EPFL

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Physical and Chemical Analyses of Materials

SEM: Basics

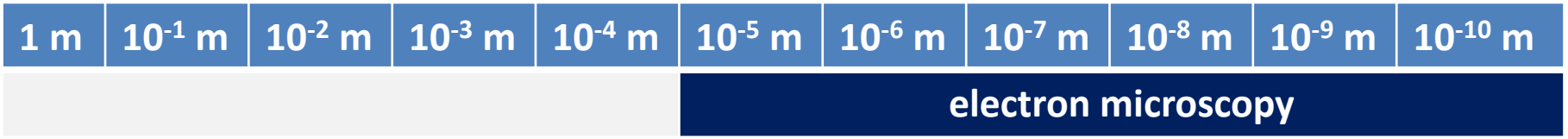
Introduction

⇨ Scanning Electron Microscopy SEM is related to electron microscopy.

⇨ The principle of SEM was demonstrated by Manfred Van Ardenne and Max Knoll in 1938 from the modification of a TEM.

⇩ The first prototype dedicated to massif samples was built by Vladimir Zvorykine in 1942 in the USA.

⇨ Conventional microscopes use an electron beam from 0.1 to 30 keV. These electron energies allow the study of samples from 10^{-5} to 10^{-10} meter size.



⇨ SEM is dedicated to massive samples which can exhibit a big relief.

⇨ SEM provides surface and topographical analyses of materials.

⇨ For thin samples 10 – 100 nm, transmitted electrons can be analysed to obtain some additional structural information about the material.

⇩ This configuration needs the use of a special holder with a Transmitted Electron Detector (TED).

⇨ SEM requires the use of a high vacuum (10^{-5} to 10^{-6} mBar) that brings additional constraints to the sample nature.

⇨ The sample should be conducting enough to prevent from charging effects that can defocus the primary electron beam (primary electrons being reflected by the sample).

⇩ Specific preparations can overcome the lack of conductivity of a sample.

⇨ The depth of field varies from a few centimetres at low magnification, to a few micrometres at the maximum magnification.

⇨ The analysis concerns both secondary (SE) and backscattered electrons (BSE).

⇨ It provides also a chemical analysis when coupled to XRMA.

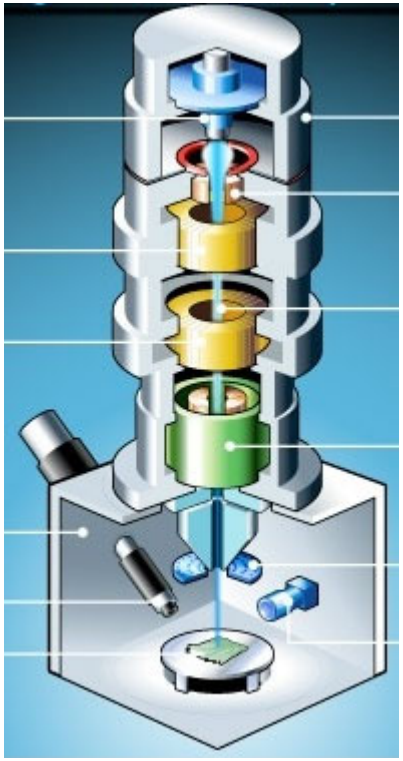
⇨ Cathodoluminescence which rely on the study of the visible light emitted by a sample can also be performed in a SEM.

SEM overview

SEM instruments

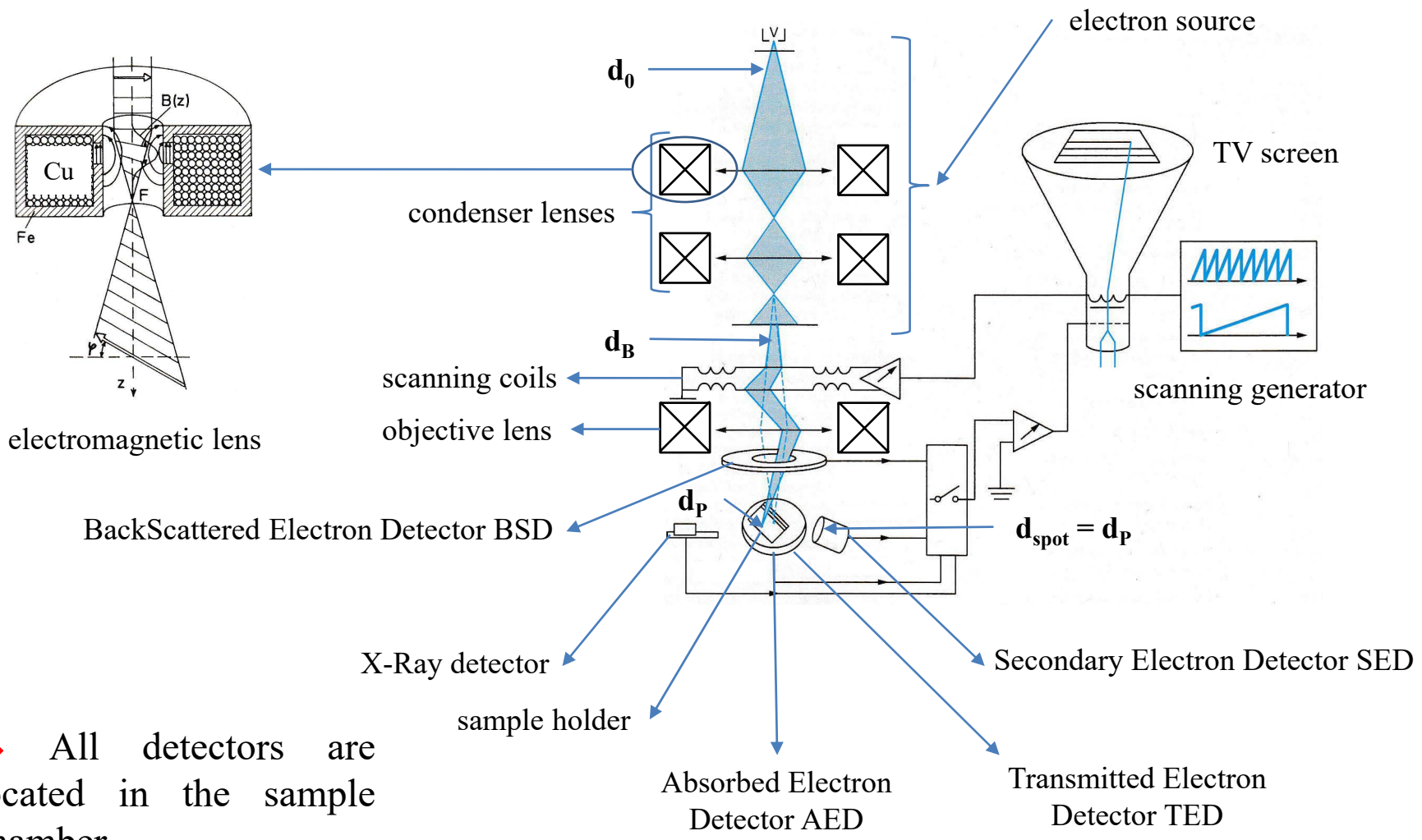
⇨ Below are shown an SEM apparatus (left side) and its operation scheme (right side).

Zeiss GeminiSEM



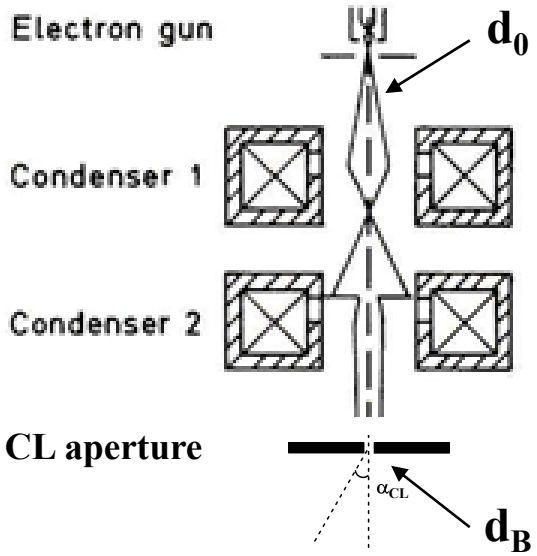
Schematic view of an SEM

Apparatus scheme



↳ All detectors are located in the sample chamber.

Electron source



⇨ The electron source is constituted by an electron gun and some condensers.

⇨ The electron gun is made of a thermionic (W or LaB_6) or field-emission source (S-FEG or C-FEG).

⇩ In SEM, LaB_6 and FEG electron sources are preferred.

