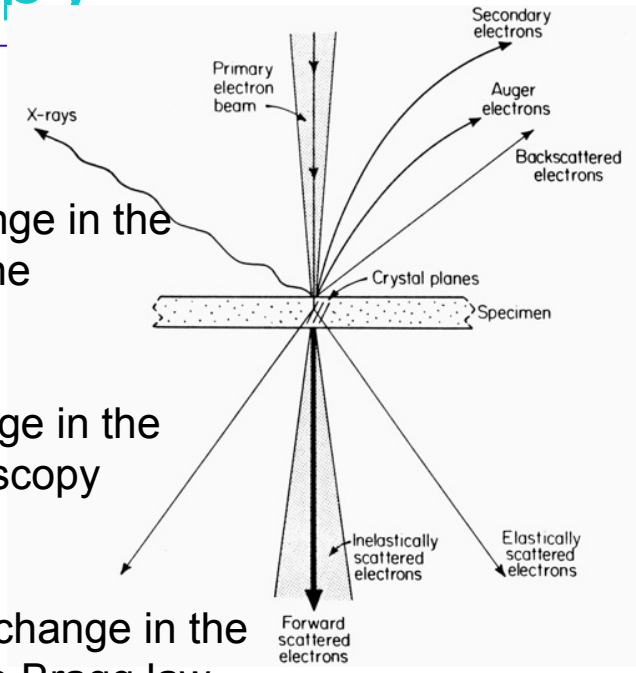
Microscopy

Electron microscopy

The „products" of the electron – material interaction:



1. ***Forward scattered electrons.*** There is no energy loss or change in the direction of the beam. It is used for the bright-field imaging in the Transmission Electron Microscope (TEM).

2. ***Inelastically scattered electrons***. Small energy loss and change in the direction of the beam. It is used in electron energy loss spectroscopy and special imaging purposes.

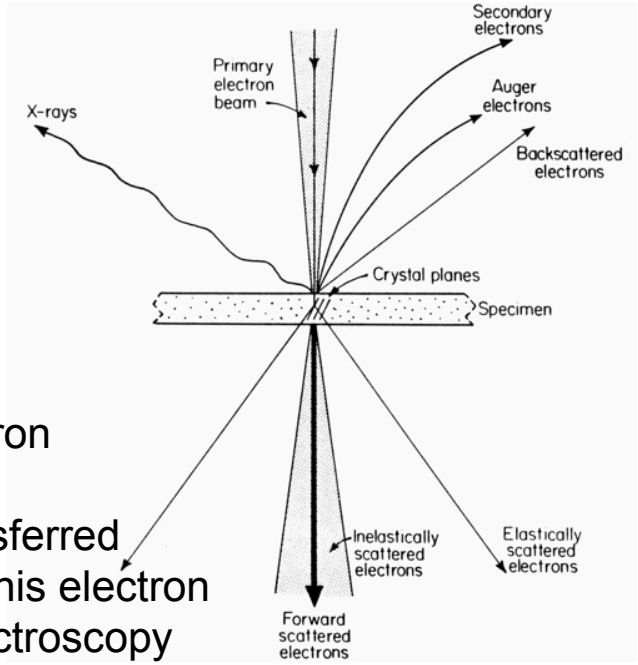
3. ***Elastically scattered electrons.*** There is no energy loss. The change in the direction of the beam is about a few degrees, determined by the Bragg law in the case of crystalline material. It is used for the diffraction mode of the TEM and for the dark field imaging of TEM and for High Resolution TEM (HRTEM) imaging.

4. ***Secondary electrons*.** They are produced on the beam side of the sample. They are ionization products of weakly bonded electrons from outer shells generated by the penetrating electron beam. By collecting these, we obtain topographic information (from the surface) in the Scanning Electron Microscopy (SEM).

5. ***Backscattered electrons***. The elastically or inelastically scattered electrons of the original beam for which the scattering angle is larger than 90 degrees.It is used for imaging in *SEM*.

Electron microscopy

The „products" of the electron – material interaction:



6. ***X-rays.*** The primary electron beam ionizes an electron of an inner shell creating an electron vacancy. The vacancy is filled by an electron from outer shells and an X-ray photon is emitted. betöltődés során röntgen foton távozik. It is the most commonly used signal in Analitic Electron Microscopy (*AEM*). It can be used to determine the chemical composition.

7. ***Auger electrons***. The primary electron beam ionizes an electron of an inner shell creating an electron vacancy. The vacancy is filled by an electron from outer shells and the energy is transferred to another electron of the outer shells, called Auger electron. This electron is shortly leaving the atom. It is used in the Auger-electron spectroscopy and gives information about the chemical composition. It is mainly used for surface investigation.

Electron microscopy

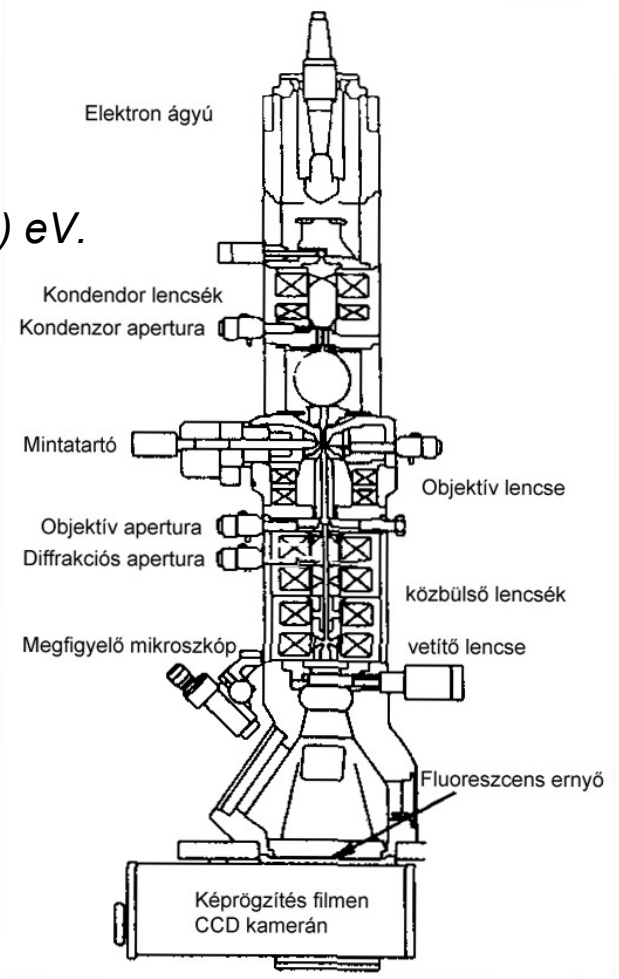
Transmission electron microscope (TEM)

Ernest Ruska 1933 (received the Nobel prize in 1986).

The typical energy used in the novel microscopes: *E = (200 – 400) eV.*

$$\lambda(nm) = \frac{h}{\sqrt{2m_e E}} = \frac{1{,}2}{\sqrt{E(eV)}}$$

$$\lambda \approx 10^{-3}\, nm$$



The main components of TEM:

electron gun,

condensor lenses,

sample space with sample holder, objective,

inner lenses,

projecting lense,

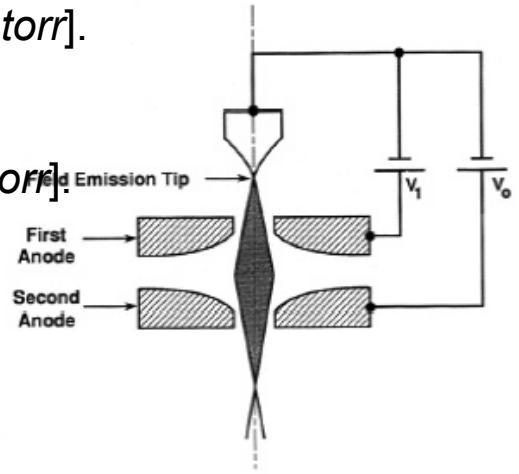
observation unit.

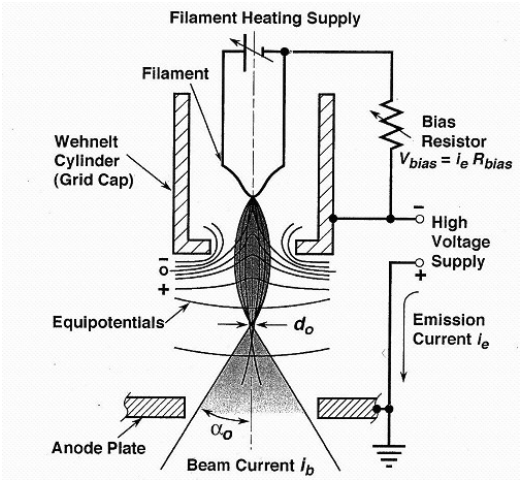
Electron microscopy

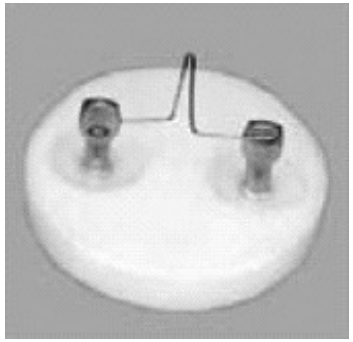
Electron gun

Incandescent cathode, the material is usually tungsten (*W*) or lantan-hexaboride (LaB_6).
The vacuum needed by this source is: (10^{-3} - 10^{-5}) *Pa* ~ [(10^{-5} - 10^{-7}) *torr*].

