EPFL

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Physical and Chemical Analyses of Materials

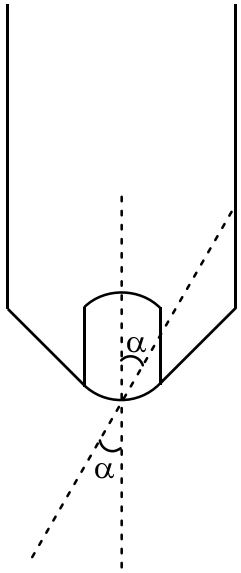
Overview on microscopic analyses

Introduction

⇨ The analysis of materials can be realised using either optical or electron microscopy.

⇨ The lateral resolution depends on the wavelength used to perform the microscopy and so, characterises also a microscopic method.

microscope objective



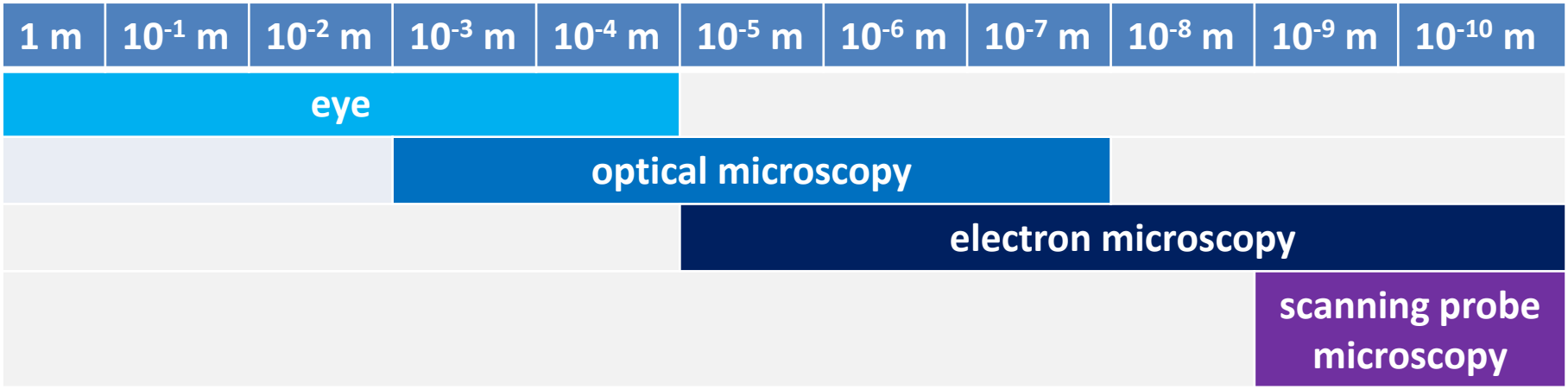
↳ The lateral resolution **d** is given by:

$$\mathbf{d} = \frac{\mathbf{0.61\lambda}}{\mathbf{n \sin \alpha}}$$

↳ **λ** is the wavelength (m), **n** is the refractive index between the lens and the observed object and **α** is the half-angle of the light cone entering the lens.

↳ To improve the resolution **d**, one can decrease the wavelength **λ** and/or increases **n** and/or **α**.

⇨ Below is presented the lateral resolving power of the different microscopies:



⇨ Here is given the resolution for different wavelengths:

↳ optical microscopy: $\boldsymbol{\lambda} = 5000$ Å, $\boldsymbol{\alpha} = 1$ rd, $\mathbf{n} = 2$, $\mathbf{d} \approx 0.15$ µm

↳ electron microscopy at 100 keV: $\boldsymbol{\lambda} = 0.037$ Å, $\boldsymbol{\alpha} = 5\times10^{-3}$ rd, $\mathbf{n} = 1$, $\mathbf{d} \approx 4.5$ Å

Optical microscopy

Optical microscopy in the visible domain

⇨ The microscopy can be carried out either in transmission or in reflexion. The detection is made by eye or by a camera (for more details, see the given literature review).

⇨ For both modes, the sample must be as flat as possible to provide a sharp image.

⇨ The resolution for a wavelength of 500 nm is about 0,15 µm.