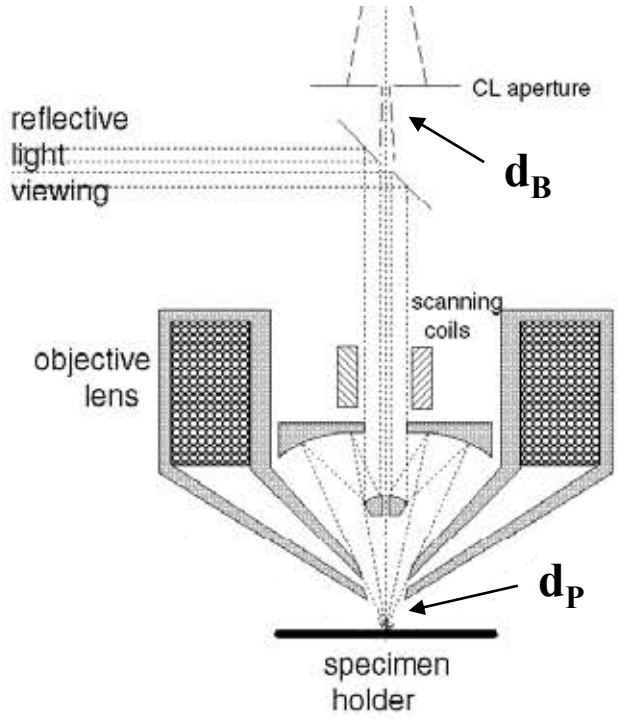
⇨ The electron beam produced by the electron gun is further focused thanks to a series of tuneable electromagnetic lenses which constitute the condensers (*i.e.* condenser 1 and 2).

⇩ The current of the beam is controlled by the size of the condenser lenses (CL) aperture. Increasing the current circulating in the lenses, decreases the focal distance of the lenses system, $\boldsymbol{\alpha_{CL}}$ is increased and the beam current is lowered.

⇨ The resulting beam is further driven to the final lens also called the objective lens. The beam entering the objective lens is from 50 to 200 nm diameter.

Objective lens

General features



⇨ The objective lens allows the focalisation of the beam onto the observed zone of the sample surface. The diameter of the probe $\mathbf{d_P}$ shone on the sample is different from $\mathbf{d_B}$.

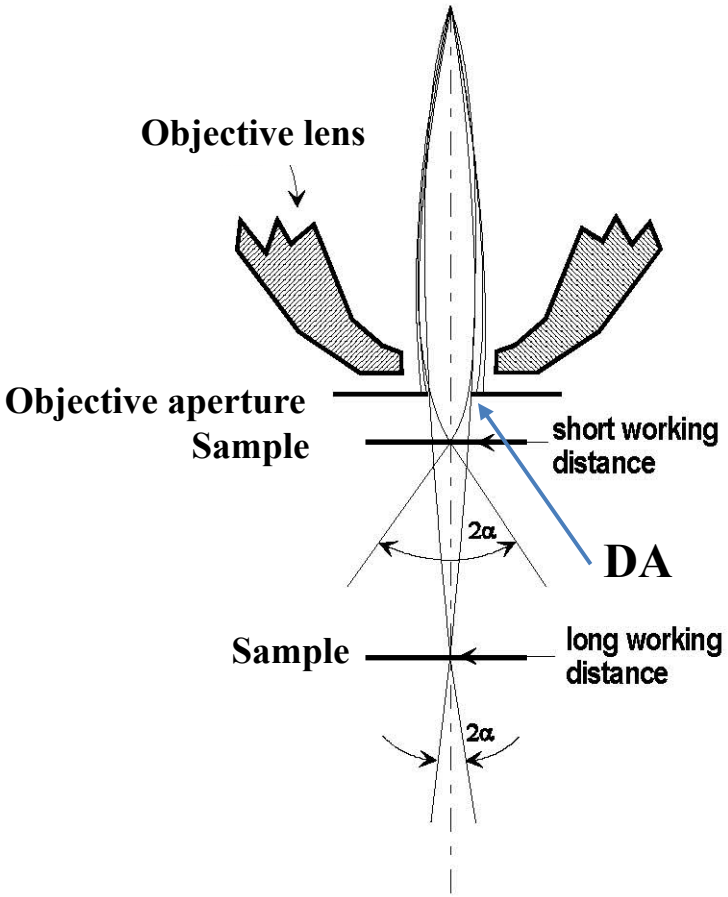
↳ It incorporates some scanning coils used to deflect the electron beam.

↳ Its primary purpose is to de-magnify the beam emitted by the CL aperture (50 - 200 nm) by a factor spanning from 1/10 to 1/100. The half-angle of the objective aperture $\boldsymbol{\alpha_{OB}}$ ranges from 10^{-3} to 10^{-2} rd.

↳ The beam size $\mathbf{d_P}$ shone on the sample can be tuned from 1 to 100 nm diameter.

⇨ An important parameter to take into account in SEM is the working distance (**WD**), that is the distance between the objective lens and the sample, that can be tuned (this is not the case in TEM because the sample must be positioned from the objective lens at the eucentric plane).

The working distance



⇨ The working distance (**WD**) determines the length of the focal point.

⇨ A long **WD** induces a big $\mathbf{d_P}$ whereas a short **WD** induces a thin $\mathbf{d_P}$.

⇨ **WD** depends on the half-angle of the objective aperture $\boldsymbol{\alpha_{OB}}$ and on the diameter of the objective aperture **DA**:

$$\mathbf{WD} = \frac{\mathbf{DA}}{2\alpha_{OB}}$$

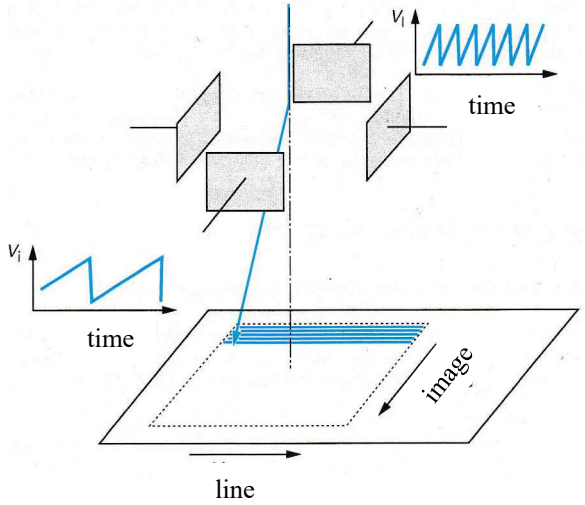
↳ $\boldsymbol{\alpha_{OB}}$ ranges from 10^{-3} to 10^{-2} rd.

↳ The **WD** ranges from a few millimetres to a few tens of millimetre.

The scanning coils

⇨ The scanning system, installed in the objective lens, is use to deviate the electron beam from its linear trajectory.

⇨ The deviation is induced by the coils stimulated by saw tooth electric signals delivered by a waveform generator. This stimulation allows to scan the sample line by line:

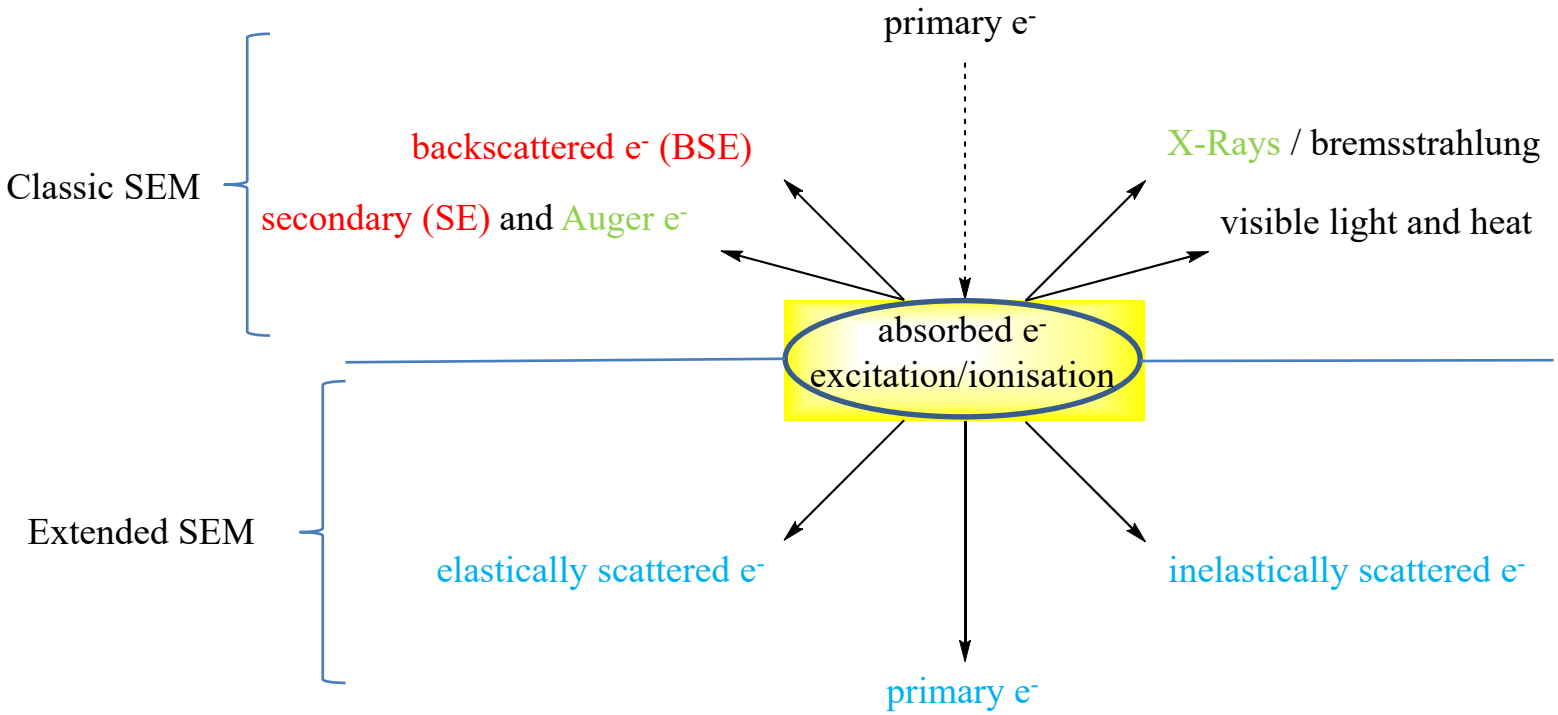


↳ The scan rates range from 16 lines per second to up to 31 250 lines per second.