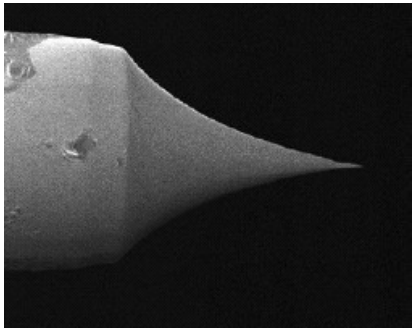
Field emission source, usually with *W* tip.
The vacuum needed by this source is much higher: 10^{-8} *Pa* ~ [10^{-10} *torr*].
In the novel TEM machines we use often field emission source with thermal heating (**Schottky source**).







Thermal heated cathode



Field emission W cathode

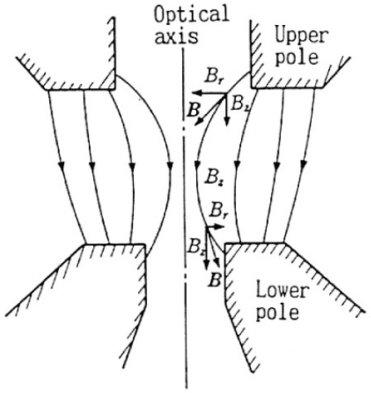
The electrons leaving the cathode are accelerated by electric field to the needed *200 – 400 keV* energy.

Electron microscopy

Electron lenses

Magnetic lenses based on the Lorentzian force.

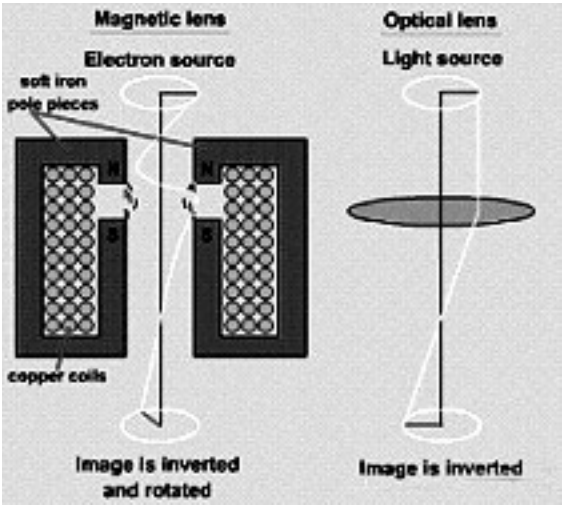
The imaging of magnetic lenses is analogous with the Imaging of thin optical lenses.



Differences to optical lenses:

Due to the $\boldsymbol{F} = e\boldsymbol{v} \times \boldsymbol{B}$ Lorentzian force, the electrons are moving spirally.

The focus distance of the lense can be adjusted by the current of the electromagnetic coil.



The optical lense rotates the image compared to the source by 180^o (the image is inverted).
The magnetic lense rotates the image by an arbitrary angle α (depending on the parameters of the lense).

The field of view of the magnetic lenses is usually much smaller, than in the case of optical lenses ($u \sim 1^o$).
This means that the numerical aperture is: $NA \sim 10^{-2}$, so the maximal resolution of the lense for $\lambda = 10^{-3}$ *nm* is: *0,1 nm*.

Electron microscopy

Optical aberrations of lenses

This resolution can be achieved by the best lenses only.

Like the optical lenses, the magnetic lenses have errors.

In the case of electron lenses the most significant errors are the **spherical aberration**, the **chromatic aberration** and the **astigmatism**.

The quality of the image is usually determined by the properties of the objective.

Spherical aberration

The spherical aberration depends on the α divergence of the beam according to equation $C_s\alpha^3$. α can be changed with the objective aperture. C_s is a constant depending on the lense. In the novel microscopes the spherical aberration is corrected by developing lenses with smaller során C_s value, so the resolution is increased.

In the case of uncorrected objective lenses we usually use only a single diffracted beam In the microscopes.

For HRTEM we need better, corrected objective lenses.

Chromatic aberration

The chromatic aberration depends on the difference of the beam to a monochromatic beam. In the case of energy filtered microscope, this aberration is not present.

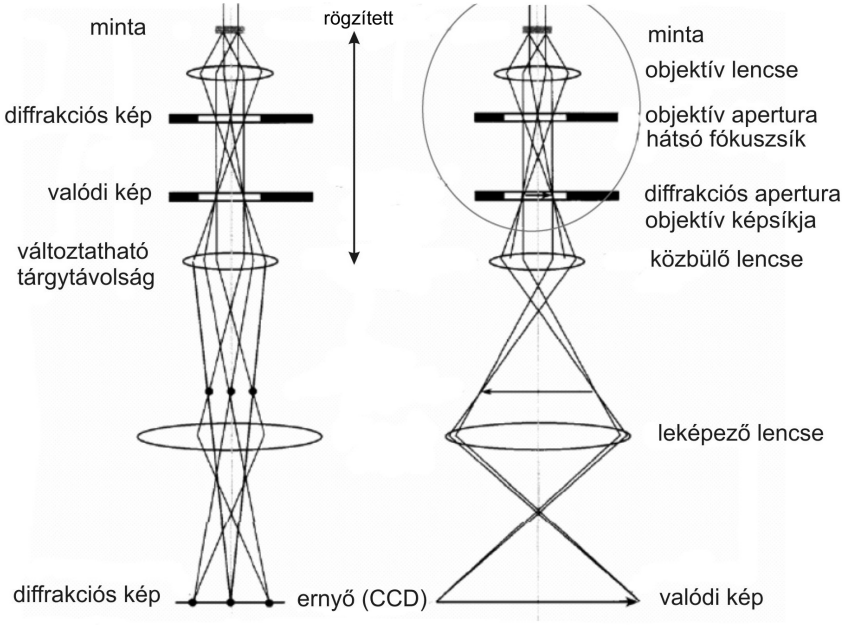
Electron microscopy, TEM

Operating modes of TEM

Diffraction mode

The object distance of the inner lense overlaps with the back focal distance of the objective lense.

In thes case we see on the screen the magnified image of the diffraction image which is produced in the focal plane.



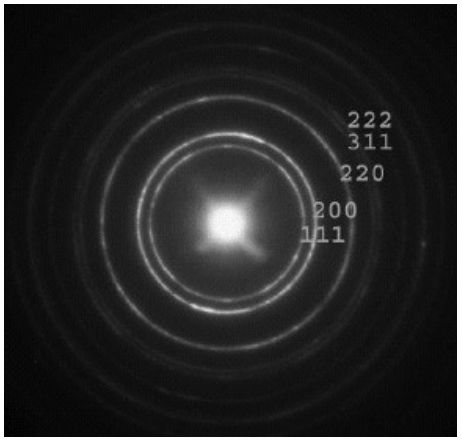
Imaging mode

The object distance of the inner lense overlaps with the image distance of the objective lense.
In this case we see on the screen the real, magnified image of the object.

Electron microscopy, TEM

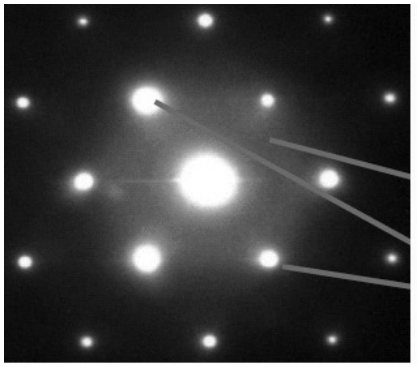
Diffraction mode

We see on the screen the diffraction image of the samples crystal lattice.



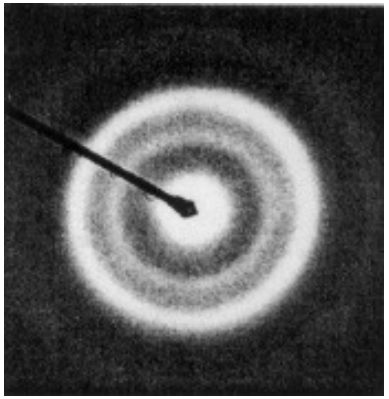
In the case of **policrystallinne sample**, since the diffraction angle is small, we see the continuous circles corresponding to the reciprocal lattice points.

