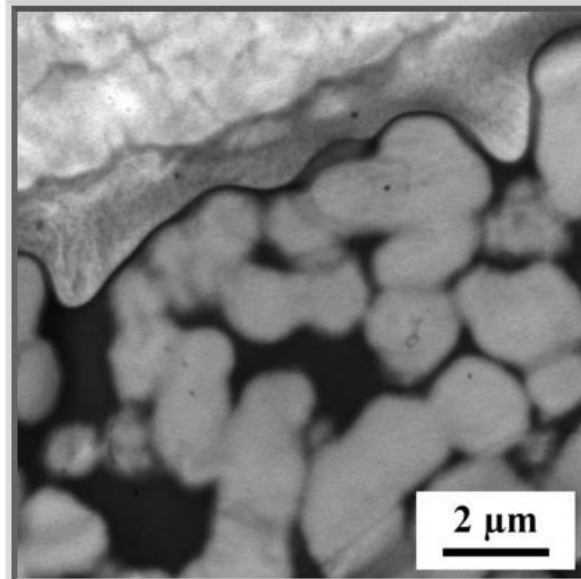
STEM/BF :: typical applications for polymer systems

Main type of contrast in STEM/BF = mass-thickness contrast:

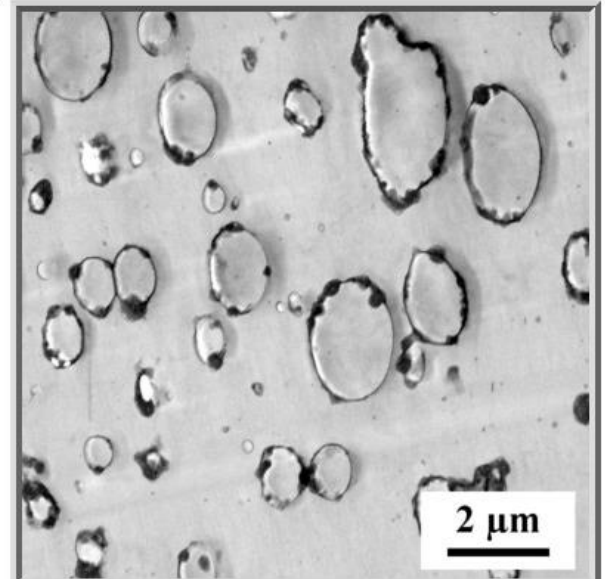
Parts of samples with higher electron density (elements with higher Z) or higher thickness absorb/scatter more electrons \Rightarrow these parts of sample appear dark in STEM/BF micrographs



(a) PS fibres



(b) PE/PE copolymer



(c) PS/PE/SBS blend

STEM/BF micrographs of various polymer systems:

(a) overall morphology of polymer microstructures – polystyrene nanofibers

preparation: 2μL of the nanofiber suspension onto Cu-grid with C-film, left to evaporate

(b) subsurface morphology of bulk polymers – surface of PP/PE copolymer particle

preparation: particle embedded in epoxy resin, RuO_4 -staining of PE, thin sections by cryo-ultramicrotomy

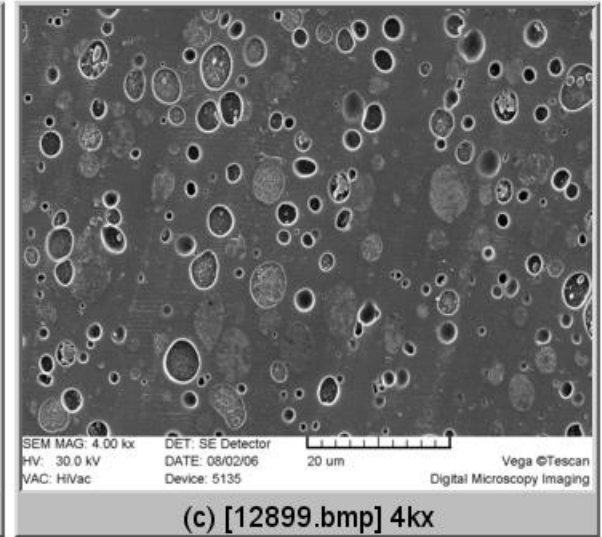
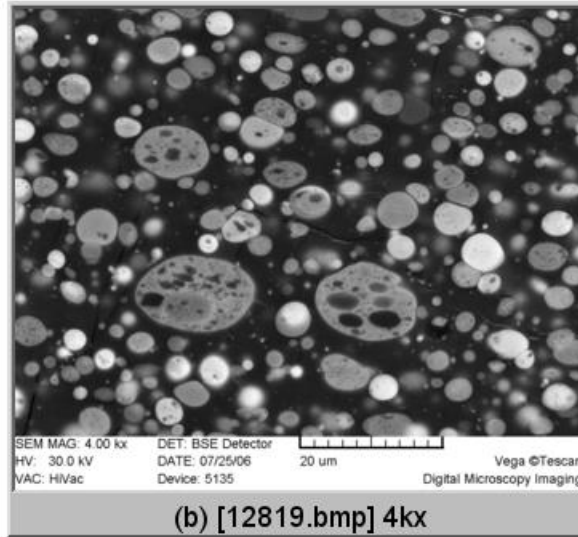
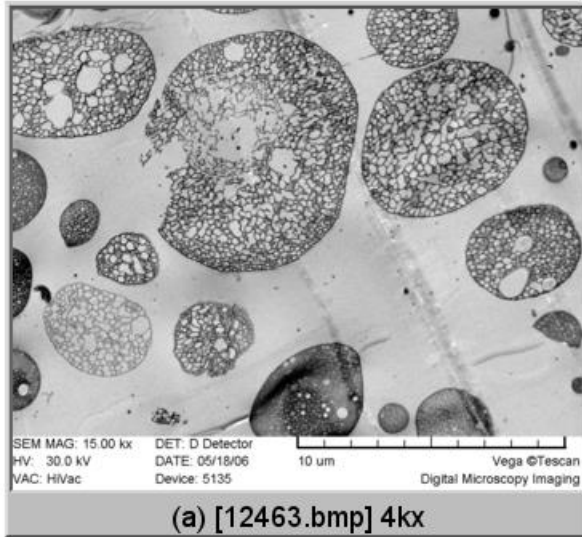
(c) internal morphology of bulk polymers – localization of SBS compatibilizer in PS/PE(80/20)

preparation: OsO_4 -staining of SBS, thin sections by ultramicrotomy at room temperature

Note: another typical example of STEM/BF – see the first example in this lecture.

