EPFL

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Physical and Chemical Analyses of Materials

Surface characterization: physical aspects

Introduction

⇨ The 3D measurement of the microgeometry is nowadays the best method to characterise a given material surface.

↳ Its precise measurement allows the identification and the quantification of surface irregularities.

↳ It also allows to draw some correlations between the surface microgeometry and its physical properties.

⇨ Surface microgeometry gathers surface morphology, surface topography and specific surface area.

↳ Morphology relates to the qualitative evaluation of the 3D-shape of a material surface

↳ Topography relates to the quantification of the characteristics of a material surface

↳ Specific surface area relates to the available surface of material per mass unit

⇨ Usually, surface morphology is studied by STEM and SEM, surface topography is explored by AFM and optical profilometry and finally, the specific surface area is obtained from BET measurements.

Surface characterization: physical aspects

⇨ Surface morphology gives some clues about the homogeneity of the studied material including chemical and / or physical aspects.

↳ Surface chemical heterogeneities can come from the migration of an alloy compound from the bulk to the surface, surface reconstruction in the presence of an adsorbed chemical compound…

↳ Surface physical heterogeneities can relate to various crystal orientations, layer by layer depositions of different geometric structures…

⇨ Surface topography gives some clues about the corrugation amplitude, the defects frequencies, the pattern of surface features, the roughness….

↳ Surface topography determination finds applications in various fields like friction, wear, lubrication, sealing, reflecting, painting, optical properties…

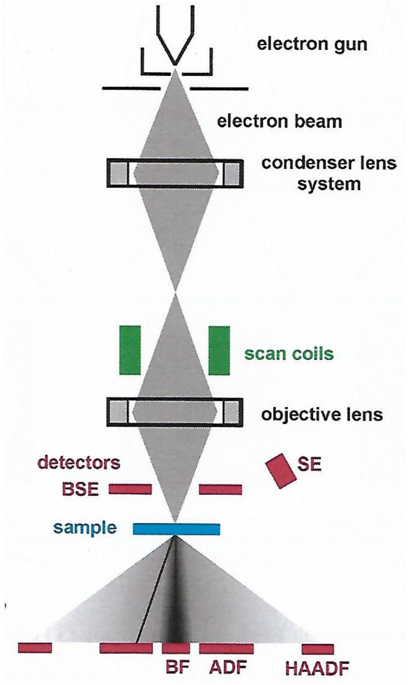
↳ Surface topography is qualified in term of roughness, waviness (corrugation) and primary profile (form), expressed as $\mathbf{R}_\mathbf{x}$, $\mathbf{W}_\mathbf{x}$ and $\mathbf{P}_\mathbf{x}$ respectively. Here, $\mathbf{x}$ represents one or more letter(s) that refer(s) to the considerer parameter, *i.e.* **a** for arithmetic, etc…

⇨ Specific surface area defines the real surface against the apparent one as it takes into account the topography of the studied surface. This notion is of importance for catalysis, adsorption….