In the case of **single crystal sample** we see the reciprocal lattice points of the crystal.



The spot in the center corresponds to the direct beam, and we also see the diffuse ring corresponding to the unelastically scattered electrons.

By using the diffraction aperture, we can obtain single crystal diffraction image even of a single crystal of a policrystalline sample. This is called selected area diffraction (SAD)



In the case of **amorphous sample**, we see diffuse rings corresponding to the Fourier transform of the pair correlation function.

Electron microscopy, TEM

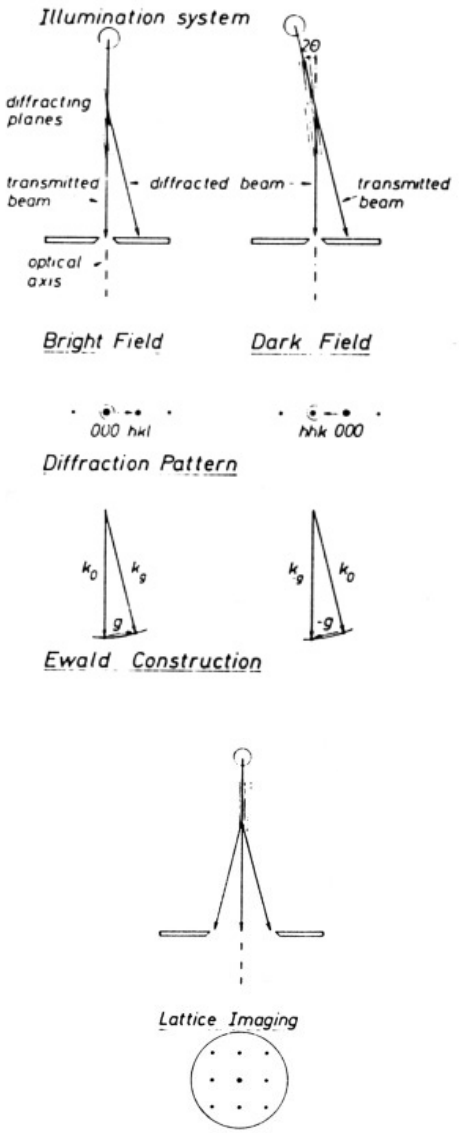
Imaging mode

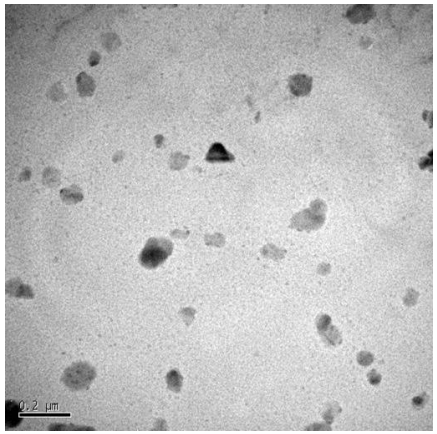
Three possible imaging:

- Bright field imaging. In this case only the direct beam is used for imaging. The contrast can be absorption or diffraction contrast.

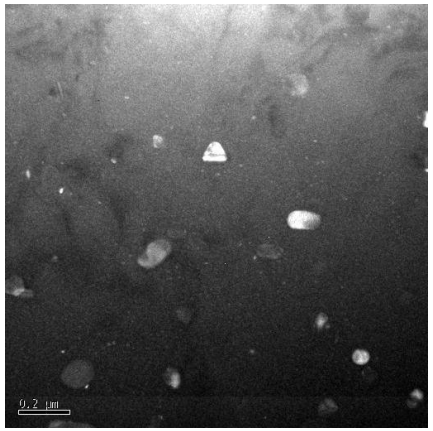
- Dark field imaging. In this case one elastically scattered beam is used for imaging. Theoretically it gives the same information.

- High Resolution Transmission Electron Microscopy (HRTEM).
- Several beams are simultaneously used for imaging.





Bright field image



Dark field image

Electron microscopy, TEM

High resolution image can be made only from thick sample ($t < 10\ nm$)

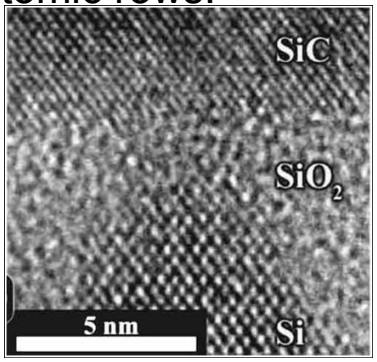
In this case neither the absorption, nor the diffraction contrast is not significant.

In the case of high resolution imaging, the different parts of the sample have different potential and the phase of the transmitted beam is changed. So in this case we see mostly the phase contrast.

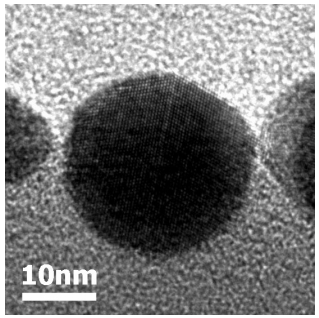
The resolution of the best microscopes is about $d \sim 0{,}1\ nm$.

In this case the lense aberrations are corrected, the source is energy filtered and the energy of the electrons is about $E = 300 - 400\ keV$.

On high resolution images we can clearly see the individual atoms and atomic rows.



Atomic rows of SiC and Si crystals

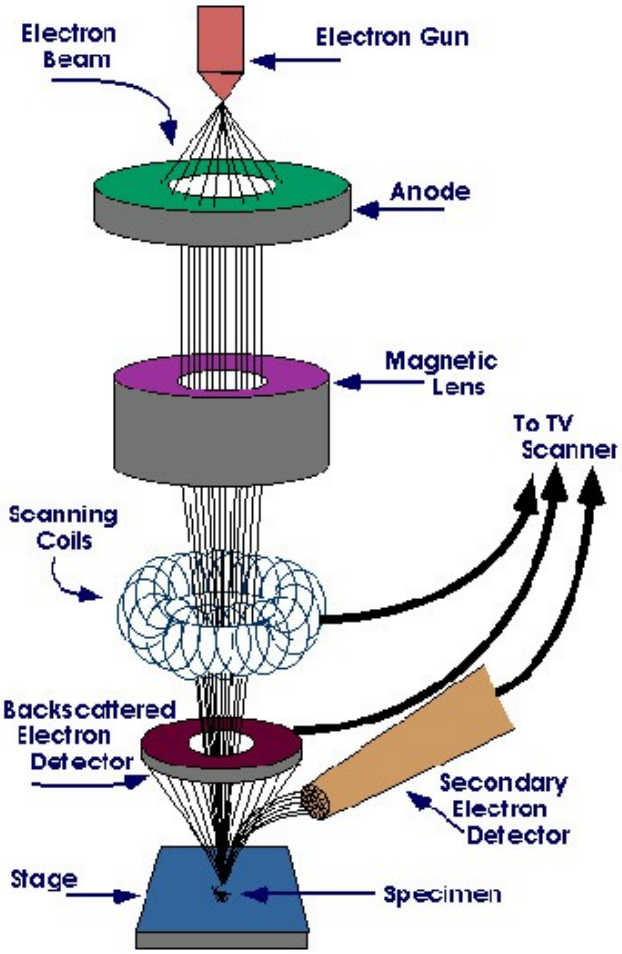


Au nanoparticle

Electron microscopy, SEM

Scanning electronmicroscope = SEM

The first microscope was built by Max Knoll in 1935.
The first commercial SEM was built in 1960.
Since then it is popular, more than 10000 is used in the world.
The SEM creates the image in a serial way, from point to point.



Source

The source is similar than in the TEM-ben, however the beam is not parallel, but it is is focussed into the sample.
The maximal energy of the electrons is usually *Emax = 30 keV*, and it can be adjusted (down) in most of the microscopes.

Electron beam

The diameter of the beam on the sample in the case of the best microscopes is about ~ *1 nm*.

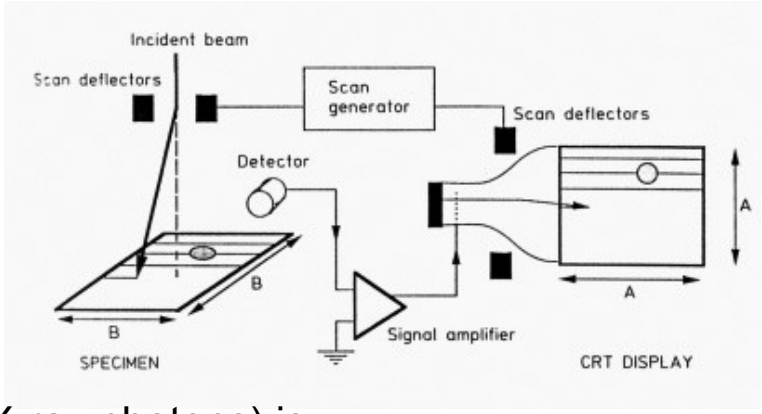
The beam is scanning the surface of the sample line by line.