↳ The waveform generator commands as well the detection/recording system.

↳ The recorded signal is numerically stored.

Electron-sample interactions

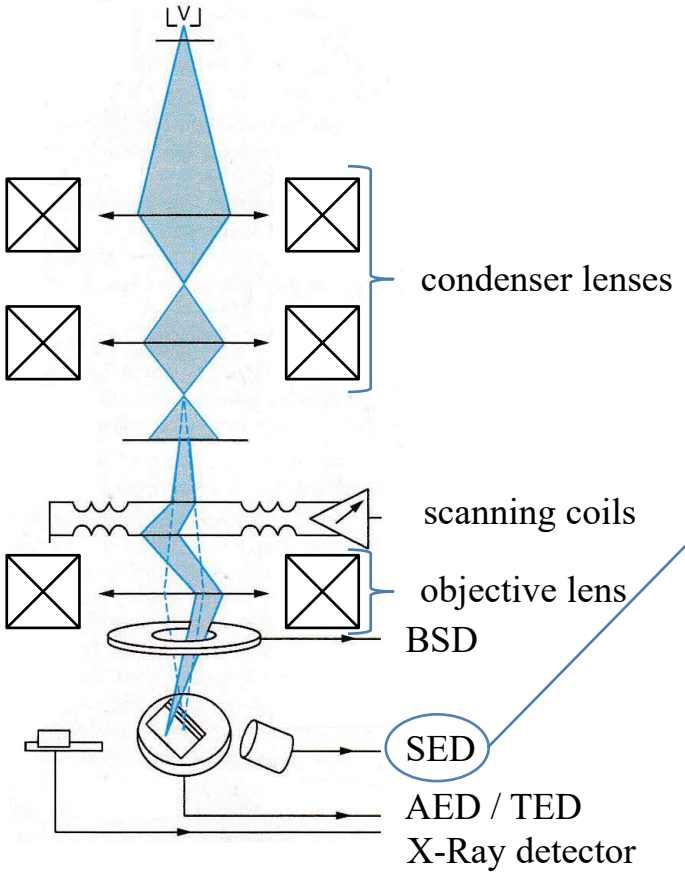


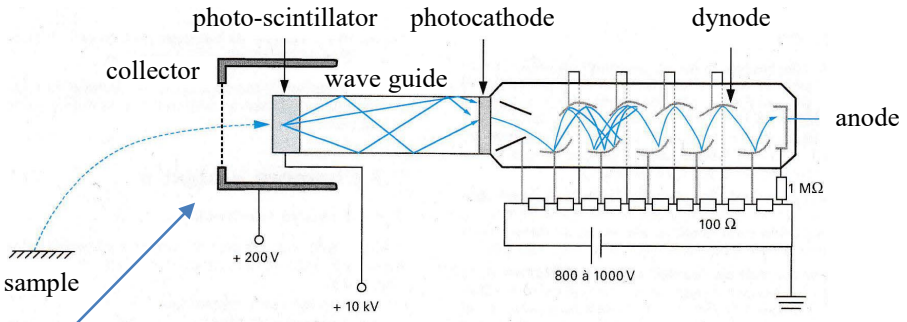
⇨ Classic SEM deals with backscattered and secondary electrons.

⇨ For thin samples (10 - 100 nm) transmitted electrons can also be analysed but it requires the use of a special sample holder equipped with a detector. This configuration is similar to that of TEM.

The detection system

Secondary Electron Detector SED



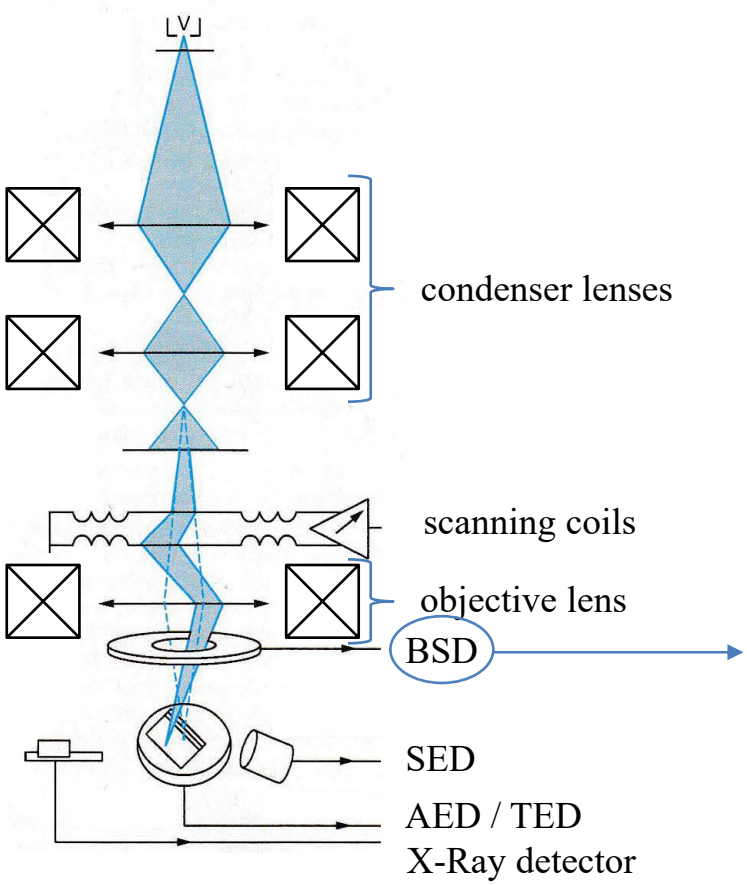


⇨ The Secondary Electron Detector (SED) is an Everhart and Thornley type detector (see detector section in "interactions beam-matter: matter emission).

↳ The collector when positively polarised attacks SE because SE are of very weak energies (5 - 10 eV).

↳ BSE can be detected by the SED when the detector is slightly negatively polarised so it repulses SE.

Backscattered Electron Detector BSD



⇨ The Backscattered Electron Detector (BSD) is an annular detector made of a diode.

⇨ The detector is divided in different sectors which allow a different polarisation of each sector leading to different image types:

↳ topography according to the distance travelled by an electron from the surface to the detector.

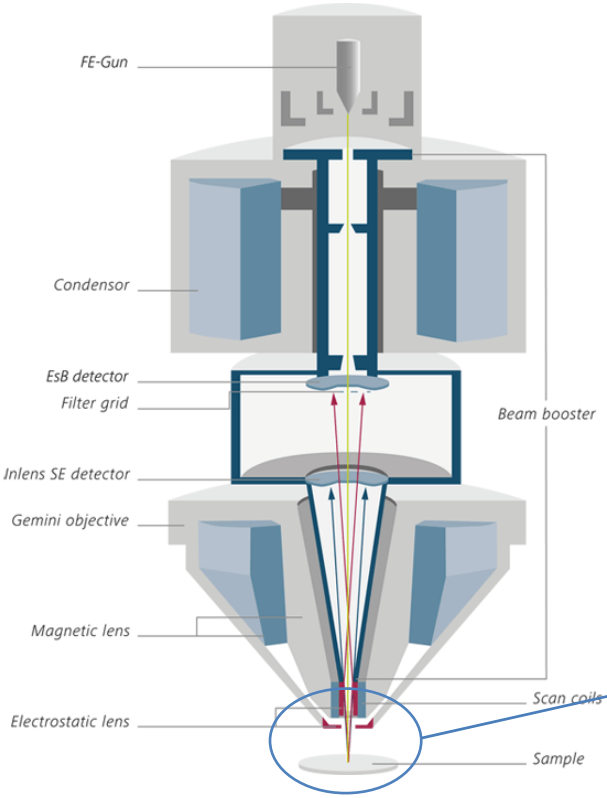
↳ chemical composition according to the energy of the backscattered electrons (BSE) which is linked to the atomic number **Z** of the target atoms excited by the primary electron beam.

⇨ More details concerning these different image modes are given in the image formation section.

⇨ BSE detected by the BSD can either arise from the sample or from the conversion of SE when the SED is negatively polarised. The last case concerns small angle backscattering studies.