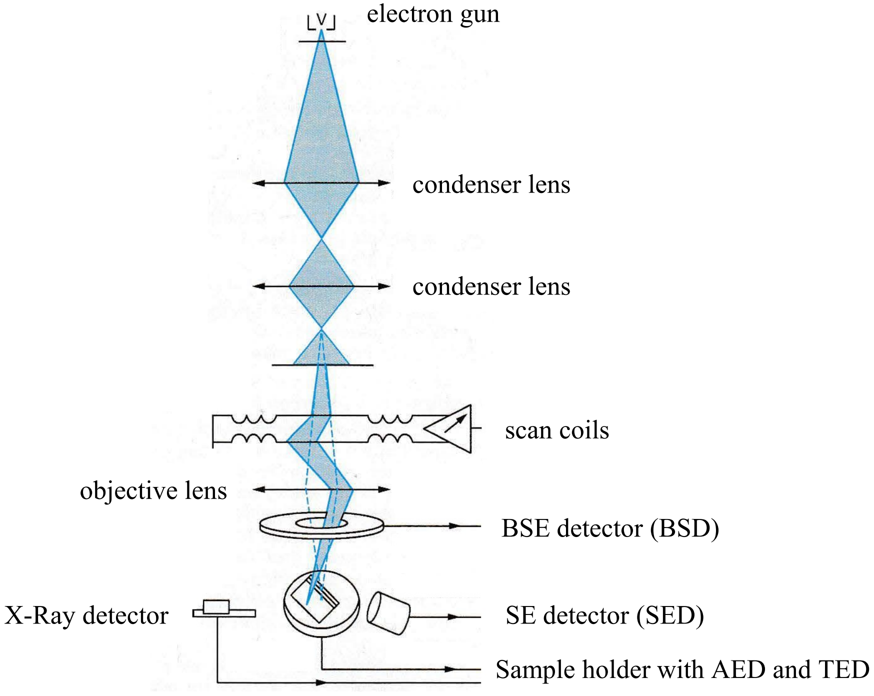
Surface studies by STEM and SEM

STEM and SEM

⇨ Surface morphology can be accessed by STEM and SEM as these two techniques provide a very good lateral resolution, 0.5 Å and 0.5 nm at the best respectively. The sub-angstrom resolution in STEM is achieved for aberration corrected microscopes. Below are the schematic figures of both apparatus:



STEM



SEM

⇨ With these two techniques, local structures can be studied at the atomic or at the nanometre scales.

⇨ The main difference between these two techniques remains into the acceleration tension of the electron constituting the primary beam which is 30 kV for SEM and about 200 kV for STEM.

⇨ Both techniques can generate sample damages due to the high energy of the primary electron beam, especially with STEM, which can change the material morphology *i.e.* partial destruction, coalescence, collapsing…

Surface morphology by STEM

⇨ Low voltage STEM microscopes operating at 0.1 to 30 kV are nowadays available to counteract the possible morphological changes that the electron primary beam can induce to the studied material.

⇨ STEM and especially ADF-STEM were found more suitable to study particles of less than 2 nm diameter than HRTEM. In contrast, for bigger particles, of more than 5 nm diameter, both techniques lead to the same results.

⇨ For a classic STEM operation, the electron beam must cross the sample, so the sample thickness must not exceed 100 nm. This maximum thickness size must be lowered in the case of low voltage STEM.

⇨ For low voltage STEM analyses, one can detect the electrons through the BSE and the SE detectors instead of the BF, ADF and HAADF detectors.

⇨ The sample size is in the millimetre range and the scanned surface is about a few hundred of nanometres.

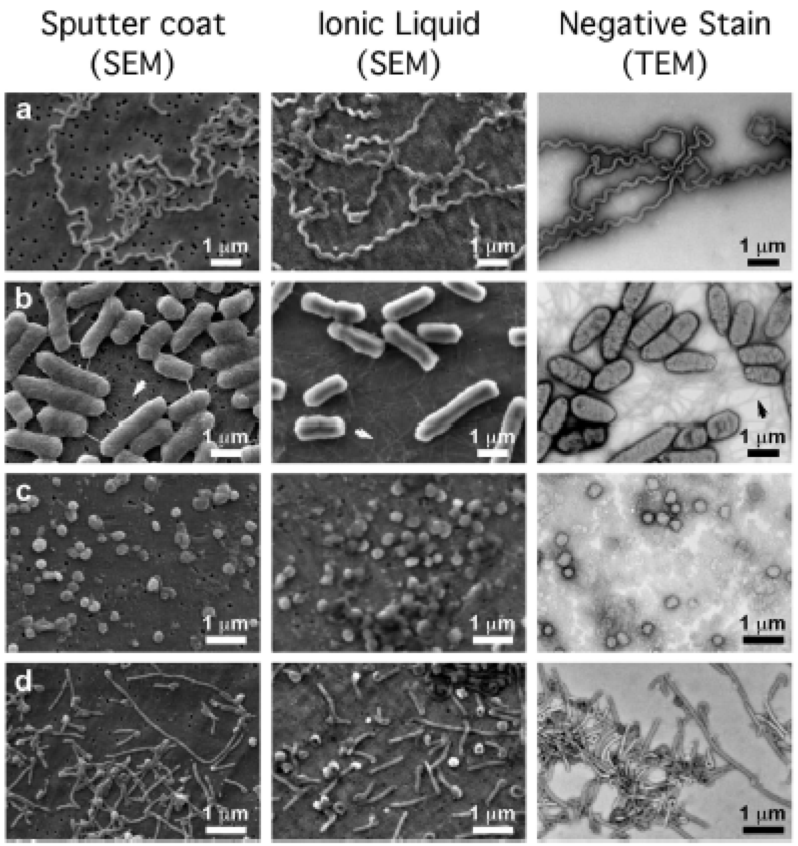
Surface morphology by SEM

⇨ SEM is naturally dedicated to morphological studies even if the lateral resolution ranges from 0.5 nm to 5 nm which is rather worst compared to STEM. The SEM working distance, the distance between the final pole piece of the lens to the sample, plays also important role on the resolution. The shorter working distance, the better resolution.