Detected signals

In the SEM we can use the **secondary electrons** (SE), the **backscattered electrons** (BSE) and the **X-ray photons** for creating the image.

Electron microscopy, SEM

The principle of the imaging



The beam scanning the surface of the sample is controlled by a scanning generator.

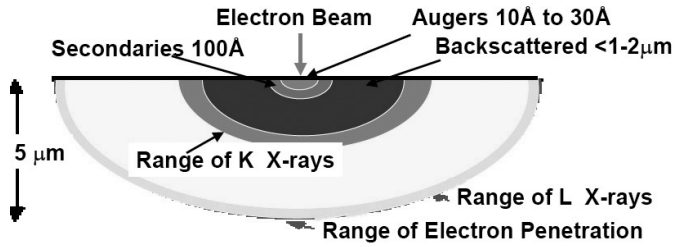
The same generator controls the intensity of the pixels of the screen point by point.

The intensity of the „products" of the beam (electrons or X-ray photons) is detected by special detectors. The signal of the detector modulates the intensity of the points of the screen.

If the emission of the surface of the sample is changing, than we see this change on the screen.

The energy of the „products" coming from the surface of the sample is different, this means that they are coming from different depth and volume.

This is determining the resolution together with the diameter of the electron beam.

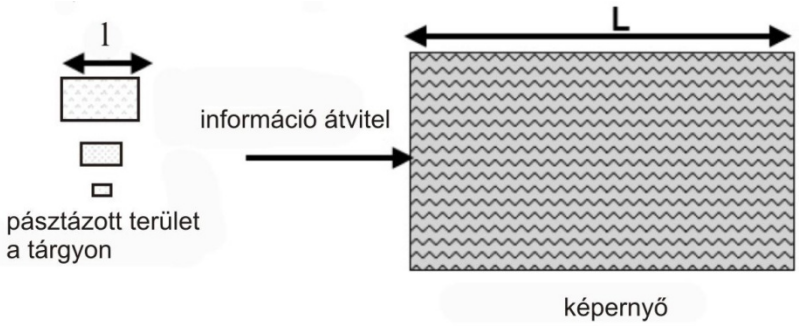


Electron microscopy, SEM

Magnification

The magnification of the SEM is determined mainly by the geometrical properties.

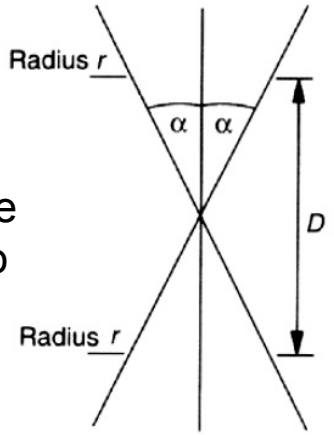
$$N = \frac{L}{l}$$



Maximal (useful) magnification:

$$N_{max} = \frac{képernyő\ \ pixekméret}{nyaláb\ mérete\ a\ mintán} = \frac{H}{nd}$$

E.g. in the case of *H=40* cm, *n= 10³* and *d = 1 nm: N = 4·10⁵.*



Depth of field:

$$D = \frac{2r}{\alpha}$$

The beam with diameter *2r* can be seen as a separate point on the screen, until its magnified image falls into one pixel of the screen.

$$2rN = K_p$$

K_p is the pixel size of the screen

$$D = \frac{K_p}{N\alpha}$$

We can see that the smallest is the magnification, the greatest is the depth of field. e.g. for K_p = *0,1 mm*, $N = 10^3$, $\alpha = 10^{-2}$
D = 0,01 mm = 10 μm.
For $N = 10^5$: $D = 10^{-4}$ *mm = 0,1 μm.*

Electron microscopy, SEM

Gemeral properties of the operation of SEM:

- We can examine thick samples too.
- It needs less preparation than the *TEM* samples.
- We have to remove the impurities from the surface of the sample before examination.
- During the SEM examination the surface of the sample is charged and we need to eliminate

In the case of **conductor samples** esetén a töltés a földelt mintatartón keresztül távozik.

In the case of **insulator samples** there are several possibilities for eliminating the charges.

1. the surface of the sample is often doped with a thin *Au* or *C* layer. The C layer has an advantage: since the C contains less electrons, it generates less background in the case of X-ray detection.

2. energy filtering of the detector signal
3. using low vacuum

Electron microscopy, SEM

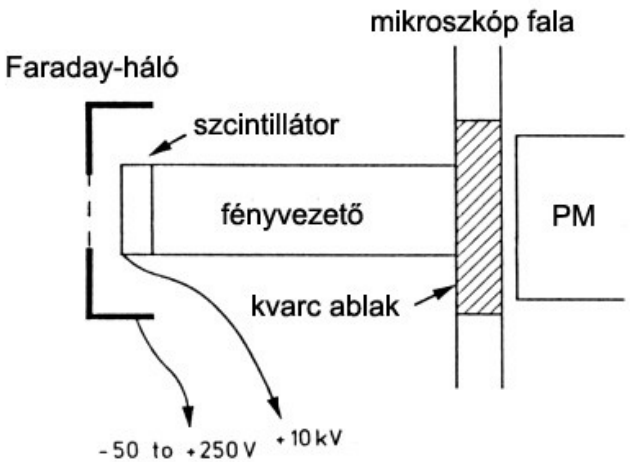
Properties of the secondary electron image

We use this in most of the cases.

The energy spectrum is broad, but the mean is low (*E < 50 eV*).

These electrons can reach the surface only from small depth (*~ 0,1 nm*).
The secondary electron image contains mainly information from a thin layer near the surface, therefore it is mainly used for morphology.

Because of their small energy, it is simple to collect the secondary electrons using a simple Everhart–Thornley detector.



A property of the secondary electron image is that in the case of low magnification, the depth of field is large.
In this case we can obtain 3D quality images.

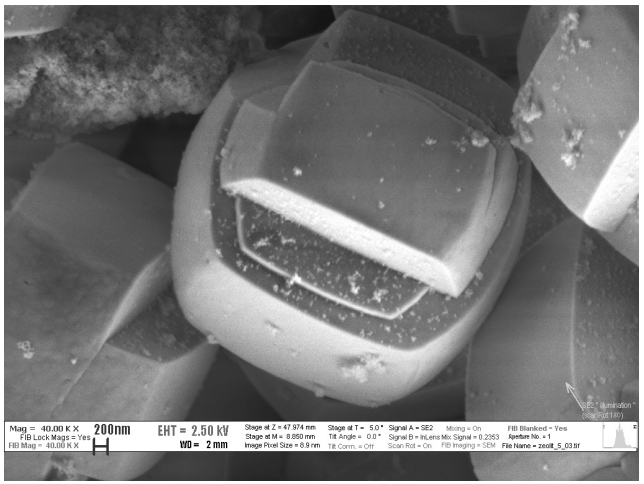


Image of a zeolite crystal, *N= 4·10*

Electron microscopy, SEM

Properties of the BSE image

The energy of the backscattered electrons is relatively large (*E ~ 10-30 keV*), their collection is harder, than in the case of the low energy secondary electrons.

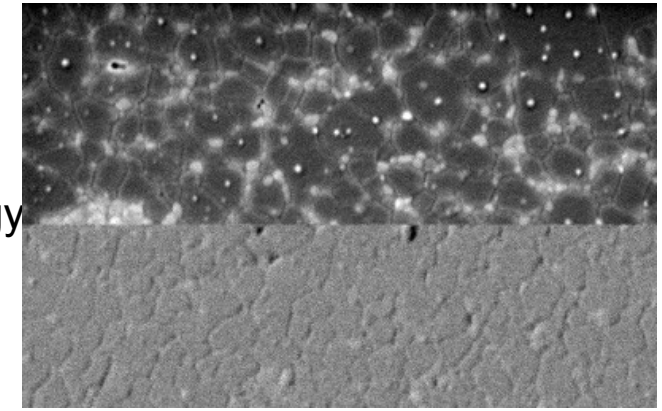
The BSE detector is usually a ring shaped semiconductor detector placed around the beam, or simply a conductor ring.

In the case of backscattered electrons, the excited region is larger than the diameter of the beam, therefore the maximal resolution is smaller than in the case of secondary electrons.

The BSE flux depends on the number of electrons of the scattering atom. Therefore the BSE image shows the so called ***Z*-contrast**.

In this image we see an *Al* sample containing *Zr* inclusions. The *SE* and *BSE* image is shown from the same region.

In the bottom in the *SE* image we see the surface morphology in the upper *BSE* image showing Z-contrast, we clearly see the *Zr* inclusions.