Through-lens detectors

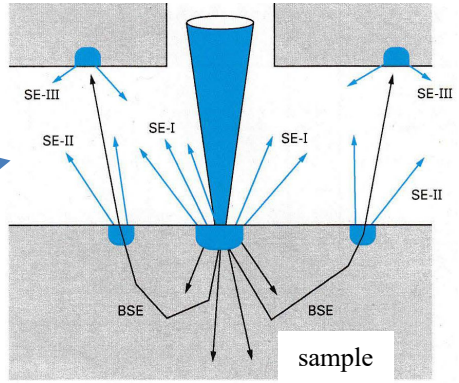
⇨ Some new-designed electronic column possess some detectors included in the lens system.



Zeiss GeminiSEM electronic column

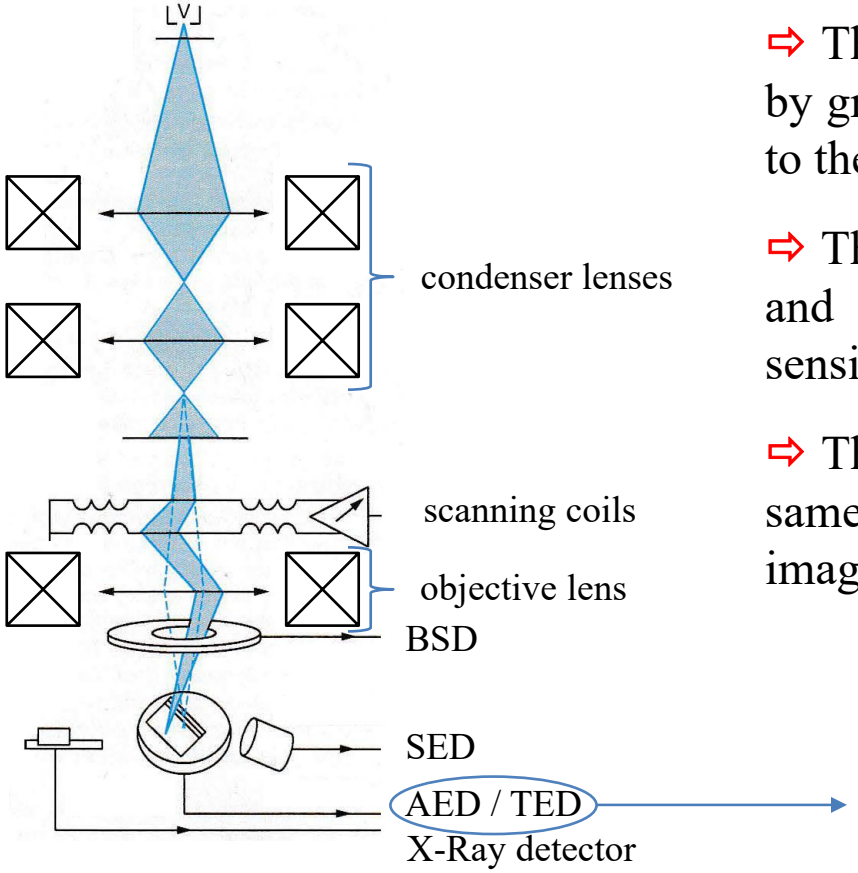
⇨ Here the SED (Everhart and Thornley type) is included between the condenser and the objective lenses. It eliminates secondary electrons SE-II and SE-III to focus only on SE-I (see scheme below).

⇨ Another detector, Energy Selective Backscattered Electron Detector EsBD is also included above the SED. This detector provides subsurface information and nanoscale composition.



⇨ The focalisation distance is reduced with an improvement of the lateral resolution as well.

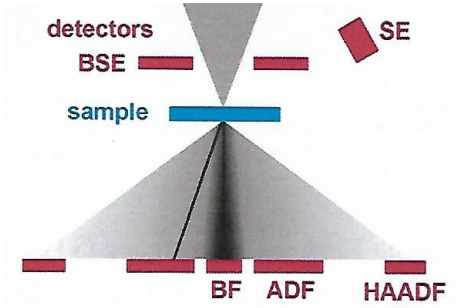
Absorbed Electron and Transmitted Electron Detectors AED / TED



⇨ The Absorbed Electron Detector AED is obtained by grounding the sample holder. The current passing to the ground is measured by a picoamperometer.

⇨ The contrast generated by the AED is rather close and complementary to that of the BSD but less sensitive to the topographical aspects of the sample.

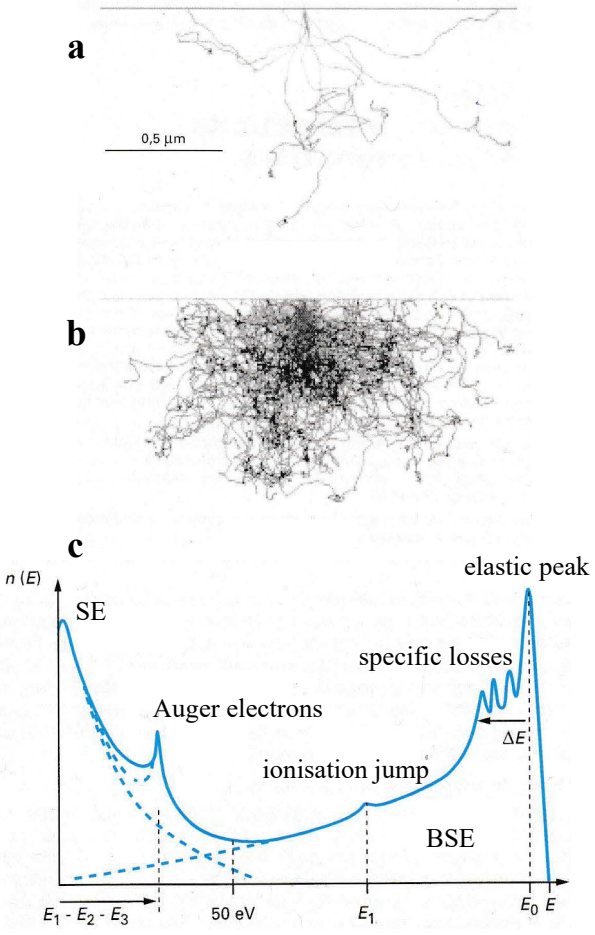
⇨ The Transmitted Electron Detector TED gives the same images than a STEM: BF-, DF- and HAADF-images:

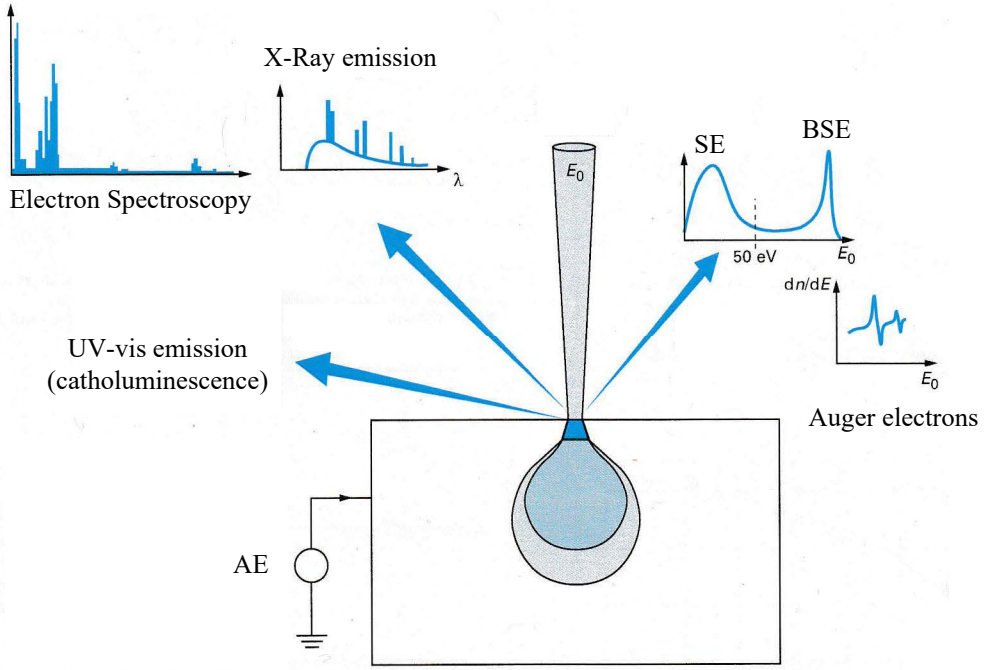


⇨ TE analysis is feasible for thin samples (10 - 100 nm thick) and for the study of replicas (see sample preparation). As with TEM, it gives structural information but with a beam energy of only 30 keV.