⇨ This type of microscopy can be coupled to IR-S or Raman-S

⇨ The transmission mode:

⇩ The sample must be thin and transparent.

⇩ This mode gives rise to a structural analysis.

⇨ The reflexion mode:

⇩ The sample can be thick and poorly transparent.

⇩ This mode gives rise to a surface analysis with white light or to a structural analysis with polarised light.

Optical microscopy with soft X-Rays

⇨ The microscopy is carried out in transmission. The detection is made by a CCD camera.

⇨ The beam (from 0.1 to 5 µm size) crosses the sample and the image is obtained from the beam absorption difference.

⇨ The resolution is about 30 nm when using a Fresnel zone plate lens.

⇨ This technic provides a structural analysis.

⇨ This type of microscopy can coupled to XRFS.

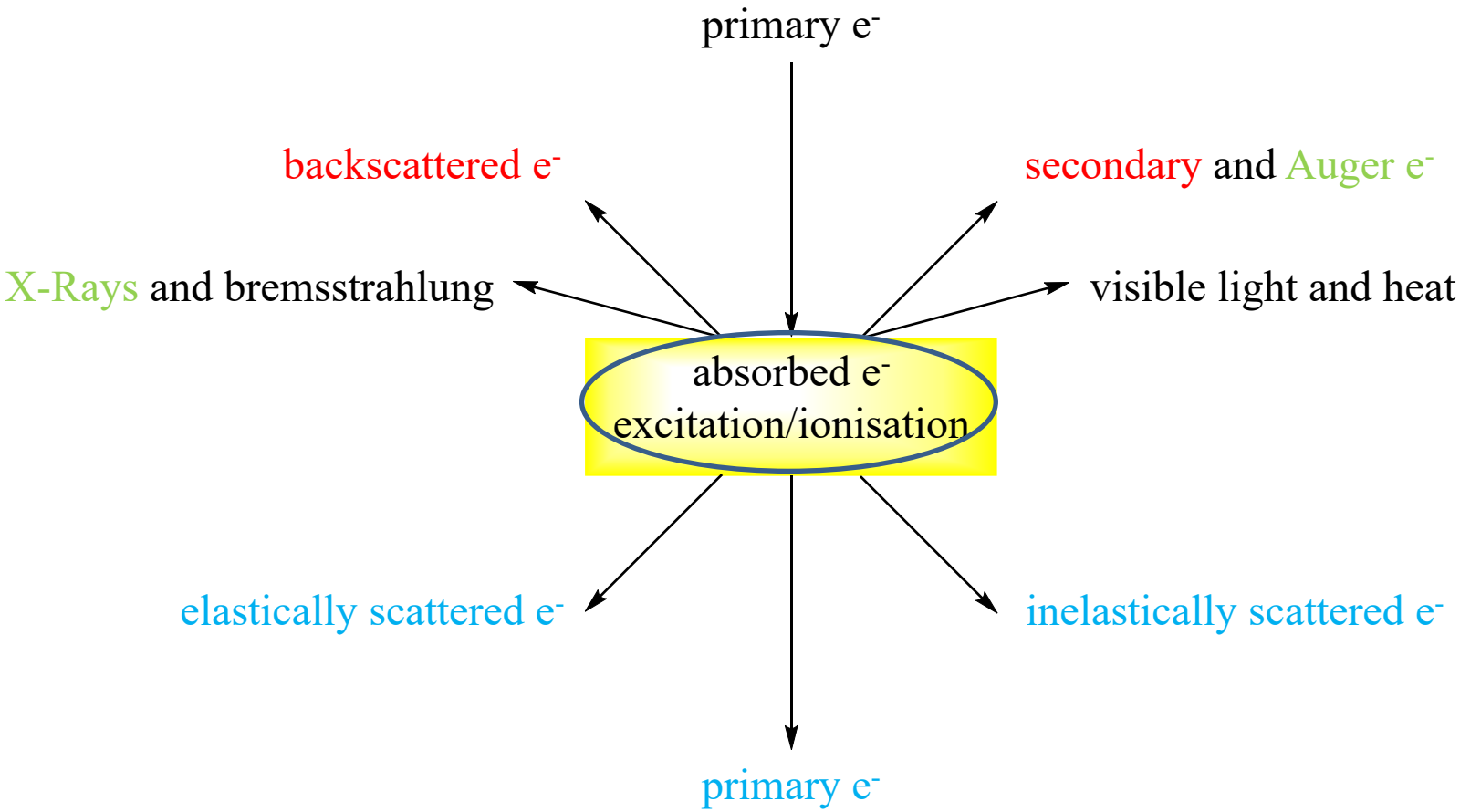
Electron microscopy

⇨ The microscopy can be carried out either in transmission (TEM) or by scanning (SEM). The detection requires specific detectors because one has to analyse electrons emitted from the sample.

⇨ The resolution depends on the electron beam energy: for $\mathbf{E_0}$ = 100 keV, **d** = 0.45 nm and for $\mathbf{E_0}$ = 1000 keV, **d** = 0.1 nm.

⇨ Electron microscopy can be coupled to XRMA and/or AES.

⇨ We can approach SEM, TEM and spectroscopy through the following scheme:



⇨ The matter modifications can be used for analytical purposes.

↳ The analysis of Auger electrons can give rise to a chemical image of a given element at the surface.

↳ The analysis of X-Rays provides a bulk chemical analysis of the studied material.

⇨ Electron microscopy is not an non-invasive method because of the inelastic scattering (excitation/ionisation) and the elastic scattering processes (thermal and chemical effects, atomic displacements) which affect the sample.

⇨ The analysis is normally realised under vacuum.

↳ For wet materials and/or materials which do not support vacuum (gels for example), atmospheric pressure SEM and TEM are available. These technics are somewhat less common.

Transmission Electron Microscopy: TEM

⇨ In this mode, only thin samples ≈ 100 nm thick at the maximum can be analysed.

⇨ In contrast with optical microscopy, the sample can exhibit a big relief.

⇨ As the analysed electrons are the transmitted ones, a sufficient electrical conductivity of the sample is not mandatory, insulating materials can be directly analysed.

⇨ The sample is deposited on a conducting grid made of Cu, Ni, Ag, Au, Pt…

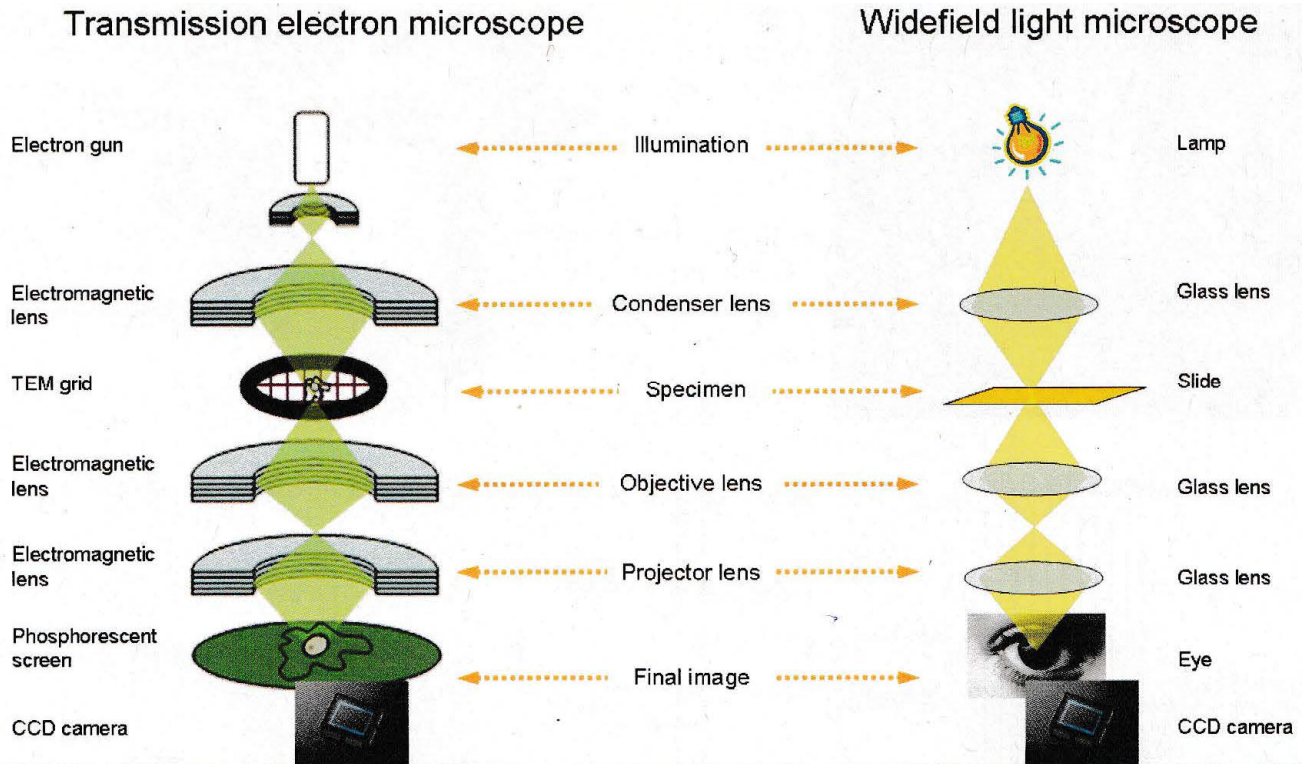
⇨ The analysis is based on both scattered and non-scattered transmitted electrons.