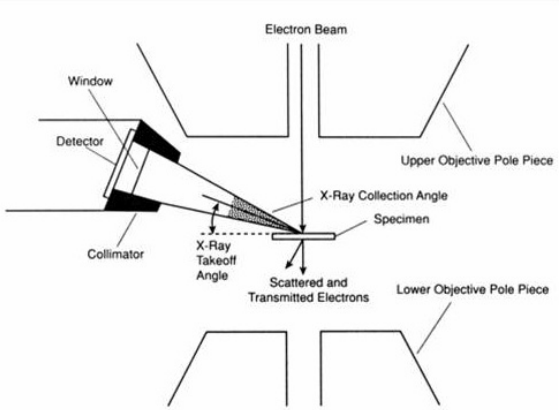
Electron microscopy, SEM

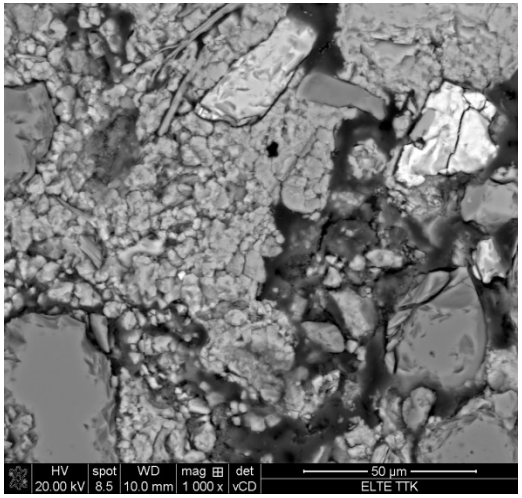
X-ray photon detection

Using an X-ray detector, we can detect the X-ray photons induced by the electron beam. The energy of the X-rays is characteristic to the source atom.

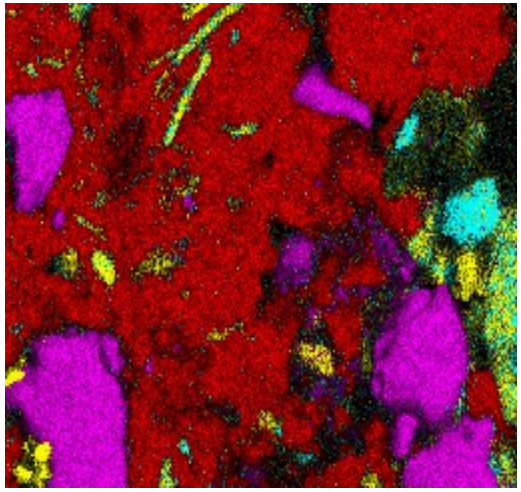
The obtained spectrum characterizes the atomic composition of the sample

This is the basis of the energy dispersive X-ray microanalysis = *EDX*.