SEM samples

Electron-sample interactions

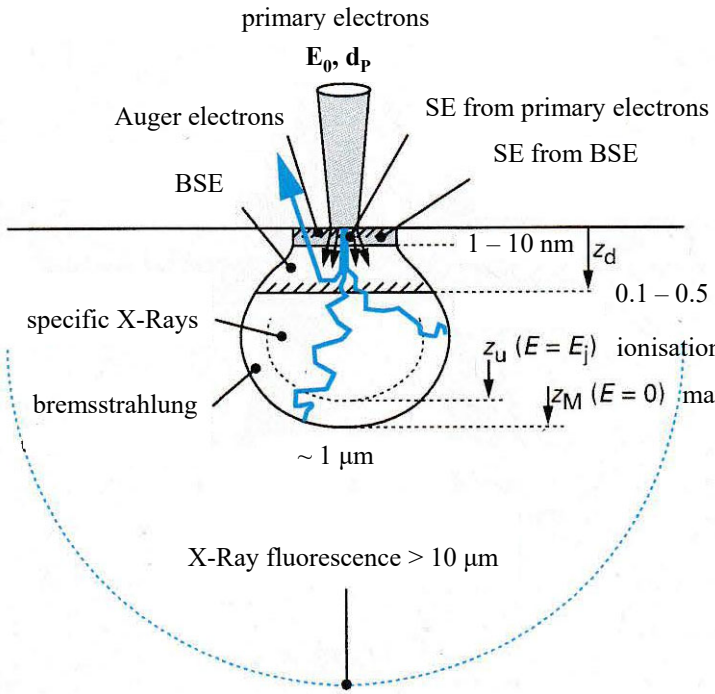




⇨ On the left side, **a** and **b** correspond to the Monte Carlo simulation of the trajectories of accelerated electrons at 20 kV in iron. **a** and **b** show a few trajectories and 200 trajectories respectively. **c** displays the electron energy losses.

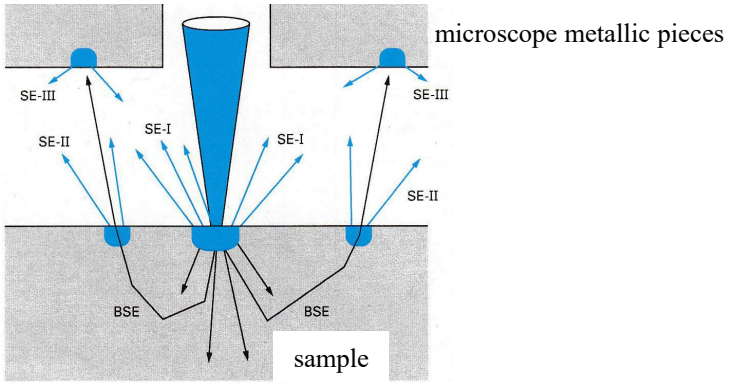
Sample relaxation

⇨ The scheme below represents the relaxation of the sample:



↳ For SE: E ≈ 5 -10 eV

↳ For BSE: E ≈ E_0



⇨ The relaxation scheme shows the different zones for the specific emissions after the electron-matter interaction.

Sample preparation

⇨ As with TEM the sample must resist to the high vacuum (10^{-5} to 10^{-6} mBar) imposed by the use of an electron beam.

↳ If it is not the case, environmental SEM can be carried out (see sample chamber).

⇨ The sample size is about 1 to 2 centimetres.

⇨ The sample must be conducting enough to prevent from charging effects that can defocus the primary electron beam, the primary electrons being reflected by the sample.

↳ Charging effects can cause the blurring of the image.

↳ Conducting and semiconducting materials do not require a specific preparation.

⇨ When the material is not conducting enough, it is possible to perform the microscopy at a lower electron beam energy, around 1 keV or less.

↳ It prevents from charging effects.

↳ It enhances the secondary emission (SE, Auger electrons…).

↳ It suffers from a lower lateral resolution.

⇨ Another alternative remains into the deposition of a conducting film like Au, Au-Pd or C.

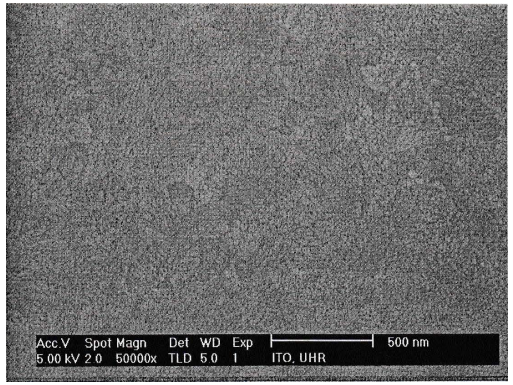
⇨ The deposition thickness ranges from a few nanometres to 50 nm. A typical thickness is about 10 – 30 nm.

⇨ A coating by Au or Au-Pd, enhances the production of SE and favours a excellent lateral resolution.

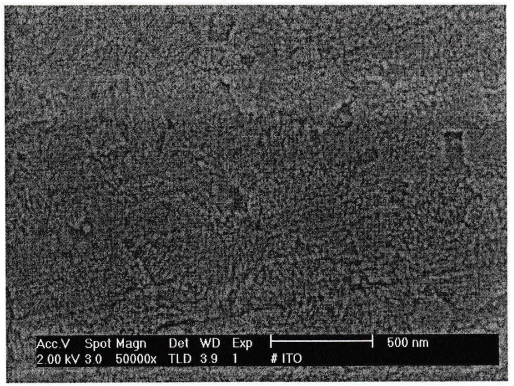
⇨ The presence of a film can mask some surface details. In this case, it is of importance to perform the analysis at a few keV prior to any film deposition.

⇨ The film nature must be considered when XRMA is carried out because of potential interferences. For XRMA analyses, a carbon deposition is more indicated.

Au deposition on a spider



bare Indium Tin Oxide (ITO)

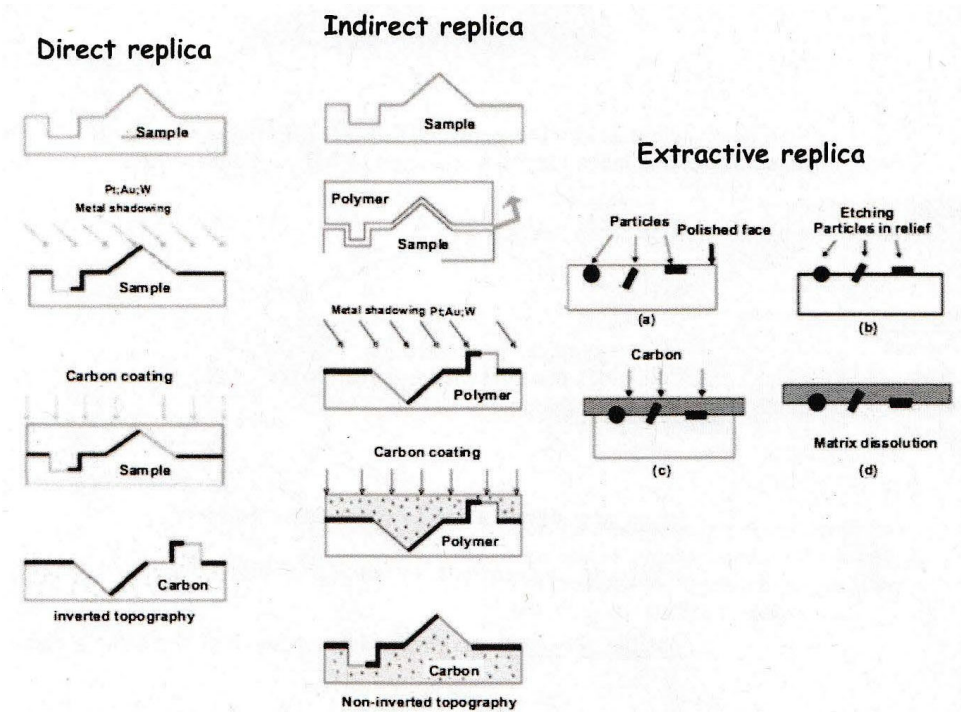


carbon deposition on ITO

⇨ For topographical studies, the method of replicas is also available.

↳ In this method one can either make a direct or an indirect replica of the material surface.

↳ Extractive replicas can be use to extract and study chemical species located at the surface or in the bulk of a material.

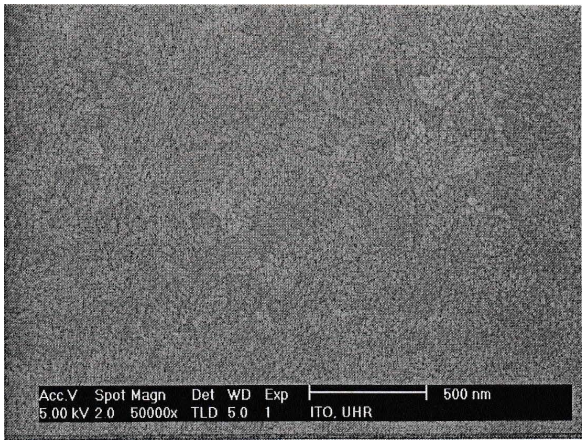


Charging effects

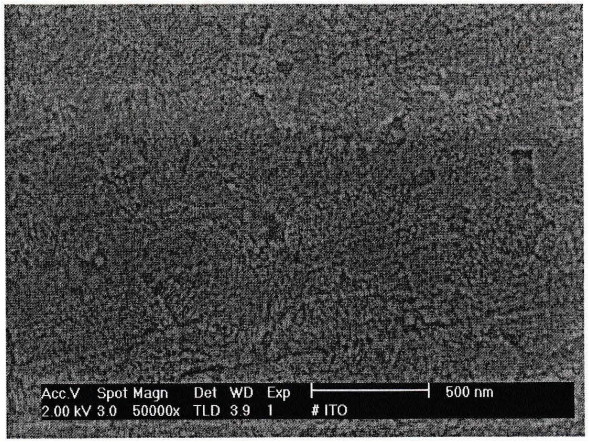
⇨ The sample charging causes image artefacts. The image can become blurred due to the deflection of the electron primary beam which causes a loss of resolution and sometimes the displacement of the image in the **x-y** plan by the primary beam defocusing.