⇨ SEM compared to TEM and at least STEM offers a 3D view due to significant contrasts.

⇨ For a classic SEM operation, the detected electrons are emitted from the material surface, so there is no criteria to respect for the sample thickness. The sample size is in the centimetre range and the scanned surface is about a few micrometres, depending of the chosen magnification (from 100 to 200 000).

Comparison between surface morphologies accessed by SEM and TEM



⇨ Studies from C. G. Golding et al., *Nature Scientific Reports*, **2016**, *6*, 26516.

⇨ SEM compared to TEM and at least STEM offers a 3D view due to significant contrasts.

⇨ SEM offers a good morphology determination compared to TEM. HAADF-STEM exhibits sharper images than BF-TEM (see after).

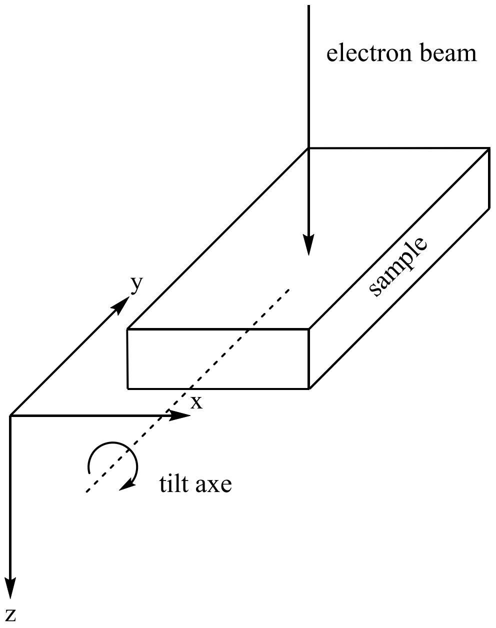
Comparison of conventional sputter coating SEM sample preparation methods (coated with gold, on plain uncoated filters) with ionic liquid treatment (after deposition on pre-coated aluminum filters) and conventional TEM (methylamine tungstate negative staining) for the observation of microbes: (**a**) Leptospira biflexa, (**b**) Salmonella Senftenberg, (**c**) vaccinia, and (**d**) Ebola virus.

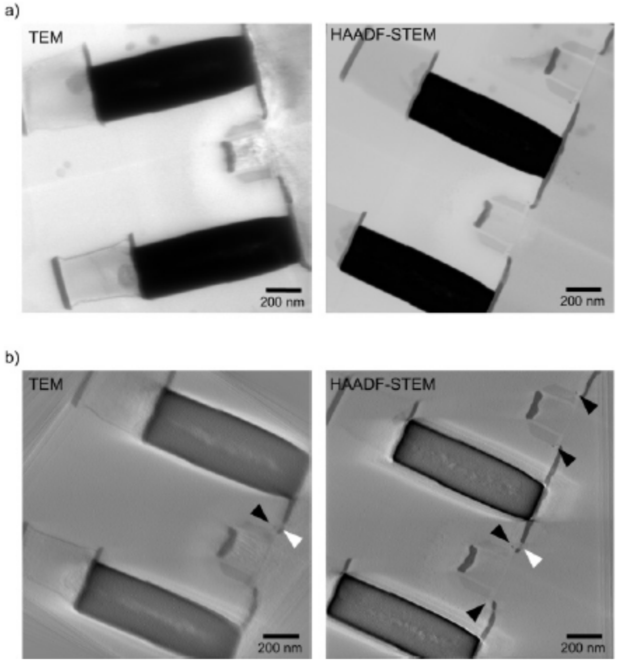
Surface topography by STEM

⇨ The surface topography of a material can not be directly assessed by STEM.

⇨ It requires the reconstruction of a 3D image from around 100 2D-images obtained at different tilt angles of the sample. This technique is known as electron tomography.

⇨ The acquisition of the tilt series is performed by a sequential tilting of the sample along one axis. All the tilts are of equal angle and must cover the highest accessible tilt range to obtain the best 3D-image accuracy.