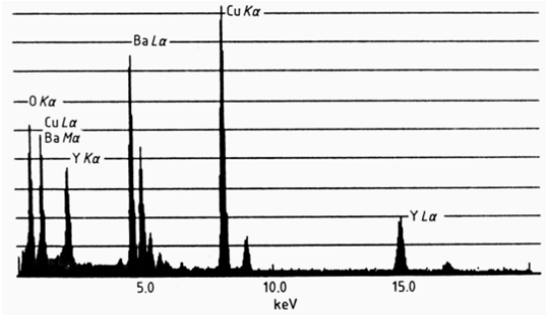


BSE electron image



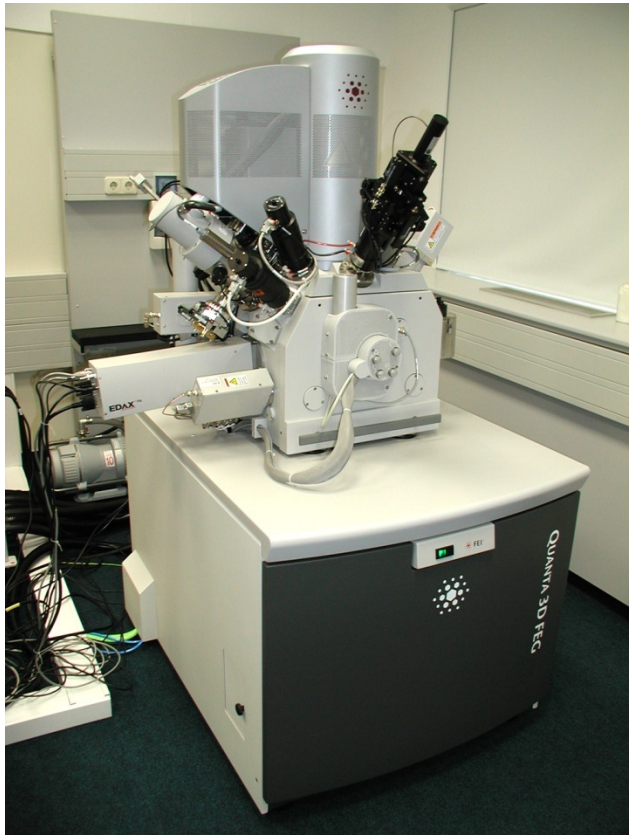
X-ray element map

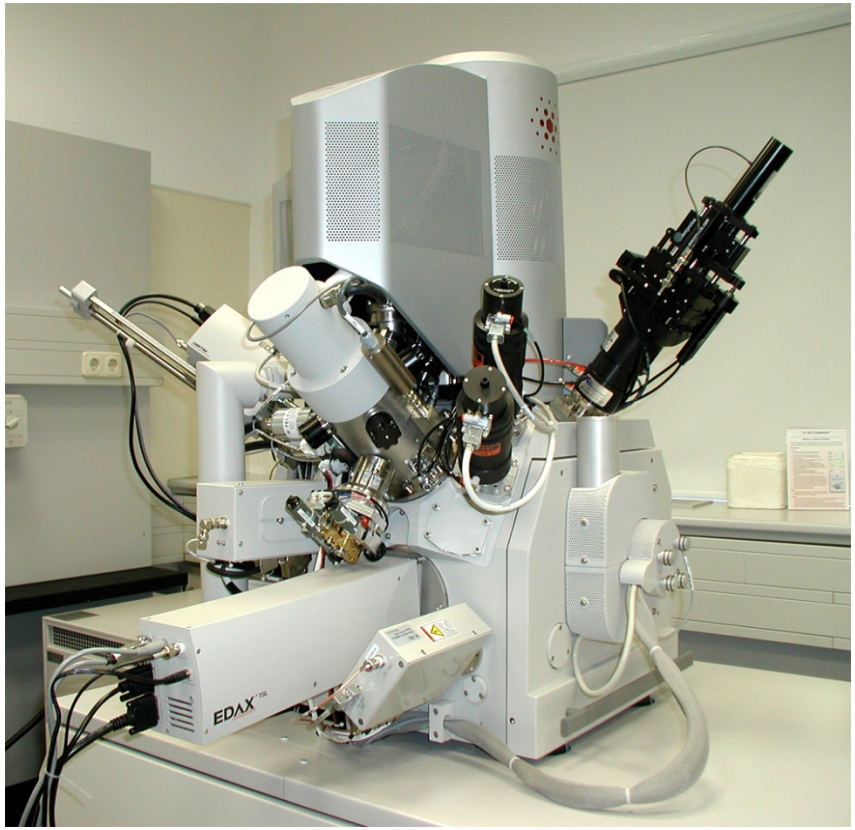
Example for creating an element map



EDX spectra for $YBa_2Cu_3O_7$ high temperature superconductor

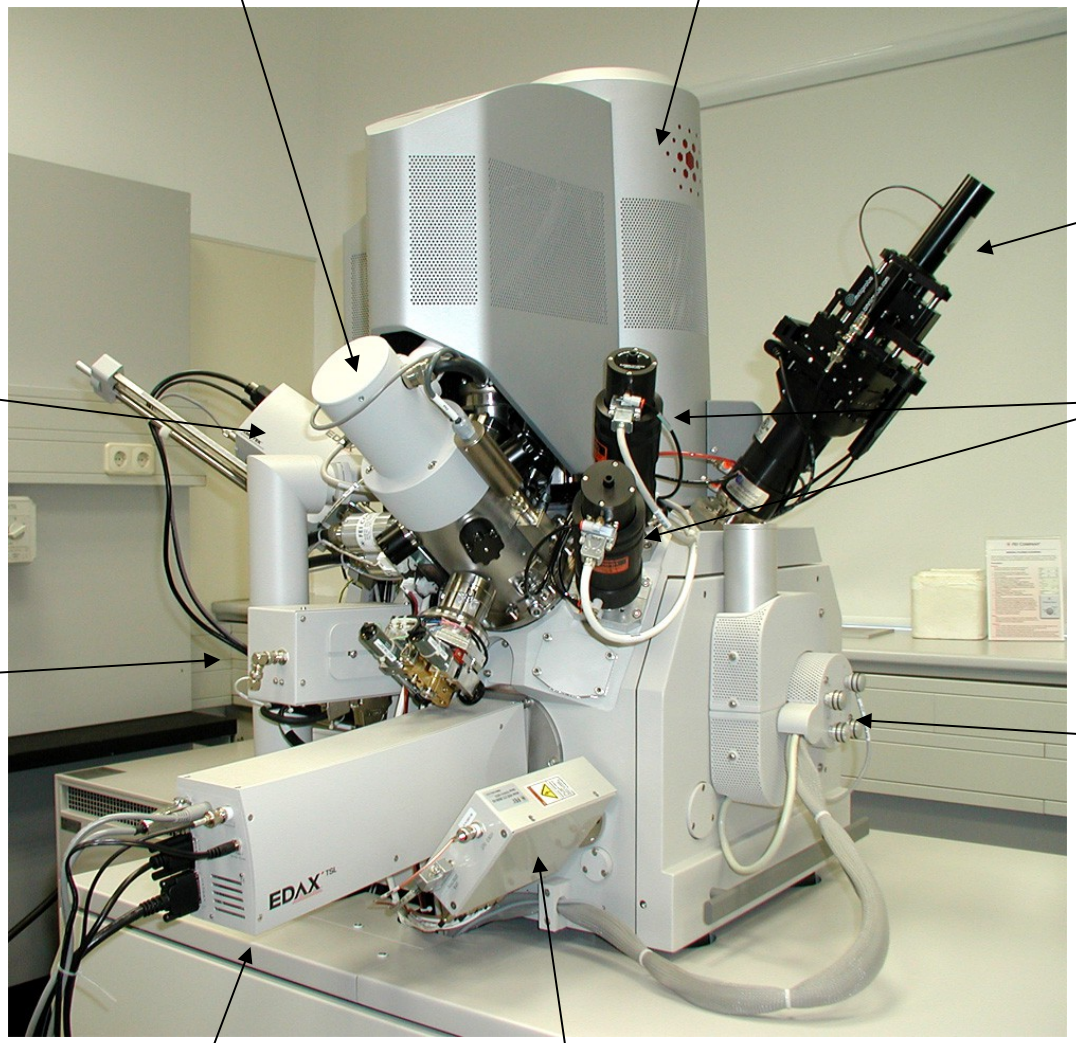
FEI Quanta 3D SEM/FIB



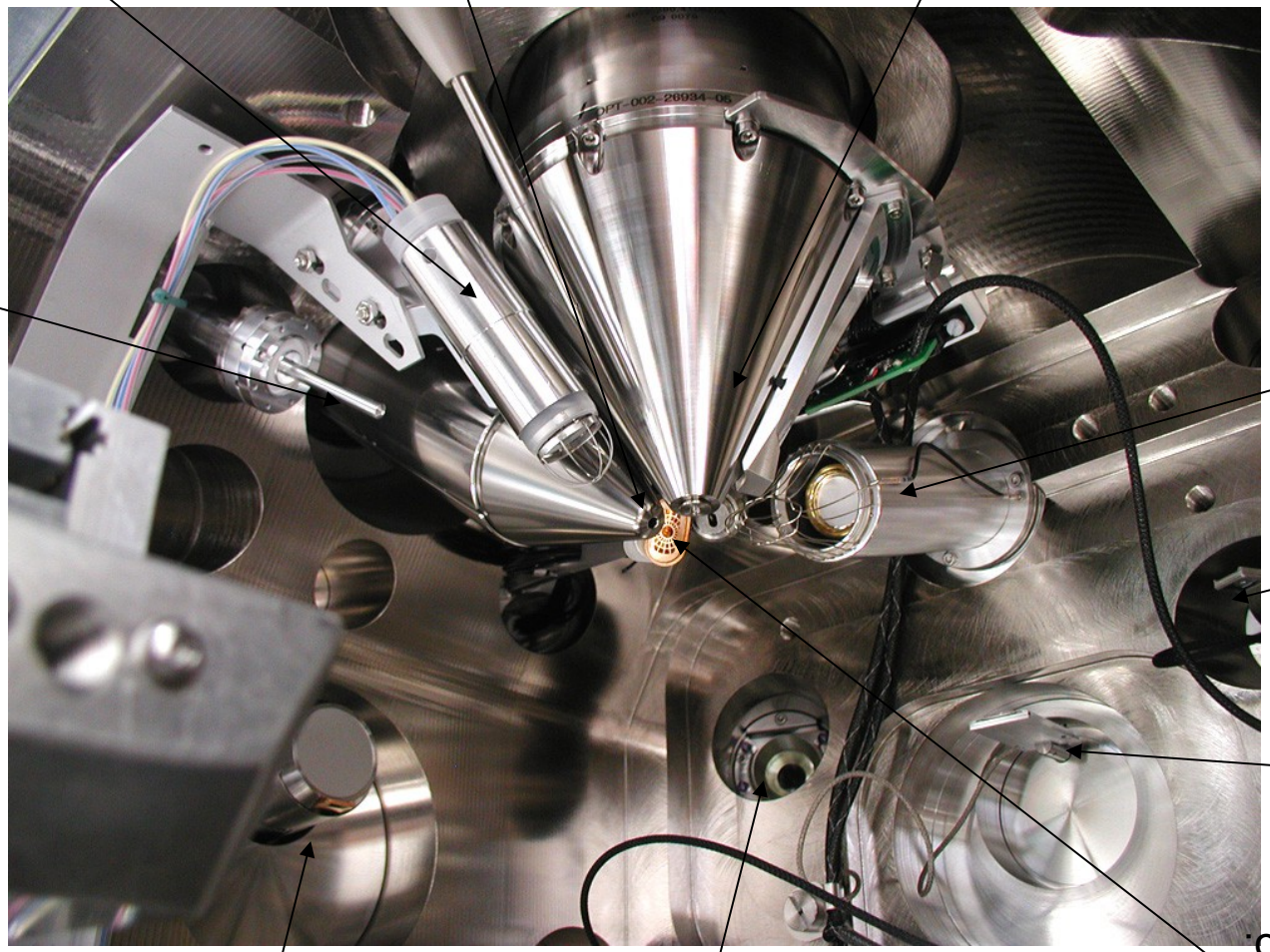


The new device of ELTE TTK Materials Science Center:
FEI (Philips) Quanta 3D SEM/FIB

FEI Quanta 3D SEM/FIB



FEI Quanta 3D SEM/FIB



Scanning tunneling microscope, STM

Scanning probe microscopes

There are several types of SPM microscopes.

Among these, we will study the STM and AFM.

Scanning tunelling microscope = STM

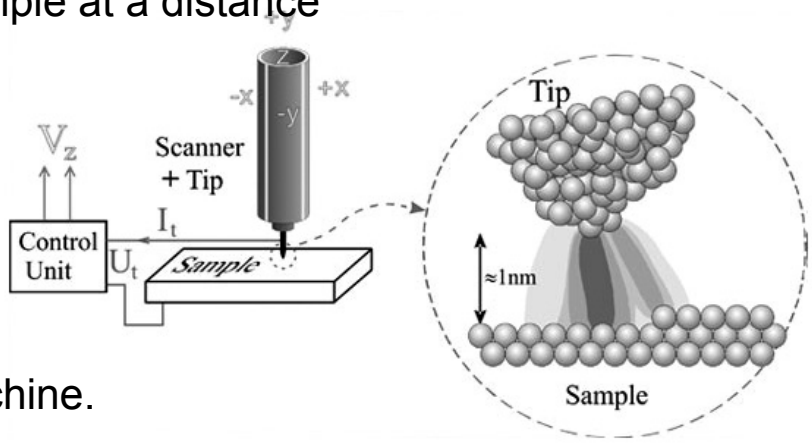
Binnig and Rohrer (physicists in Switzerland) developed in 1982, received the Nobel-prize in 1986.

The *STM* can create high resolution images of the surface of conducting materials.

Working principle

A sharp needle is moving above the surface of the sample at a distance of about 1 *nm* and is scanning the surface line by line.

Ẇe apply a tension of about a few *V* between the tip and the sample. Due to the tunneling effect (known from quantum mechanics), a tunneling current will flow between the tip and the sample.



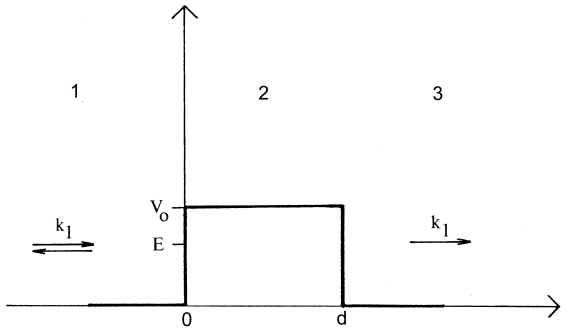
We can achieve even athomic resolution with this machine.