⇨ If the charging effect is too intense, the primary electrons can be totally backscattered by the sample, causes the blindness of the detector that can display a bright white spot instead of the sample image.

⇨ The left image shows a charging effect that degrades its sharpness compared to the one obtained from the treated sample by carbon deposition (right side).



bare ITO



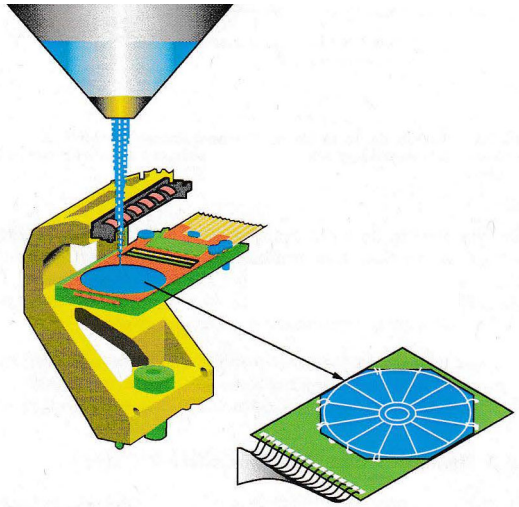
carbon modified ITO

↳ ITO is anchored on the SEM holder by its insulating side which prevents the electron purge.

↳ Images were recorded with a Through-Lens Detector (TLD).

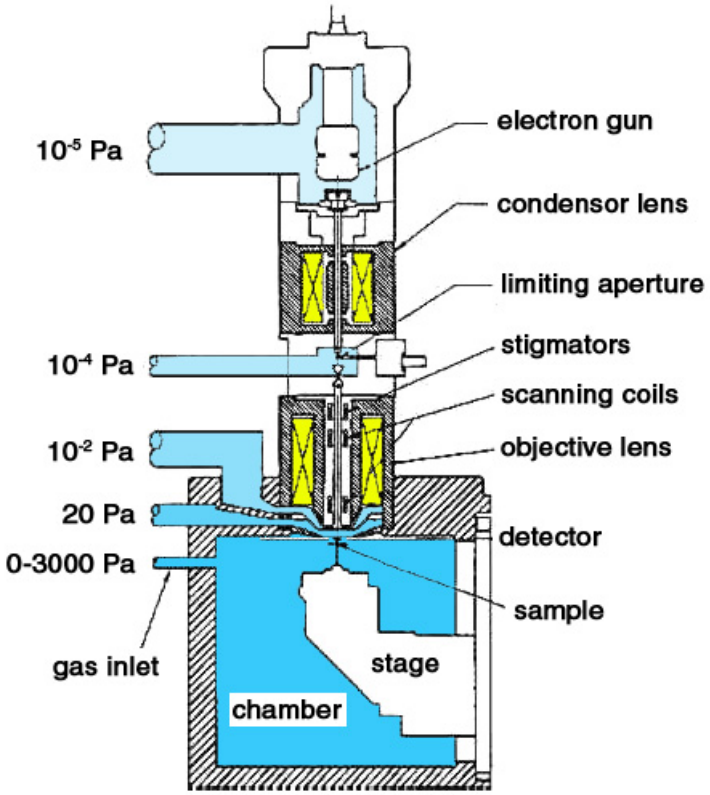
Sample chamber

⇨ The sample is deposited and stuck to a specimen 3-axes holder using a conductive adhesive. When a TED is required, one must use a specific holder as depicted on the right side.



⇨ SEM requires the use of a high vacuum (10^{-5} to 10^{-6} mBar) that brings additional constraints to the sample nature (see sample preparation).

⇨ When a sample is sensitive to the high vacuum of the sample chamber or for studies which require an atmospheric pressure and/or the need of a gas environment, specifically designed chambers are available:



⇨ This technique relates to ESEM: Environmental SEM.

Image formation

Aberration and astigmatism corrections

⇨ For conventional SEM (thermionic electron source), the diameter of the beam $\mathbf{d_P}$ shone onto the sample is only governed by the aberrations of the objective lens.

⇨ For high-resolution SEM (FEG electron source), the diameter of the beam $\mathbf{d_P}$ shone onto the sample is governed by the aberrations of the objective lens and those related to the electron source.

⇨ For conventional SEM, taking into account the aberrations of the objective lens, one obtains:

$$\mathbf{d_P} = \sqrt{\left(\frac{4\mathbf{I_p}}{\pi^2\mathbf{B}} + \frac{2.28}{\mathbf{E_0}}\right)\frac{1}{\alpha_{OB}^{\ 2}} + \frac{1}{4}\mathbf{C_s}^2\alpha_{OB}^{\ 6} + \left(\frac{\Delta\mathbf{E}}{\mathbf{E_0}}\right)^2\mathbf{C_c}^2\alpha_{OB}^{\ 2}}$$

↳ In this equations, $\mathbf{B}$ is the electron gun brightness ($A \cdot m^{-2} \cdot sr^{-1}$), $\mathbf{I_P}$ is the probe current (A), $\boldsymbol{\alpha_{OB}}$ is the half-angle of the objective aperture (rad), $\mathbf{C_S}$ (nm) and $\mathbf{C_C}$ (nm) are the coefficients for spherical and chromatic aberrations respectively. $\Delta\mathbf{E}$ represents the energy peak broadening of the electron beam (see the chapter on electron sources).

⇨ Except for microscopes equipped with a cold cathode, only the aberration of the objective lens has to be taken into account.

↳ Working at a half-angle of the objective aperture $\boldsymbol{\alpha_{OB}}$ from 10^{-3} to 10^{-2} rd leads to an optimal reduction of the influences of the aberrations.

↳ The working distance **WD** conditions the value of $\boldsymbol{\alpha_{OB}}$. In addition, the objective aperture size **DA** plays also a role on the value of $\boldsymbol{\alpha_{OB}}$ (see slide 8).

↳ Technical progresses in lens fabrication allow to reduce both lens aberrations and the size of the electron column.

⇨ The emergence of electron energy filtration devices favours the reduction of chromatic aberration (see electron sources).

⇨ A series of 8 coils surrounding the electron beam allows an astigmatism correction by a constant tuning of the current flowing in this octopole.

↳ This octopole generates an anisotropic electromagnetic field which compensates the astigmatism and the field curvature.

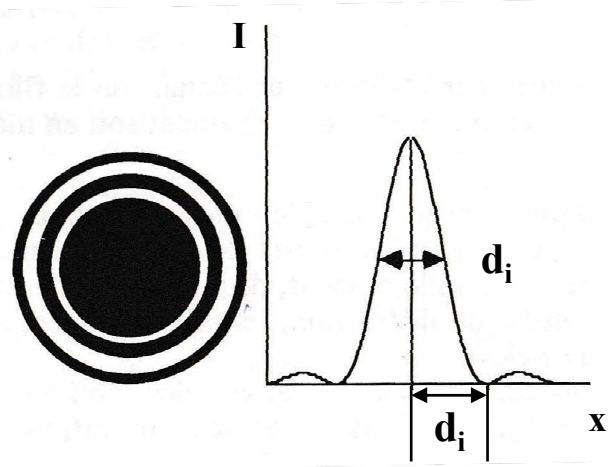
↳ The device is installed in the objective of the SEM.

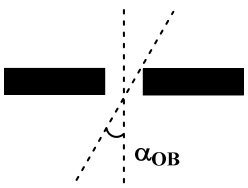
Resolution, magnification and depth of field

Resolution

⇨ The resolution of a microscope stems from its ability to separate two points vicinal points.

⇩ In the following schemes, are represented the diffraction pattern corresponding to the image of a point of diameter $\mathbf{d_i}$ (left side), also named an Airy pattern and its corresponding signal intensity **I** as a function of the distance **x** also called the intensity distribution.