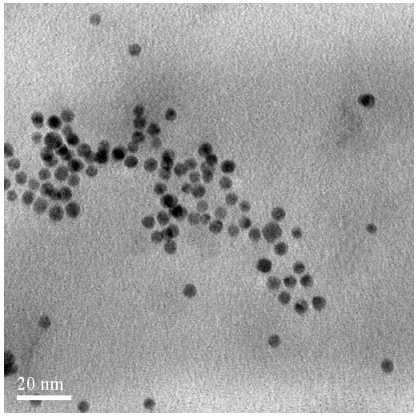
⇨ The analysis is realised in a static mode. To obtain some information from bigger surfaces a scanning mode is also available: STEM

⇨ This mode gives images and mostly structural information including the thickness measurement of the analysed material.

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

⇨ TEM could be compared to transmission optical microscopy:





TEM image of synthesised gold nano-particles: I. Arnaud, J.P. Abid, C. Roussel and H.H. Girault, *Chemical Communications*, **2005**, *6*, 787-788.

Scanning Electron Microscopy: SEM

⇨ In this mode, there is no requirement regarding the samples thickness as it concerns surface imaging. The sample can exhibit a big relief but should be conducting enough to prevent from charging effects that defocuse the primary electron beam (primary electrons reflected by the sample).

⇩ If the material is not conducting enough, deposition of a conducting film (Au or C) on the material and/or performing the microscopy at low beam energy is feasible. The nature of the deposited film must be taken into account when chemical analyses are realised (interferences).

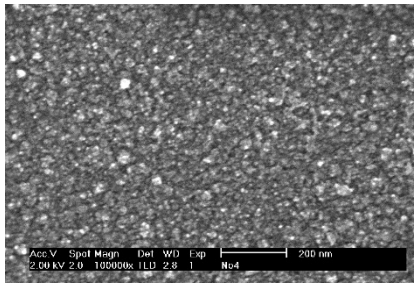
⇨ The depth of field varies from a few centimeters at low magnification, to a few micrometers at the maximum magnification. For thin samples 10 – 100 nm, transmitted electrons can be analysed to obtain also some structural information about the material.

⇨ The sample is deposited and stuck to a specimen 3-axes holder using a conductive adhesive.

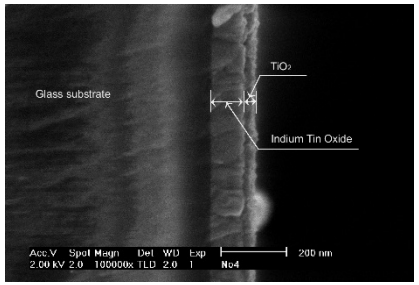
⇨ The analysis concerns both secondary and backscattered electrons. This mode gives surface images and allows also the determination of the surface topography.