Scanning tunneling microscope, STM

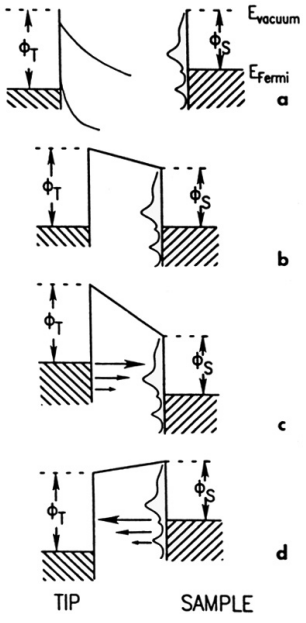
Basic facts of quantum mechanics

The probability of 1→3 transition: $P = \frac{j_3}{j_1} \sim e^{-2\kappa d}$

$\kappa^2 = \frac{2m(V_o - E)}{\hbar^2}$, m is the mass of the electron.



In the case of metals, the electrons are in a potential trap of height Φ.



If the two metals are close enough to each other, a contact potential is created and due to the tunneling effect a current will flow until the Fermi levels are lined up and equilibrium is reached.

If we apply a voltage U_t between the tip and the sample, then we shift the Fermi-levels by eU_t energy.

If $U_t < 0$, then the Fermi level of the tip is shifted up.

If $U_t > 0$, then the Fermi level of the tip is shifted down.

Scanning tunneling microscope, STM

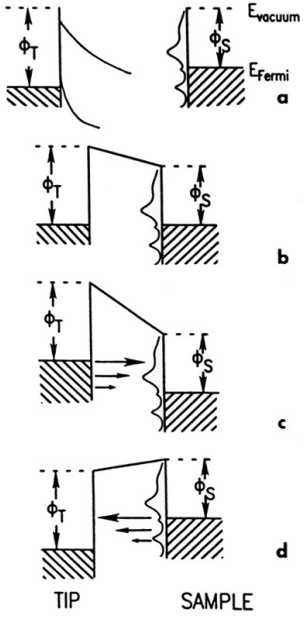
Due to the Pauli principle, the current may flow only from filled shells to unfilled shells, and the current is proportional to the difference of the density of state = DOS functions between the filled and unfilled shells.

We suppose only elastic tunneling effect.

The current between the tip and the sample is equal to the sum of the currents between all energy levels and can be expressed with an integral between E_F and $E_F + eU_t$.

$$I_t \sim \int_{E_F}^{E_F + eU_t} P(E) D_t(E - eU_t) D_s(E) dE$$

$$I_t \sim e^{-2\kappa d}$$



There is a very strong dependence on the distance.
E.g. if the sample to tip distance is $d = 1\ nm$ and the current is $I_t = 1\ nA$, and if d is increased by $\Delta d = 0{,}1\ nm$-t nő, then the current changes to: $I_t = 0{,}13\ nA$.

The atomic resolution is possible due to this strong dependence on distance.

Scanning tunneling microscope, STM

If the voltage U_t is small, then the probability P is independent of the energy.
We can choose the metal of the needle so that its electron density function is constant near the Fermi energy.

In such case:

$$I_t \sim \int_{E_F}^{E_F + eU_t} D_s(E)dE$$

We also see that:

$$\frac{\partial I_t}{\partial U_t} \sim D_s(E)$$

If we swith off scanning, the needle is hold in the same position, and we change the voltage and measure the tunneling current, then the derivative of the so obtained curve will be proportional to the electron density function of the sample at that point.

This is the basis of the tunneling spectroscopy.

Scanning tunneling microscope, STM

Schematics and working principle of STM machine

The needle is moved by using a cylinder made of pieso electric material.

The pieso effect can be described by a tensor.
The order of magniude of the elements of the tensor: *~ 1 nm/V*

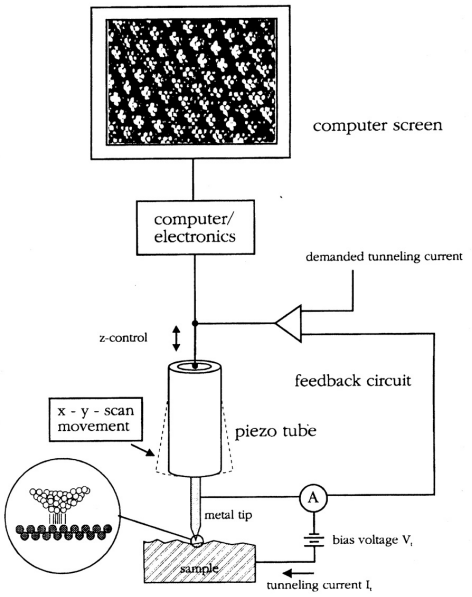
We can move in *x, y, z* directions.

The needle is usually made from *Pt-Ir* alloy.

In order to keep constant the parameters (e.g. constant current mode) we need a feedback circuit.

The microscopic image is created serially.

The voltage can be changed in the *mV – V* range



Scanning tunneling microscope, STM

NT-MDT (russian)

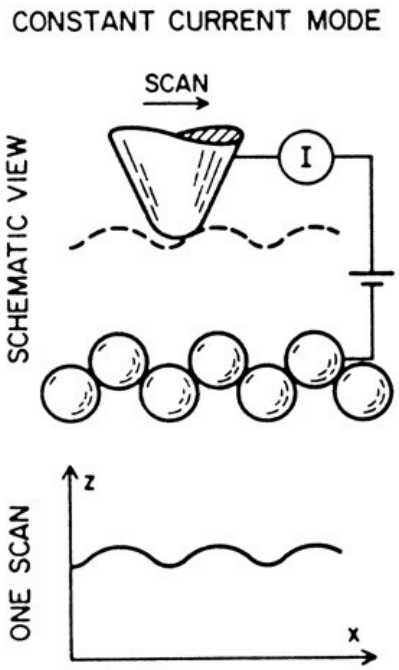
Veeco (USA)

Scanning tunneling microscope, STM

Operating modes of STM

Constant current mode

The feedback keeps constant the current.
The height changes of the surface is followed by the tip.
The tip height *z* is plotted as a function of *x – y.*



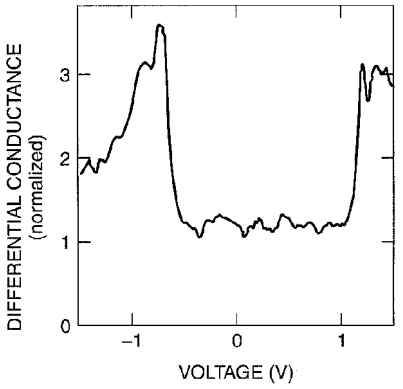
Constant height mode

The feedback is switched off.
The position of the tip is constant.
The current *I* is plotted as a function of *x – y*.

Spectroscopic mode

The scanning is switched off. The voltage U_t is changed.

We measure $\frac{\partial I_t}{\partial U_t} \sim D_s(E)$ as a function of U_t .



Electron density function of metallic C nanotube

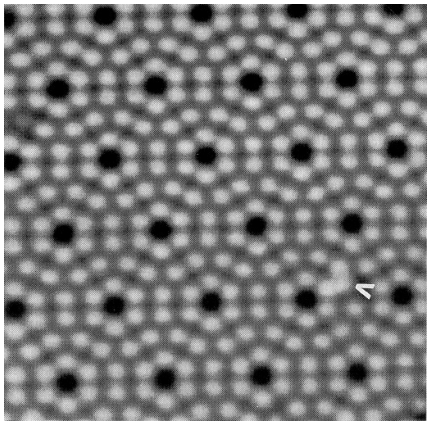
In the case of the best newest *STM* machines:
maximum **horizontal resolution** ~ *0,1 – 0,2 nm*,
maximum **vertical resolution** ~ *0,04- 0,05 nm*.

Scanning tunneling microscope, STM

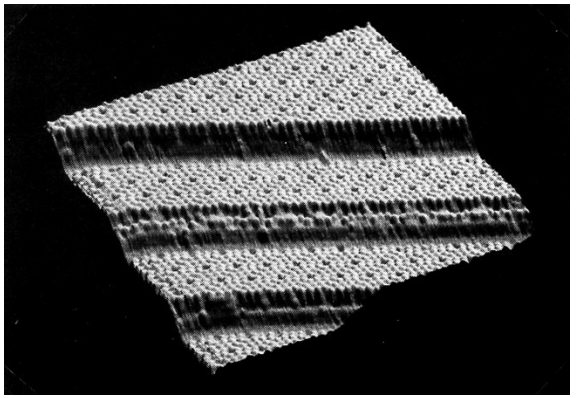
Properties of the STM

- Each setup, recording and image processing is controlled by the computer.
- The machine is sensitive to mechanical noises, we have to use noise filtering.
- Only conducting materials can be examined by STM.
- The purity of the surface is needed. The layer structured materials (e.g. graphite) can be easily examined.
- The oxidizing materials (e.g. *Si*) can be measured only in vacuum.