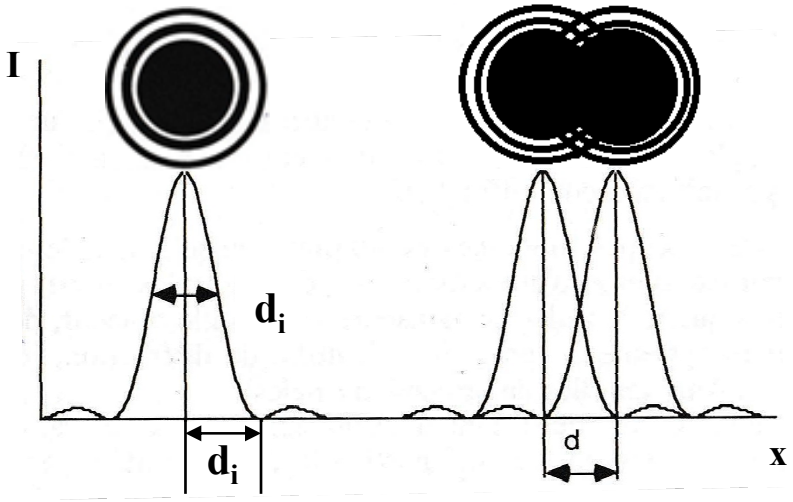
objective aperture

⇩ The width of the disk of confusion $\mathbf{d_i}$ (nm) at small half-angles $\boldsymbol{\alpha_{OB}}$ in vacuum is given by:

$$\mathbf{d_i = \frac{0.61\lambda M}{\alpha_{OB}}}$$

⇩ The width $\mathbf{d_i}$ depends on the beam wavelength $\boldsymbol{\lambda}$ (nm), the objective magnification **M** and the half-angle $\boldsymbol{\alpha_{OB}}$ of the objective aperture.

⇨ The resolution **d** of a microscope is the lowest distance needed to obtain a resolved system. It is associated to the diameter $\mathbf{d_i}$ of the image of a point: $\mathbf{d = d_i}$.



↳ **d** is taken equal to the diameter of final primary electron beam emitted by the objective lens $\mathbf{d_P}$.

⇨ For optimizing the lateral resolution **d**, one has to:

↳ decrease the diameter $\mathbf{d_P}$ of the primary electron beam emitted by the objective lens by preferentially tuning **WD**. The shorter **WD**, the higher resolution is achieved

↳ limit the spreading of the emitting zones of SE

↳ Ensure a sufficient electron intensity to provide the highest detected electrons/ background electrons ratio

⇨ The best lateral resolution **d** depends on the operating parameters but also on the nature of the electron gun (brightness **B**).

⇩ The typical lateral resolution **d** ranges from 0.5 nm to 5 nm.

Magnification

⇨ The magnification is defined by two practical limits between which an image is clear.

⇨ The magnification **M** is linked to the lateral resolution **d** as: $\mathbf{M_{max} = \frac{\varepsilon}{d}}$, **ε** being a constant ranges from 0.1 to 0.2 mm.

⇩ For a typical value **ε** = 0.1 mm and for **d** = 5 nm, $\mathbf{M_{max}}$ is 20 000 whereas for **d** = 1 nm $\mathbf{M_{max}}$ is 100 000.

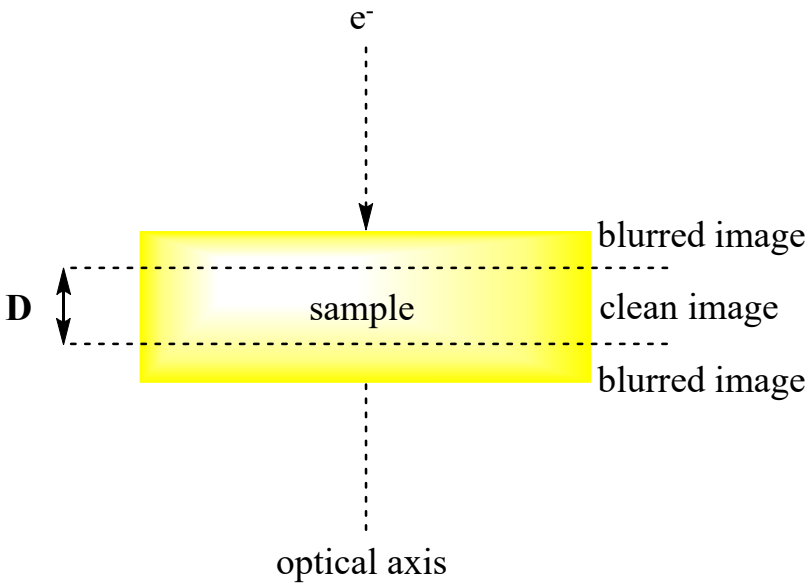
⇩ The estimation of $\mathbf{M_{min}}$ leads to a value of 100. The calculation takes now into account the size of the resulting image and the number of lines used to build the image.

⇨ For standard SEM, the magnification **M** spreads from 100 to 200 000.

⇩ The images realised at a big magnification must be taken with a short **WD**.

Depth of field

⇨ The depth of field **D** can be described as follows:



⇨ The expression of **D** is: $\mathbf{D} = \frac{\left(\frac{\varepsilon}{M}\right) - d}{2\alpha_{OB}}$

⇨ The expression of **D** depends on the **ε** constant (0.1 mm), the magnification **M**, the lateral resolution **d** (nm) and the half-angle of the objective aperture $\boldsymbol{\alpha_{OB}}$.

↳ As an example, for **ε** = 0.1 mm, $\boldsymbol{\alpha_{OB}} = 2\times10^{-3}$ rd and **d** = 5 nm, **D** ranges from 0.5 mm to 1.25 µm for **M** rating from 50 to 10 000.

⇨ SEM exhibits a widespread range of depth of field that allows the study of thick samples.

↳ For maximizing **D**, one has to operate with a long **WD**.

SEM images

Images and contrasts

⇨ SEM is essentially used for surface imaging.

⇨ The images are formed from the emission of surface electrons including SE and BSE.

⇨ Different contrasts can be observed: topographic, chemical, crystalline…

⇨ The contrast **C** represents the relative variation of the signals $\mathbf{S_1}$ and $\mathbf{S_2}$ coming from two vicinal points **1** and **2** of the image:

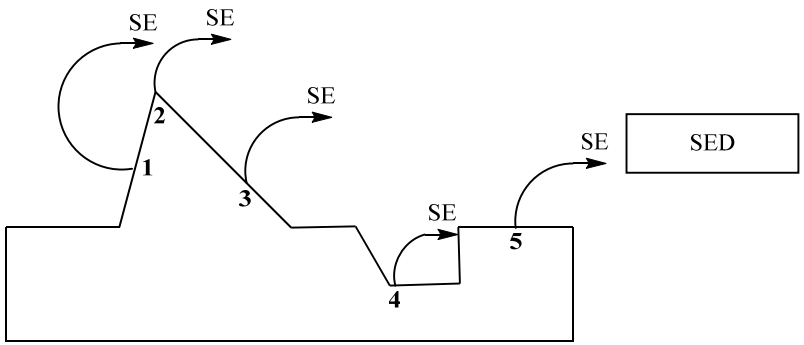
$$\mathbf{C} = \frac{\mathbf{2}\left(\mathbf{S_1} - \mathbf{S_2}\right)}{\mathbf{S_1} + \mathbf{S_2}}$$

Contrast in SED detection

⇨ The contrast provided by SE are: tilt, shadow and edge contrasts.

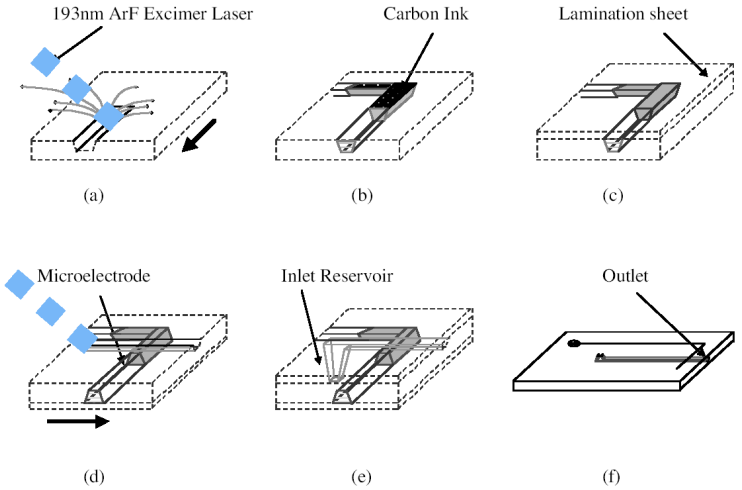
⇨ There is always a contribution of BSE in an SE image, mainly the ones backscattered at high angles thus detected by the SED.

⇨ These contrasts are depicted in the following scheme:

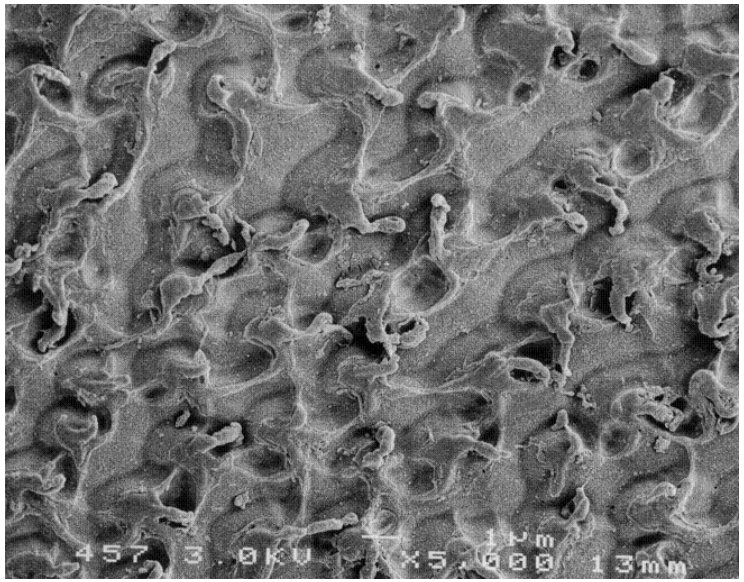


1: shadow contrast, 2: edge contrast, 3: tilt contrast, 4: shadow contrast, 5: reference signal.