STEM/BF :: Polymer blends :: OsO₄ staining

- OsO₄ staining is a typical method for visualization of morphology in polymer blends.
- It can be used when our systems contains a component with double bonds.
- Osmium is bonded selectively in these regions.



HIPS/E514

STEM/BF: OsO₄ selectively bonded to rubber particles containing PB

Absorption and diffraction: ⇒ rubber particles dark

HIPS/E514

SEM/BSE: OsO₄ selectively bonded to rubber particles containing PB

Material contrast ⇒ rubber particles bright

HIPS/E514

SEM/SE: LN₂ smoothed surface + permanganic etching

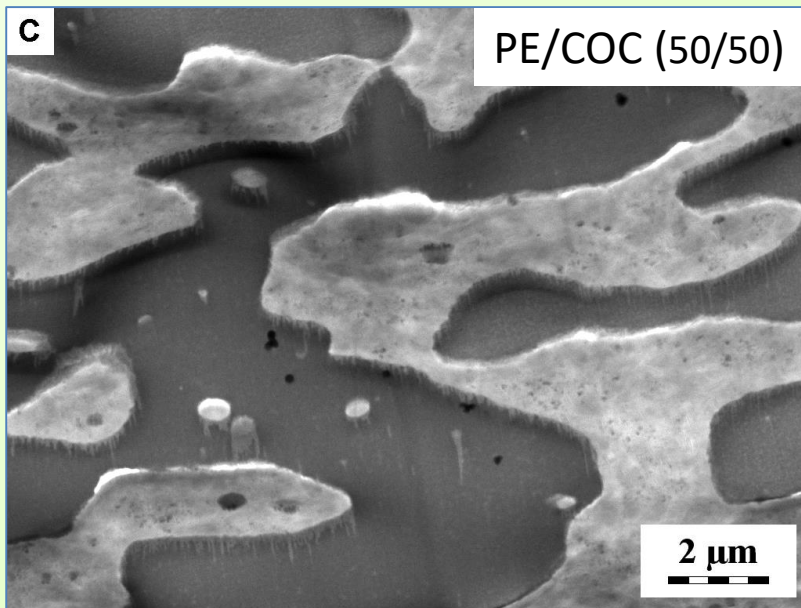
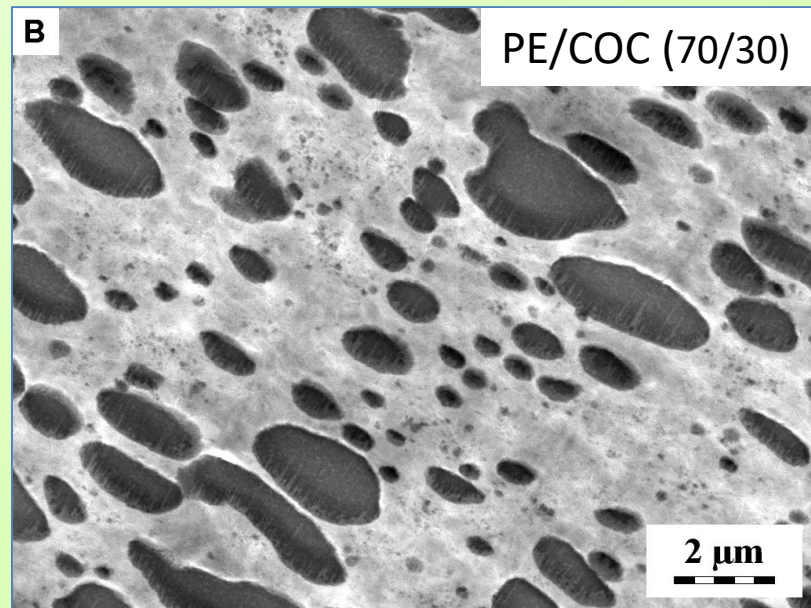
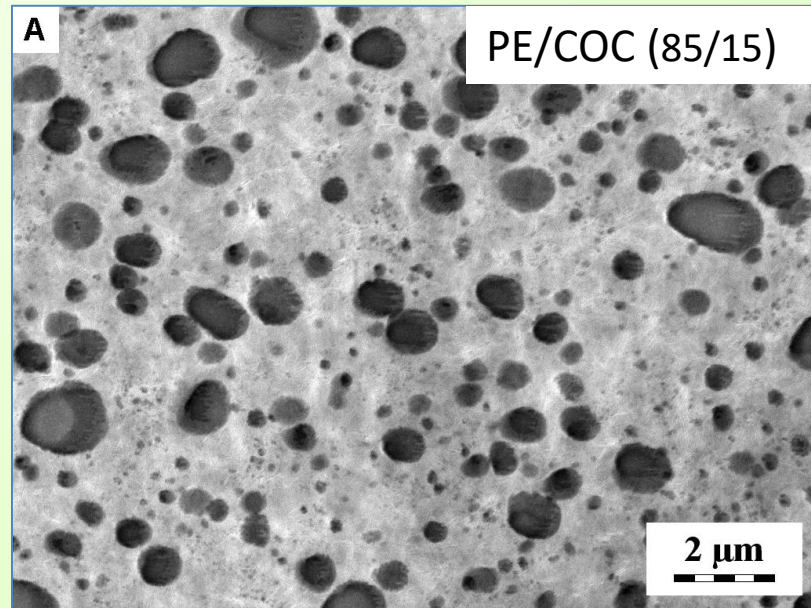
Topographic contrast ⇒ edge effect

Note #1: the most common sample preparation – fracturing in LN₂ – no useful results.

Note #2: more about polymer-specific sample preparation – end of this lecture.

STEM/BF :: Polymer blends :: RuO₄ staining

- RuO₄ staining is a sister method to OsO₄ staining – less predictable, but more universal.
- It can be applied to any polymer system, but we can only estimate the result...
- Ru is more reactive and attacks all components –with different speed.
- Here: STEM + RuO₄-staining of PE/COC blends.