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

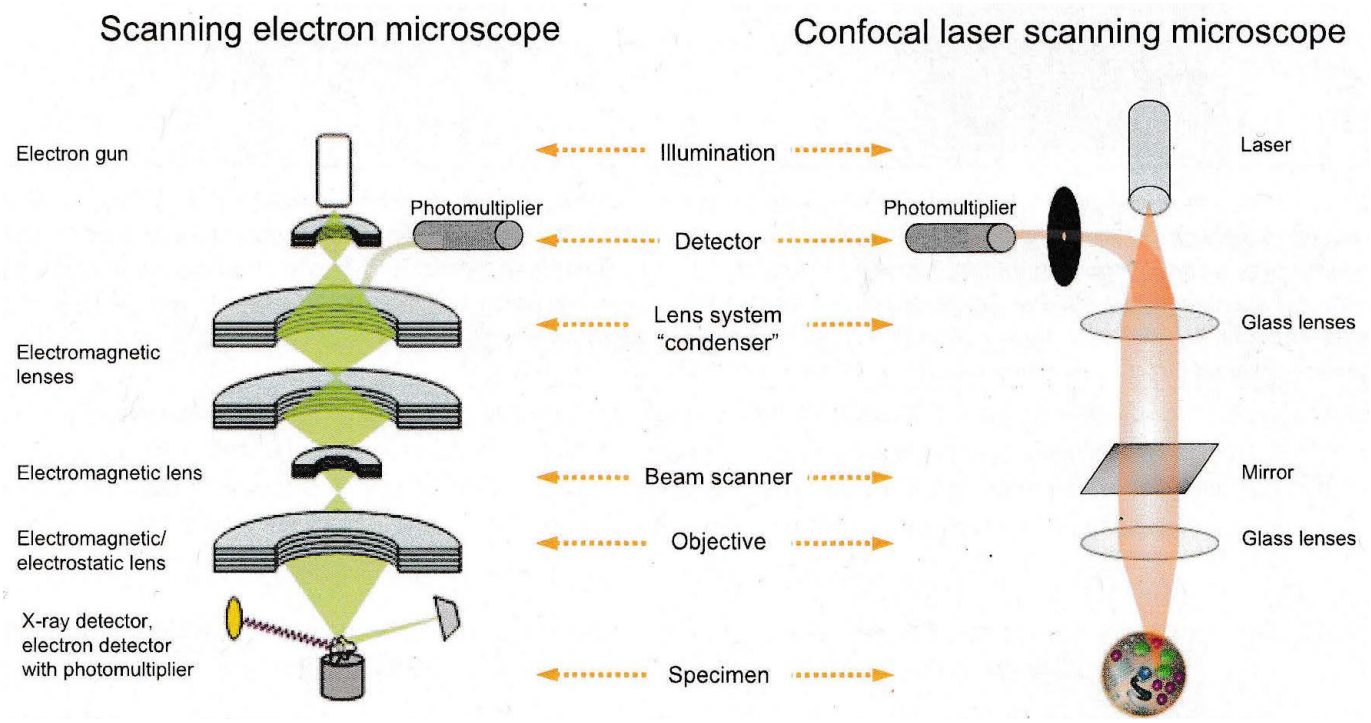
⇨ SEM could be compared to reflexion optical microscopy:



Top view



Cross-section view



SEM images of a TiO_2 layer generated at the surface of an ITO electrode: J.F. Liu, C. Roussel, G. Lagger, P. Tachini and H.H. Girault, *Analytical Chemistry*, **2005**, *77*, 7687-7694

Scanning probe microscopy

⇨ In the following, the term scanning probe microscopy will refer to Scanning Tunnelling Microscopy (STM) and Atomic Force Microscopy (AFM).

⇨ Both technics use stylus-type instruments in which a sharp probe scans the material surface to detect some changes in the surface structure at the atomic level.

⇨ The stylus moves up and down according to the surface topography.