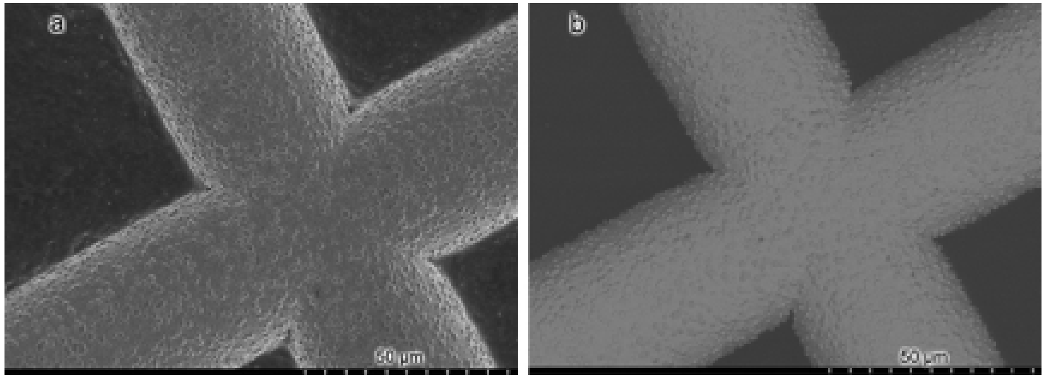
↳ BF-TEM / HAADF-TEM images (a) and the 3D reconstructed images based on tilt series of BF-TEM / HAADF-TEM images (b) of a transistor.

↳ C. Kübel et al., *microsc. microanal.*, **2005**, 11, 378

Surface topography by SEM

⇨ The three dimensionality of a typical SEM picture is more subjective than real. Nevertheless, topographic information can be obtained by pairs of SEM pictures showing the surface at different sample tilt (stereometry) or from differently placed detectors at a fixed sample orientation.

⇨ The best surface topographic information are provided by SE as shown in the following pictures in which **a** and **b** stand for the SEM images obtained from SE and BSE of the sample respectively:



⇨ Topographic information can be obtained also from BSE but it requires the use of a annular BSD separated in different sectors, the signal of different pairs are subtracted to enhance the surface topography as already discussed in the chapter dedicated to SEM.

⇨ An automatic technique for measuring heights in SEM lies on a combination of stereometric and focusing methods.

↳ In this approach the primary electron beam is electrically tilted such than the plane containing the tilting axis is coincident with the focal plane of the objective lens. As a result, the objective lens tracks the surface topography.

⇨ To gain into accuracy, one can reduced the primary electron beam energy down to 0.5 or to 1 keV.

↳ The interaction of the primary electrons is more efficient with the surface layer of the material.

↳ The better interaction provides a sufficient emission of secondary electrons.

↳ However, the decrease of the primary electron energy causes the decrease of the SEM lateral resolution.

⇨ Another important drawback in the determination of surface topography by SEM lies on the surface charging effects that will lead to the primary beam defocusing.

↳ However either gold or carbon deposition can counteract the charging effects. Even though the deposition layer is rather thin (10 – 30 nm), it may affect the initial surface topography of the sample.

Surface studies by STM and AFM

STM and AFM

⇨ STM and AFM were developed in 1981 and 1986 respectively by a research team at IBM Zurich. Both apparatus share many components as AFM can be view as an evolution of STM for insulating material studies.

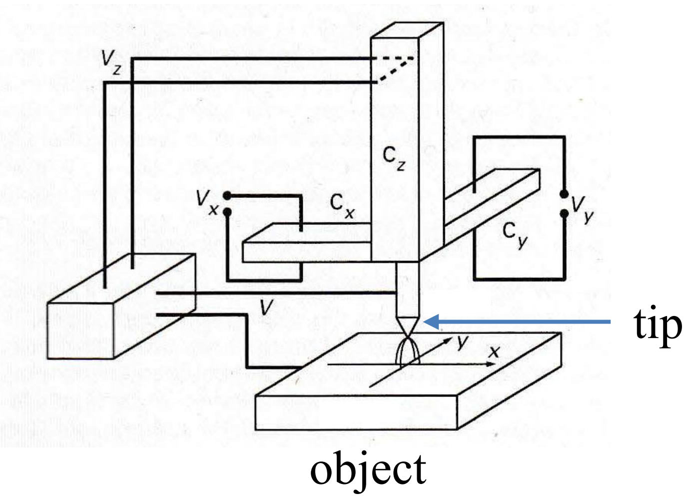
⇨ Whereas the principle of STM lies on the recording of a tunnelling current, AFM is based on the interaction forces established between the tip of a cantilever and the scanned surface.

↳ While STM is dedicated to the study of conducting and semiconducting materials, AFM can be used whatever the conductivity of the studied material, for any surfaces.

⇨ Compared to STEM and SEM, STM and AFM give rise to a direct measurement of the surface topography according to the movement of the tip along the **z** axis while scanning the surface. The magnification can rise up to 1 000 000.