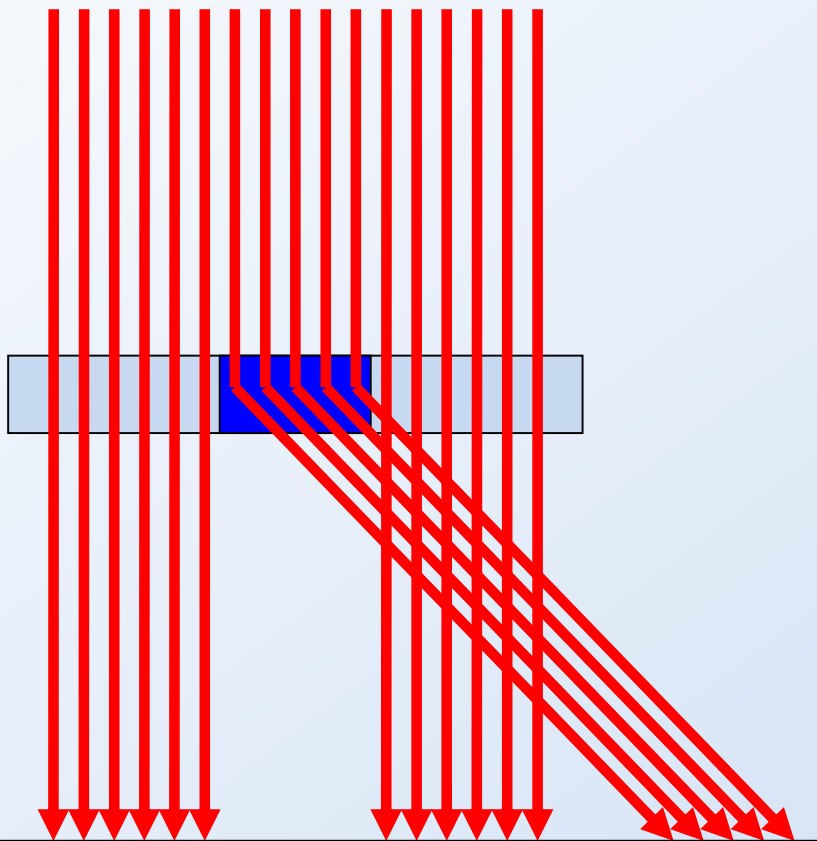


Note: more about polymer-specific sample preparation – end of this lecture.

SEM/STEM limitation :: No classical electron diffraction

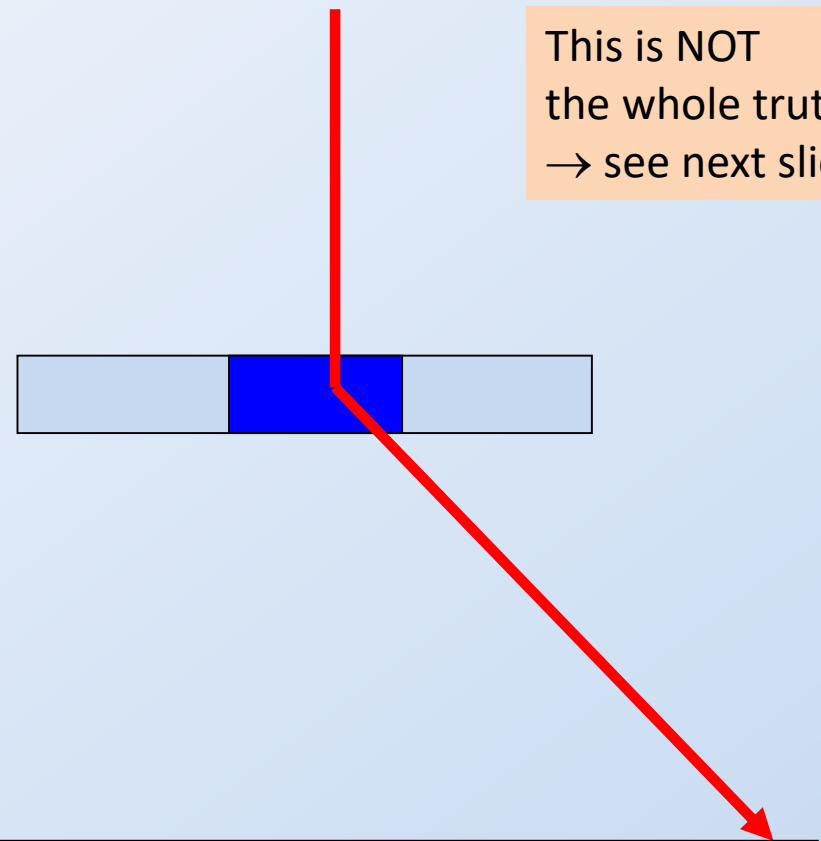
Why the (classical) electron diffraction cannot be observed in SEM/TE = STEM?

TEM: the sample is submerged in the broad beam \approx parallel rays go through simultaneously
 \Rightarrow scattering + interference \Rightarrow TEM/SAED



TEM detector

STEM: the sample is scanned by thin focused convergent beam \approx 1 ray
 \Rightarrow no (classical) diffraction



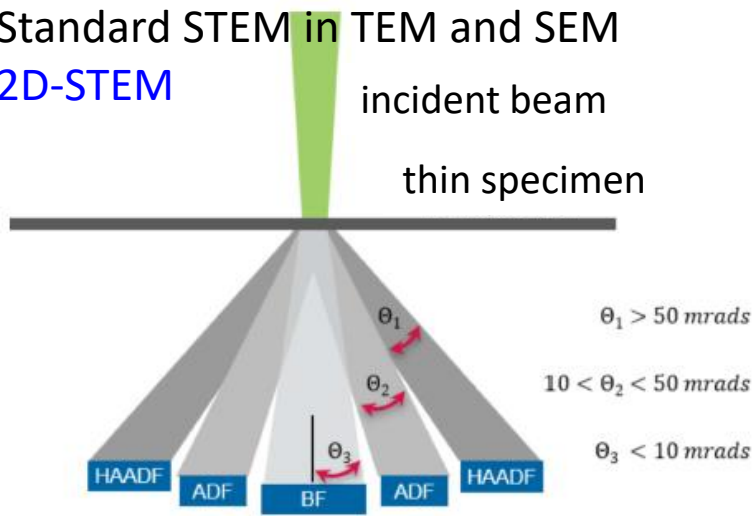
STEM detector

This is NOT
the whole truth!
 \rightarrow see next slide

Recent development :: Electron diffraction also in SEM

4D-STEM = modern TEM and SEM microscopes with pixelated STEM detectors.