Scanning Tunneling Microscopy: STM

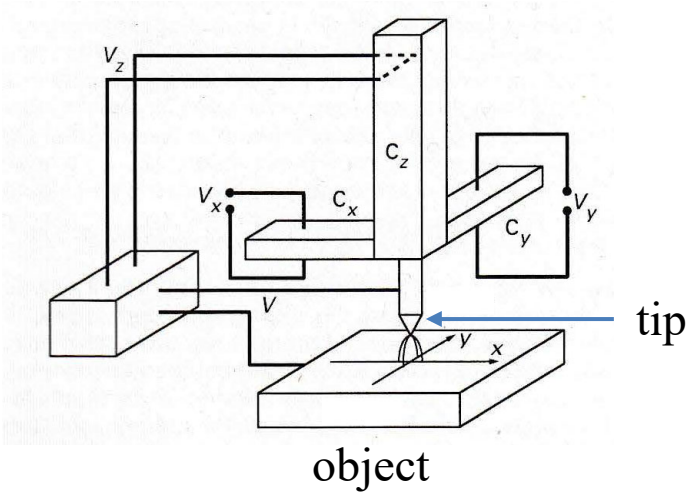
⇨ In STM, the surface electronic density of a conductor or semi-conductor is measured by tunnelling effect.

⇨ A potential is applied at the tip approaching the surface and the tunnelling current is recorded.

⇨ For materials having relative uniform electronic properties, STM provides an image which represents the surface topography.

⇨ STM presents a maximum lateral resolution of 0.1 nm.

⇨ Below, a synoptic scheme of an STM microscope:



↳ The tip moves along the **x** and **y** axes.

↳ The sharp probe is set at a potential **V** versus the object and the tunnelling current is recorded.

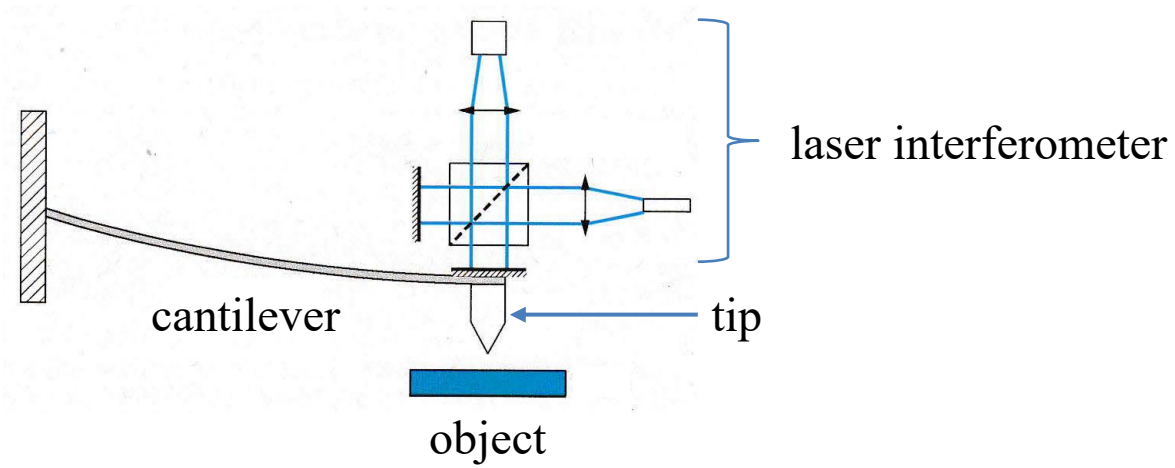
↳ Fine control of the tip position is achieved by means of piezoelectric crystals $\mathbf{C_x}$, $\mathbf{C_y}$ and $\mathbf{C_z}$.

Atomic Force Microscopy: AFM

⇨ AFM allows the surface analysis of conducting, semi-conducting and insulating materials.

⇨ AFM presents a typical lateral resolution of 0.1 nm.

⇨ The tip is fixed to a cantilever:



↳ The object moves along the **x** and **y** axes.

↳ The tip stays at a fix position.

↳ The deflection of the cantilver determines the surface topography.

↳ The deflection is measured with a laser interferometer.

⇨ AFM can operate under different modes: contact, resonating, tapping, pulsed, friction…