A



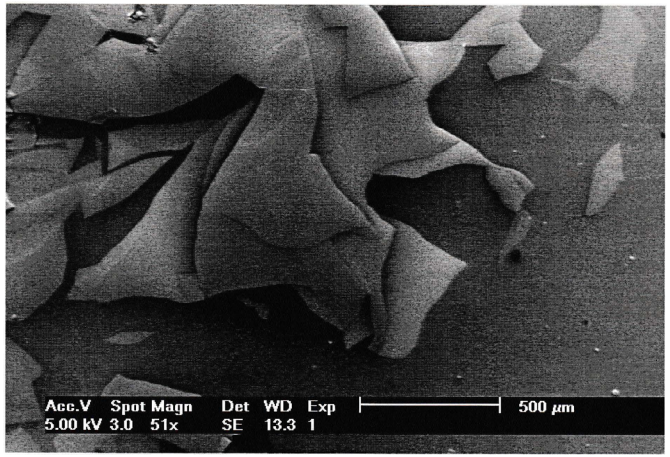
B



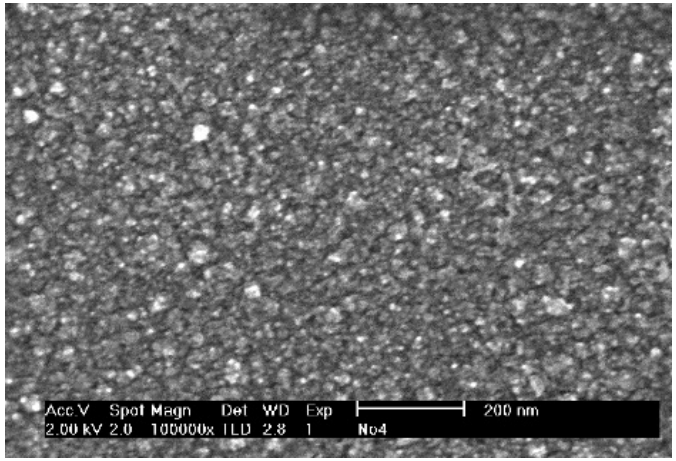
↳ All these contrasts can be enhanced by the tilting of the sample during the analysis thanks to the 3D-axes SEM holder.

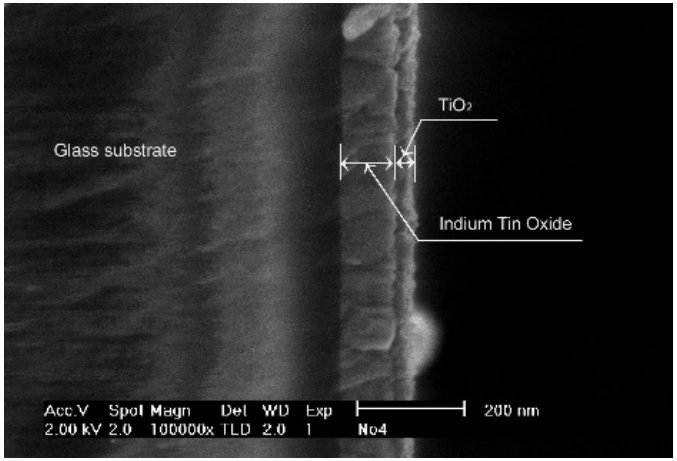
↳ On the right side: the fabrication of micro-electrochemical cells in PET plastics by laser photo-ablation **A** and the SEM observation of the bottom of the drilled micro-channel **B** (step d).

⇨ Observation of a TiO_2 amorphous gel deposited on a glass slide:



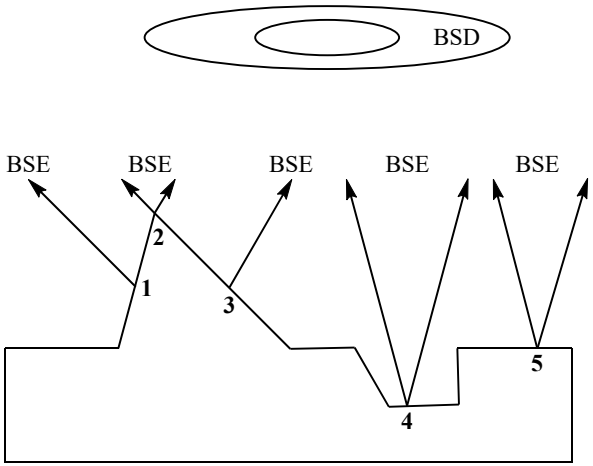
⇨ Observation a TiO_2 crystallised gel (anatase) deposited on an ITO slide. Top view on the left side and cross-section view on the right side:





Contrast in BSD detection

⇨ The contrast provided by backscattered electrons is depicted below:



1: shadow contrast, 2: edge contrast, 3: tilt contrast, 4: shadow contrast, 5: reference signal.

⇨ BSE can be detected by the SED when the detector is slightly negatively polarised so it repulses SE.

↳ The images are strongly contrasted and less sharp.

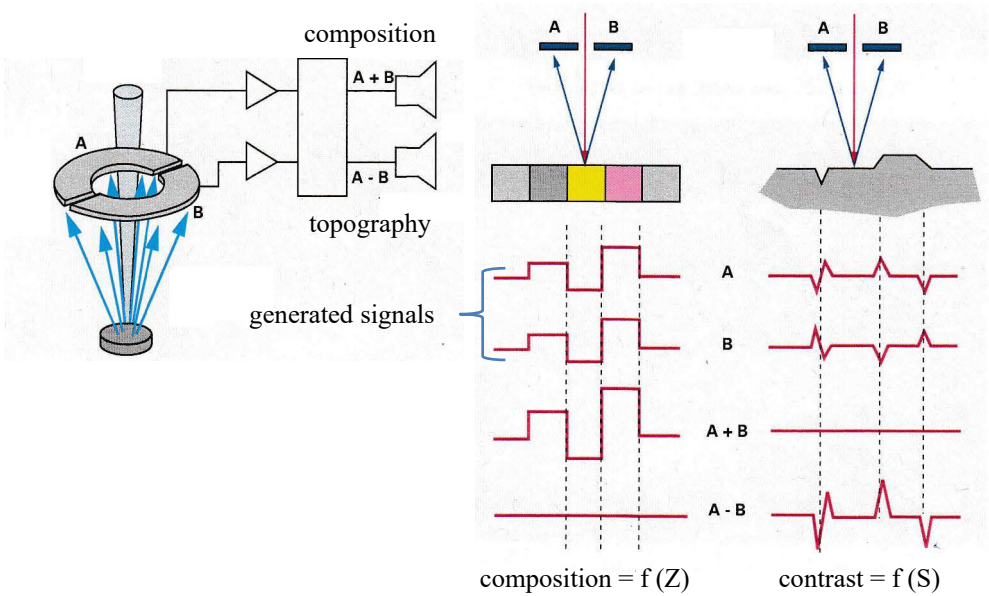
⇨ BSE can be detected by the BSD.

↳ The images are less contrasted and the relief levelled. The surface appears more flat than it is really. Playing with the different sector of the BSD, the topographical contrast can be enhanced.

⇨ BSE detected by the BSD can also provide a composition contrast of the sample.

⇨ For materials with a big relief, the topographical contrast exceed the composition one.

⇨ The BSD which is an annular detector is divided in different sectors. This configuration allows a different polarisation of each sector leading to different image types: topography or composition.



⇨ The composition contrast is achieved by the energy of the BSE which is linked to the atomic number **Z** of the target atoms excited by the primary electron beam.

↳ In this mode, the signals coming from sectors **A** and **B** are summed.

⇨ The topography contrast is achieved by the subtraction of the signals coming from sectors **A** and **B**.

↳ The two signals which are offset and so inverted, give rise when subtracted to an amplification of the sample relief.

Other contrasts

⇨ Among the numerous possible contrasts observed in SEM, one can cite:

⇩ surface crystalline contrast when diffraction occurs

⇩ magnetic contrast obtained by the magnetism of a material or material zones that affect the electron trajectories

⇩ electrical potential contrast caused by local variations of the conduction of a material

Other imaging

⇨ Absorbed electron imaging using the AED

⇨ Transmitted electron imaging using the TED

⇨ Cathodoluminescence imaging using a UV-Vis detector which allows the determination of the band gap energy of a semiconductor

⇨ XRMA and AES imaging