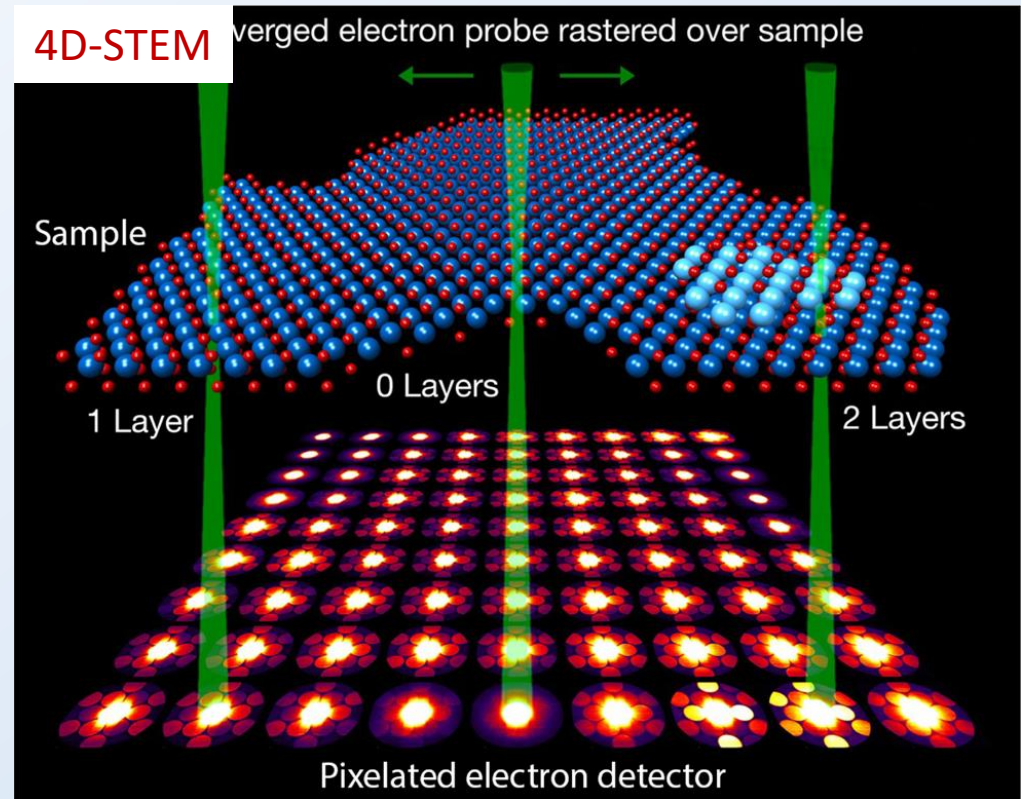
Standard STEM in TEM and SEM
2D-STEM



2D-STEM = standard STEM detectors:

- BF, ADF, HAADF: one XY-position on sample \Rightarrow one signal on detector
- Result: 2D-STEM micrographs

4D-STEM



4D-STEM = fast pixelated STEM detectors (2D pixel array detectors) + thin scanning beam:

- impossible in the past: beams in STEM were convergent + computers/detectors were slow
- but now: non-convergent beams also in STEM \Rightarrow nano-beam diffraction (NBD)
- plus fast HW: 2D-array of 2D-NBD patterns \Rightarrow 4D-STEM = four-dimensional datasets

Part 7

Sample preparation

- ❖ General methods of sample preparation for SEM
- ❖ Specific sample preparations for:
homopolymers, copolymers, blends, composites, micro/nanoparticles...

Notes:

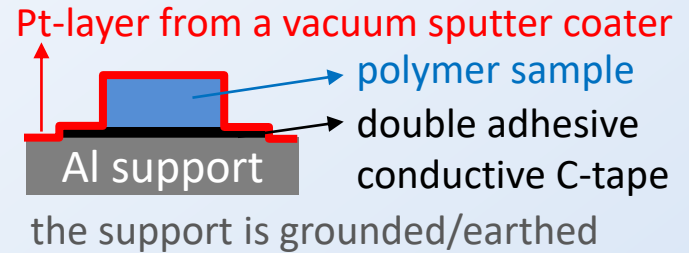
- Sample preparation is not a main subject of this course, but keep in mind the following rule:
bad sample + perfect microscope = bad result
good sample + average microscope = good result

SEM :: General methods of sample preparation

Key problems: (A) How to make samples conductive? (B) How to look inside the sample?

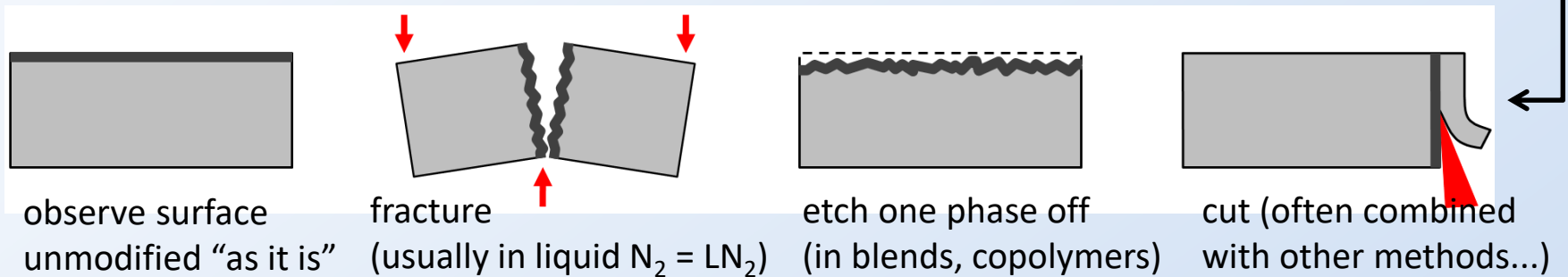
Ad A) Conductivity of polymers: Easy solution.

→ commercial devices (sputter coaters etc.) yield a thin conductive layer of Pt, Au, C...



Ad B) Revealing internal morphology: More difficult.