Examples:



7 x 7 reconstruction of *Si* (111) plane



Steps on the surface of *Si* sample

Atomic Force Microscopy

Atomic force microscope

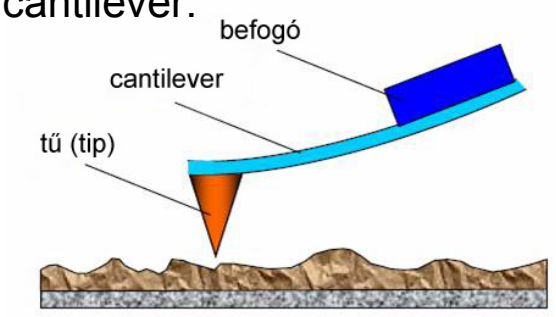
The AFM was developed based on STM technique.

In general, the same machine is used for STM and AFM operating modes, only the measuring head should be changed.

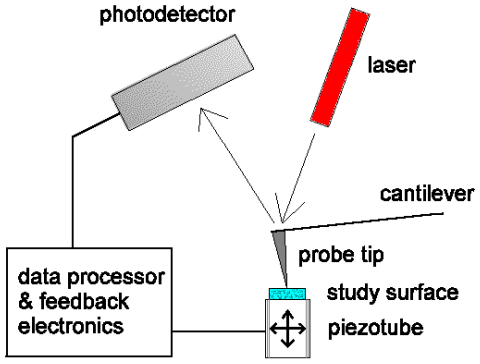
Here also a sharp needle is moving in the nm proximity of the sample. We measure the force acting between the tip and the surface of the sample.

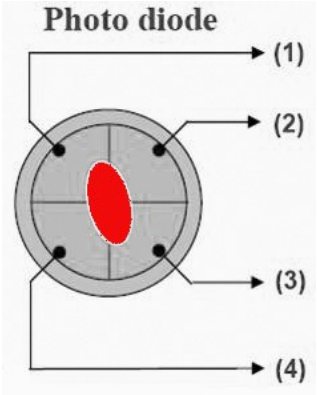
The *AFM* tip is placed at the end of a cantilever (elastic holder).

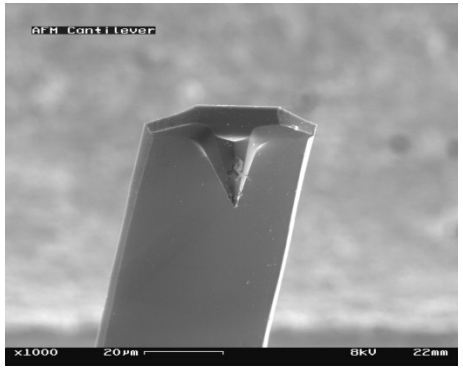
The force acting on the tip is measured by the deformation of the cantilever.



A laser the beam is reflected from the surface of the cantilever and the deformation is measured by a photo diode divided into four sections.

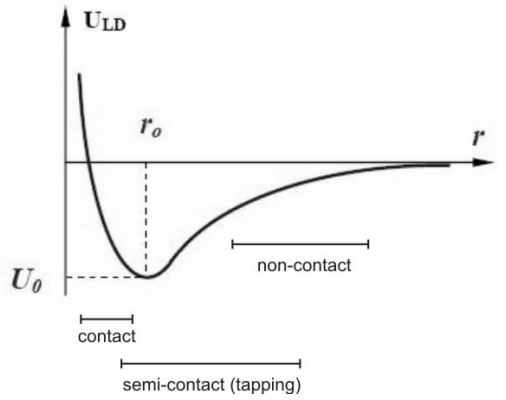






Atomic Force Microscopy

AFM operating modes



Non-contact mode:
In the first approximation the Lennard–Jones potential describes the Interaction between the tip and the sample:
($F = -grad\ U_{LP}$).

In the non-contact mode the tip is moving above the surface of the sample in a distance of about *1-100 nm*. Here the main acting forces are the Waals (attractive) forces.

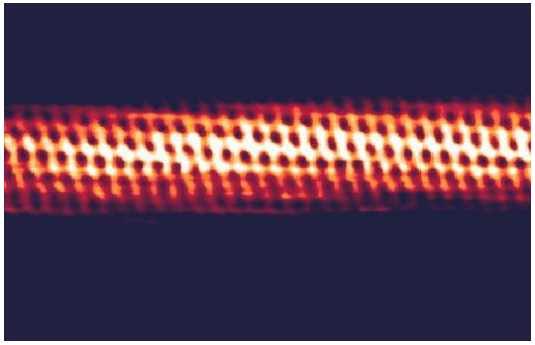
The force between the tip and the sample can be:
electrostatic force (attractive – repulsive),
magnetostatic force (attractive – repulsive),
Capillary force (attractive – repulsive).

Contact mode

In the contact mode the distance between the tip and sample < *1 nm*.

Here the forces are repulsives.
Reason: Coulomb forces between the partially overlapping nuclei and the Pauli principle.

Since the gradient of the curve is the highest here, we can also achieve atomic resolution.



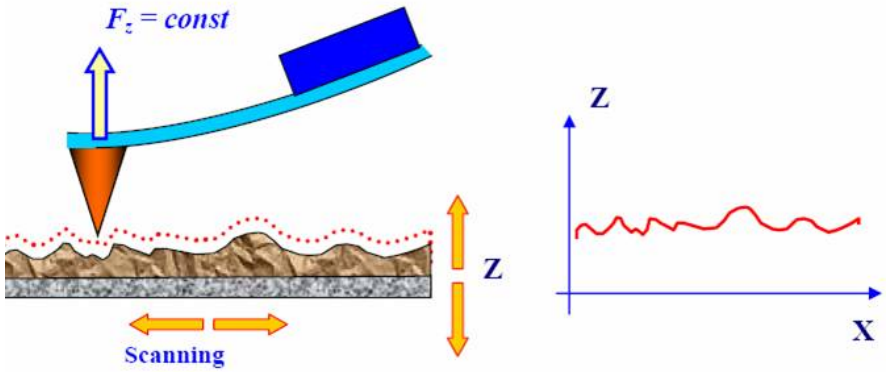
Szén nanocső mérése kontakt módusban

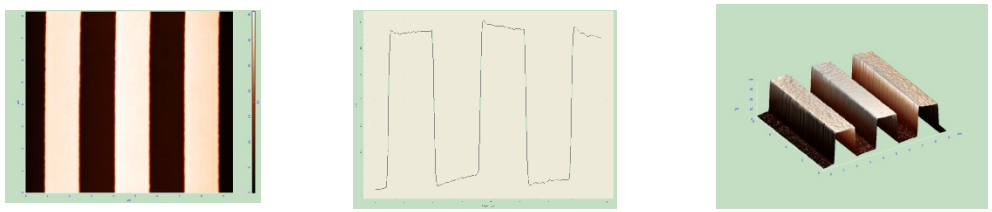
Atomic Force Microscopy, AFM

The most used operating mode either in contact or non-contact mode is the **constant force mode**.

The feedback electronics keeps constant the force acting between the sample and tip by changing the z tip to surface distance.

The microscopic image is created by plotting the *z(x,y)* function.





Contact mode measurement of calibration grid (2D, intersection, 3D)

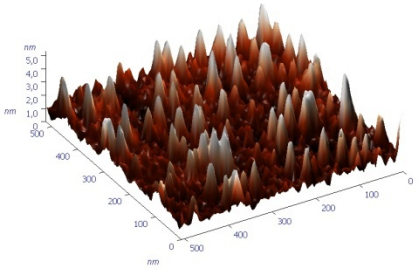
Atomic Force Microscopy, AFM

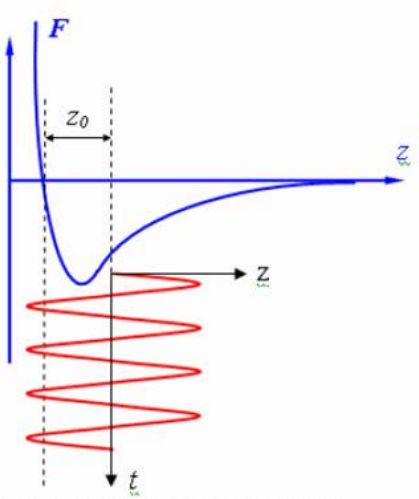
Dynamic mode (semi-contact, tapping mode)

The cantilever is vibrating with its natural frequency (eigenfrequency) and the amplitude of the oscillation is large enough to enter in the contact region (so it is tapping on the sample) for a short period during each cycle.

This mode is favorable, since the interaction is short, so the surface of the sample is usually not harmed, unlike in the case of contact mode, where the contact is constant.

We can register the **change in the amplitude**, or the **change of the phase**, and it is plotted as a function of the *x-y* coordinates of the sample.





Contact mode measurement of nanostructures of ion implanted Al_2O_3 (sapphire) sample