→ morphology of the surface usually uninteresting, unless we study morphology of particles
→ morphology of the interior (phase structure, crystalline structure) should be revealed



(1) **Nanopowders:** deposit on a support, sputter with Pt, observe in SEM/SE.
(if the size of the nanoparticles is below $\sim 10\text{nm}$, it is better to use TEM)

(2) **Micropowders:** deposit on a support, sputter with Pt, observe in SEM/SE.

(3) **3D-samples:** reveal internal structure as suggested above, sputter with Au/Pt/C, observe...
...no material contrast (homopolymers, copolymers, blends) \Rightarrow SEM/SE
...material contrast (microcomposites, nanocomposites) \Rightarrow SEM/BSE

* STEM: thin sections like for TEM
→ next lecture

* EDX: samples like for SE/BSE

(4) **More details and/or specific cases** → see next slide & good textbooks...

SEM :: Sample preparation for specific polymer systems

Homopolymers

- (1) amorphous: morphologically homogeneous – only fracture surfaces
- (2) semicrystalline => amorphous x crystalline regions
 - a) smoothing + etching + SEM/SE
 - b) ultramicrotomy + staining + TEM/BF

Copolymers

- (3) statistical, random, branched and star copolymers: amorphous => case (1)
- (4) alternating: amorphous (case 1) or semicrystalline => case (2ab)
- (5) block copolymers: microphase separation, wide range of morphologies (2ab)
- (6) block copolymers as compatibilizers: ultramicrotomy + staining + STEM/BF

Polymer blends

- (7) miscible: morphologically homogeneous => case (1)
- (8) immiscible => phase morphology, interphase adhesion, compatibilization...
 - a) fracturing in LN2 + SEM/SEmorphology, adhesion
 - b) smoothing in LN2 + etching + SEM/SE ..morphology for precise studies
 - c) ultramicrotomy + staining + STEM/BF ..morphology, compatibilization

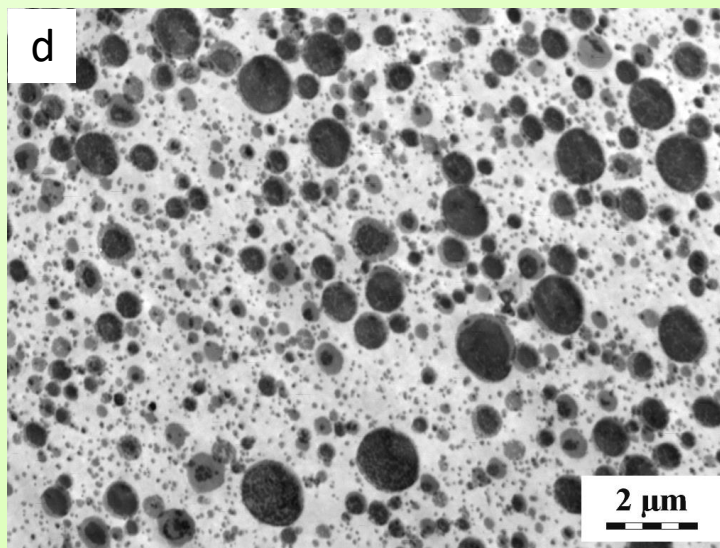
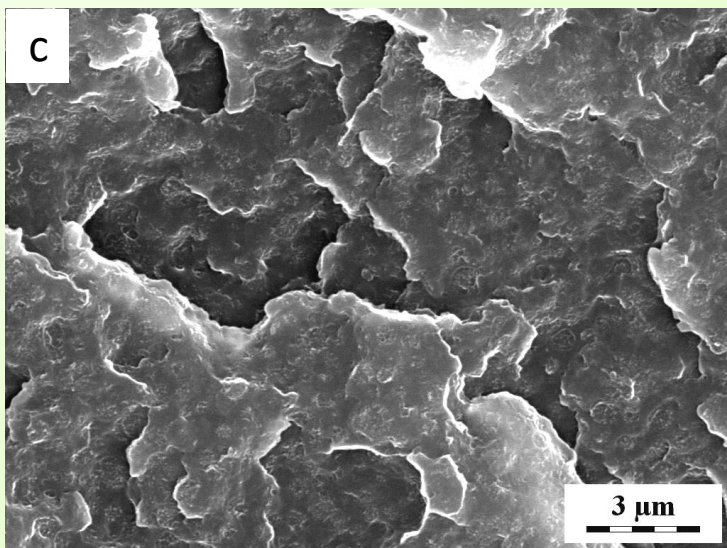
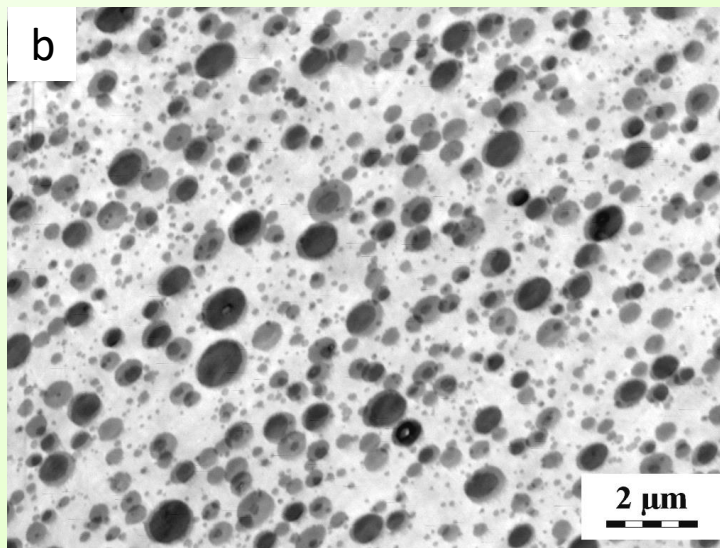
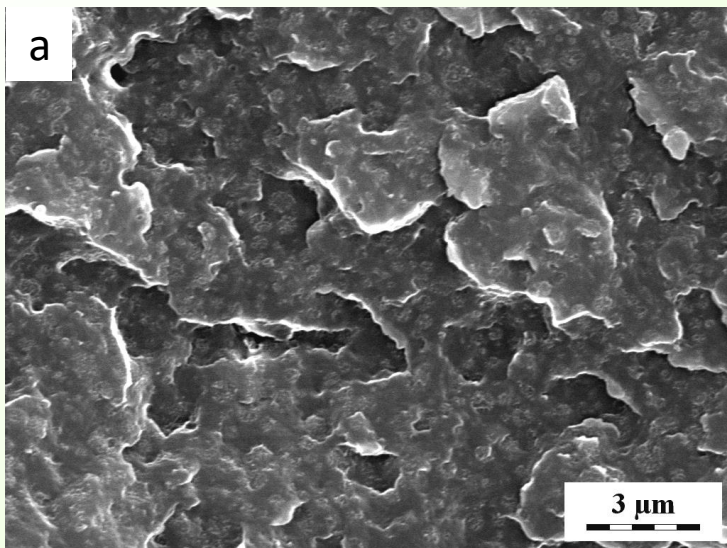
Polymer composites

- (A) microcomposites: fracturing + SEM/SE, BSE, EDX (cutting/smoothing difficult)
- (B) nanocomposites: TEM/BF preferred (higher magnification than average STEM)

More details & systems -> textbooks such as [[Sabbatini 2022](#), Chapter 6]

=> the reference to [[Sabbatini 2022](#)] (and some others) -> next slides

Example :: The right sample preparation is important!



Fracturing in LN₂ is one of the most common methods, but not always the best.

For polymer blends, the UMT combined with staining reveals the morphology much better (in case of good compatibility).

Another useful method for polymer blends: smoothing and etching - Part3, Edge effect.

More methods: see refs. in the previous page.

SEM/SE of LN₂ fracture surfaces (a,c) and STEM/BF of RuO₄-stained ultrathin sections (b,d) of polymer blends PA66/sPS: (a,b) 80/20 a (c,d) 70/30.

SEM :: Sample preparation – useful references

General textbooks about electron microscopy, including sample preparation methods:

- [1] Watt IM. The principles and practice of electron microscopy. 2nd edn. Cambridge (UK): Cambridge University Press; 1997.
- [2] Brandon D, Kaplan WD. Microstructural characterization of material. Chippenham.(UK): Wiley; 2008.

Textbooks about polymer microscopy, including sample preparation methods:

- [3] Sawyer LC, Grubb DT. Polymer microscopy. 2nd edn. London (UK): Chapman & Hall; 1996.
- [4] Slouf M, Vackova T, Lednický F, Wandrol P: Polymer surface morphology: Characterization by electron microscopies. In: Polymer surface characterization. (Sabbatini L, Ed.) Berlin: Walter de Gruyter, 2014, pp. 169–205, ISBN 978-3-11-027508-7.

A few papers coming from our department, describing the most useful techniques (there are many other papers – I just included those I have read carefully 😊):

- [5] OsO₄ staining: Fortelny I et al.: Appl. Polym. Sci. 100 (2005) 2803–2816.
- [6] RuO₄ staining: Slouf M et al.: J. Appl. Pol. Sci. 91 (2004) 253–259.
- [7] Smoothing and etching: Slouf M et al.: Polym. Eng. Sci., 47 (2007) 582-592.

Part 8

Other SEM methods

- ❖ Variable-pressure SEM
- ❖ Low-energy SEM
- ❖ 3D-SEM

Notes:

- The above three groups of methods (VP-SEM, LE-SEM, 3D-SEM) represent modern and popular trends in the field of SEM.
- Moreover, there are some classical methods, which are not so frequently applied to polymers systems: WDS, EBSD, CL, AES... ⇒ these are just briefly listed in the supplement

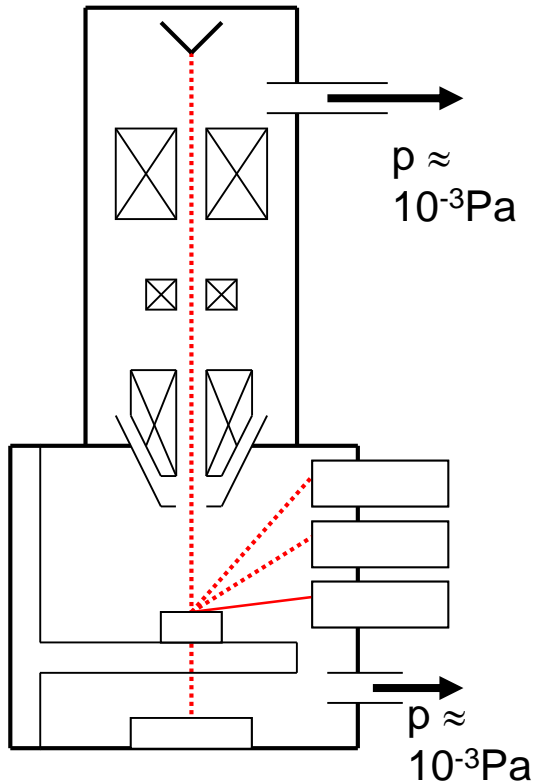
Variable-pressure microscopy

Slides above: standard SEM at high vacuum, BUT vacuum in the chamber can be lower...

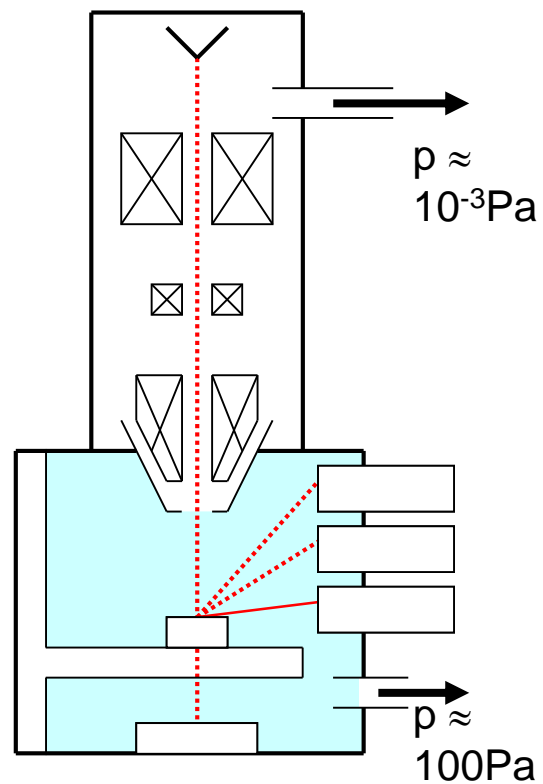
High vacuum SEM = **HV-SEM**

Low-vacuum SEM = **LV-SEM**

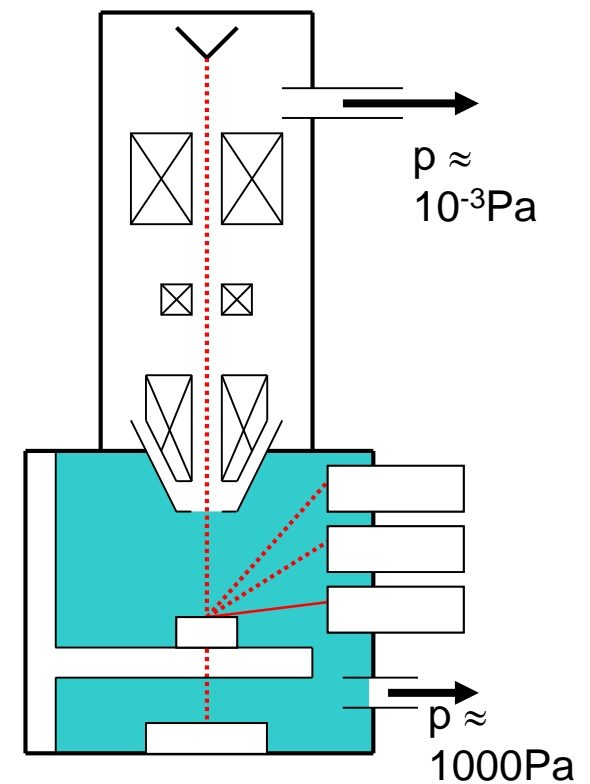
Environmental SEM = **ESEM**



conductive specimens
(or surface-coated
(always dry



non-conductive specimens
(also frozen samples
(samples containing ice!



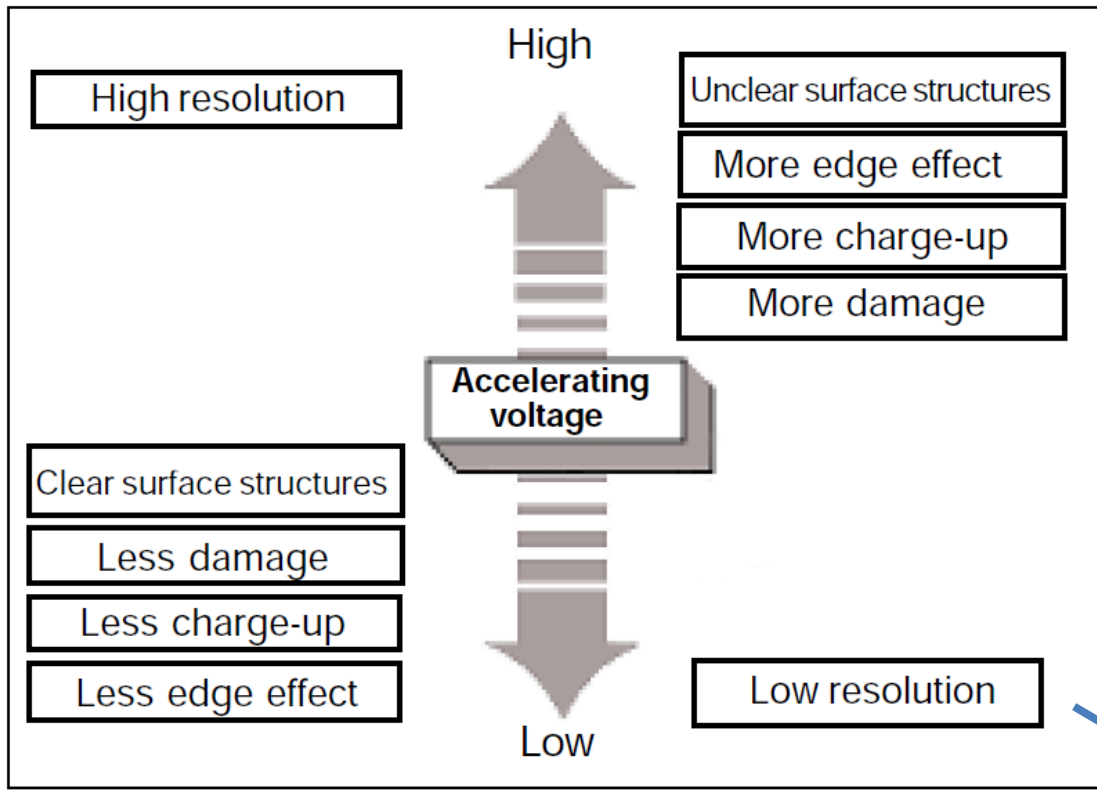
non-conductive specimens
(also wet specimens
(samples containing water!!

* LV-SEM and ESEM modes are sometimes denoted as **VP-SEM** = Variable-Pressure SEM.

* VP-SEM microscopy is not covered in detail \Rightarrow a specific subject for another lecture.

Low-energy SEM microscopy

Slides above: SEM at high energies, but below 5 keV \Rightarrow low-energy microscopy...



Note: low-voltage vs. low-energy:

- ❖ classical/older SEMS:
the landing energy [keV] is equal to the accelerating voltage [kV] (energy of e^- at sample surface)
- ❖ modern/new SEMs:
the electrons can be decelerated just before they impact on the specimen; i.e. the landing energy [keV] may be **lower** or equal to the accelerating voltage [kV]

<http://www.jeolusa.com/RESOURCES/ElectronOptics/DocumentsDownloads/tabid/320/Default.aspx>

High accelerating voltage \approx high energy has just two advantages:

1. Higher resolution at high magnifications.
2. More signal = easier work (if the sample is not damaged).

Low accelerating voltage \approx low energy has many advantages, BUT...

1. The signal is usually lower = the work is a bit more difficult for the user.
2. The low-energy microscopy requires modern microscope – difficult on older SEMs.

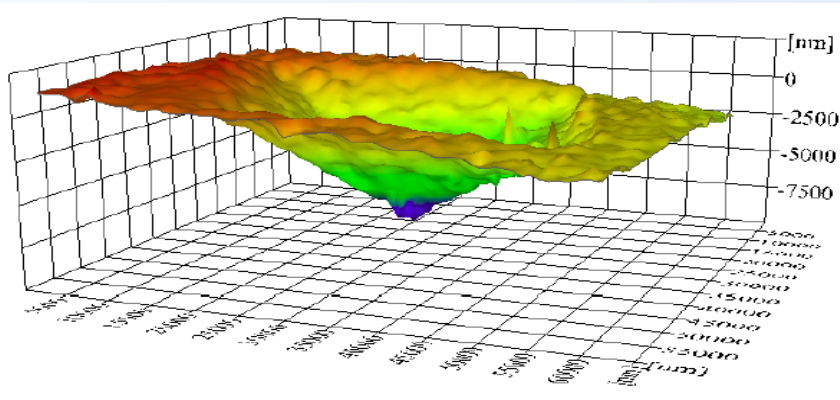
See supplement #3
in section on SEM/SE
as an example

3D-SEM microscopy

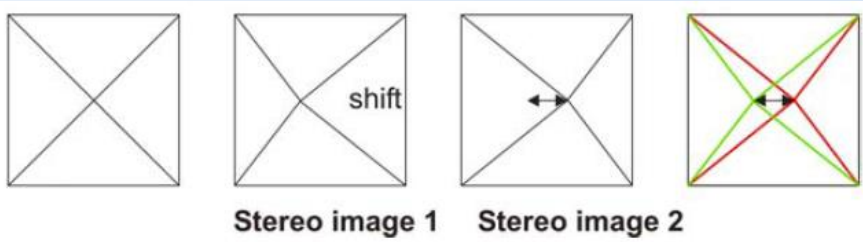
Slides above: 2D-micrographs, BUT with modern SW/HW \Rightarrow 3D-microscopy...

(a) 3D visualization of the sample surface

- ❖ Example: image of 3D-surface showing the Vickers indentation



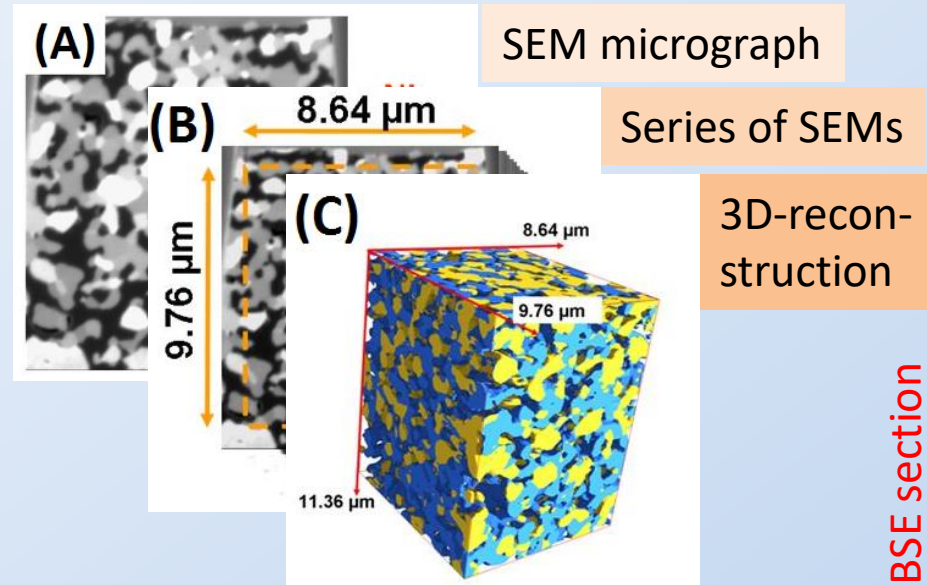
- ❖ Principle: calculations based on two (or more) micrographs with different tilts



- ❖ What to you need to get this?
SEM microscope with eucentric stage
Special software (commercial solutions)

(b) 3D visualization of the sample interior

- ❖ Example: 3D-structure of a porous material



- ❖ Principle & what to you need to get this?
 - it is easy 😊, you just need to get the series of (aligned) SEM images
 - 1st possibility: SEM microscope with an ion beam (FIB SEM or Dual-beam SEM)
 - 2nd possibility: a microtome that can do physical slicing inside your SEM
 - Plus SW for 3D-reconstruction

See also MED-SEM in BSE section

Supplement #5: Less common SEM methods

Classical methods of SEM, less frequently used, and very rarely applied on polymers...

WDS/WDX (Wavelength Dispersive Analysis of X-rays).

Analogy of EDS/EDX – it uses the same signal (X-rays), but differs in technical details.

WDX yields higher resolution, better SNR, and more accurate detection of trace elements.

EDX suffers from lower resolution, worse SNR, but is cheaper, simpler and faster than WDX.

EBSD (Electron BackScattered Diffraction).

The method employs the fact that BSE electrons hitting specimen surface are scattered to specific directions and intensities according to the crystalline structure of investigated material. Evaluation of EBSD patterns is difficult and requires special software, but can be employed in identification of crystallites and their orientation in the sample. EBSD is used for crystalline materials such as metals and minerals. Requires perfectly smooth surfaces. Not applicable to polymers.

AES (Auger Electron Spectroscopy).

It uses a signal, which is “a step further” in comparison with EDX/WDX.

EDX: PE kicks off SE → some e^- fills the vacancy → X-ray is emitted & detected.

AES: PE kicks off SE → some e^- fills the vacancy → X-ray is emitted → kicks off AE we detect.

AE exhibit specific energies – they can be used for analysis analogously to X-rays in EDX/WDX.

CL = CathodoLuminiscence – PE impacting on a luminescent material cause a photon emission.

ECP = Electron Channeling Patterns – electrons are channeling in the crystals...

Conclusions & summary

- ❖ **We have explained the four basic methods of SEM microscopy:**
 - SEM/SE = topographic contrast
 - SEM/BSE = material contrast
 - SEM/EDX = microanalysis
 - SEM/TE = STEM = internal structure

- ❖ **The lecture was focused on understanding and interpretation of SEM micrographs and spectra.**

- ❖ **Other pieces of information:**
 - We have learnt how to calculate velocity, wavelength and penetration depth of electrons in EM
 - We have also shown manual interpretation and a few calculations concerning EDX spectra
 - We have discussed some other aspects of microscopy, such as: magnification, resolution, why is it used...
key importance of sample preparation for SEM studies
some other methods/modes of SEM, such as VP-SEM, LV-SEM and 3D-SEM...