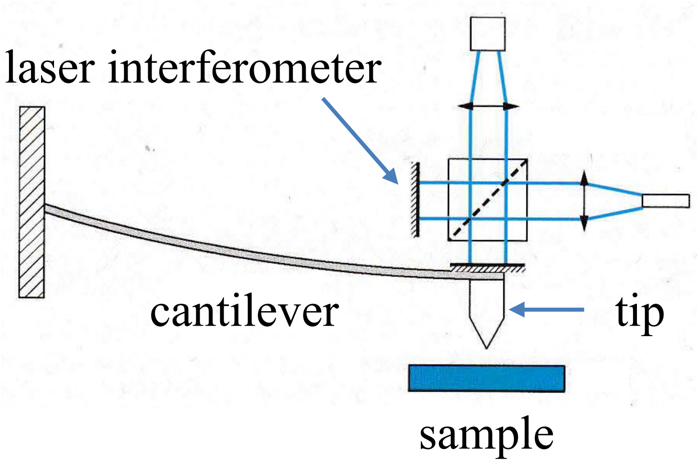
⇨ The accuracy of the vertical resolution of both techniques span from 0.01 to 0.1 Å for STM and is about 1 Å for AFM. The lateral resolution ranges from 2 – 6 Å for STM and is about 0.5 to 10 nm for AFM. Theses lateral resolutions strongly depend on the tip manufacturing.

- Below are the schemes of STM and AFM apparatus:



- In STM, the tip is directly mounted on a mobile arm animated by piezoelectric actuators.

- In AFM, the tip is situated at the end of a cantilever. The displacement of the cantilever along the **z** axis is monitored by interferometry.

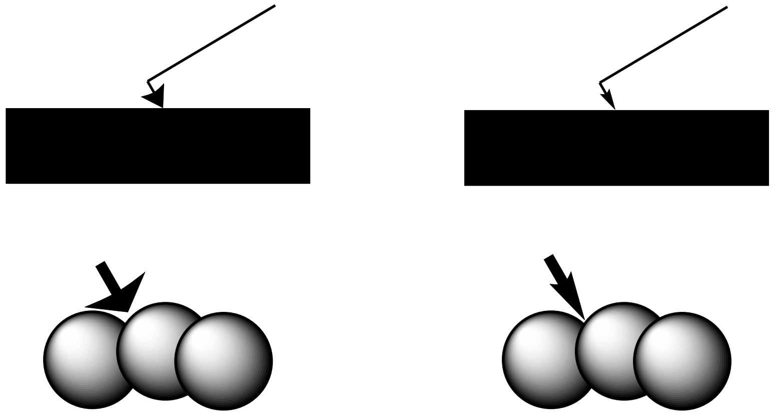


- In STM, the tip is moved by the piezoelectric actuators and the sample is still.

- In AFM, the tip is still and the sample is moved by the piezoelectric actuators.

⇨ For both STM and AFM, the accessible surface details depend on the size and shape of the tip.

↳ Steric artefacts will arise when the characteristic dimensions and angles of the tip are comparable to the surface ones, as show below for an AFM setup:



↳ An STM or AFM image comes from a convolution between the surface topography and the tip shape as described on the scheme above. The tip shape must be studied by SEM prior to any experiment to get the real vertical and lateral resolutions of the microscope.

⇨ Because STM and AFM are not based on beam-matter interactions, the obtained images are not real images but 3D-profiles of a given surface. Images are obtained when an electromagnetic beam interacts with a sample like in optical and electron microscopy.

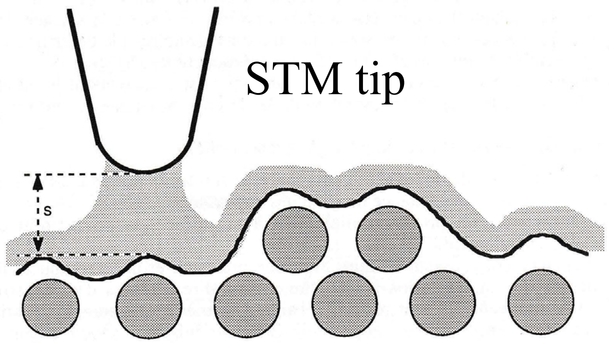
↳ As a consequence, morphological aspects can be observed by STM and AFM if morphological details provides noticeable changes in the surface profile like an inclusion, adsorptions, a growing phase...

↳ The scanned area ranges from a few μm^2 up to a few mm^2.

Surface topography by STM

⇨ As already mentioned, STM is dedicated to the study of the topography of conducting or semiconducting material.

⇨ To perform STM, the tip must be polarised against the studied sample then generating the tunnelling current recorded at the tip. Depending on the polarisation of tip, the tunnelling current can arise from either the filled or empty electronic surface states.

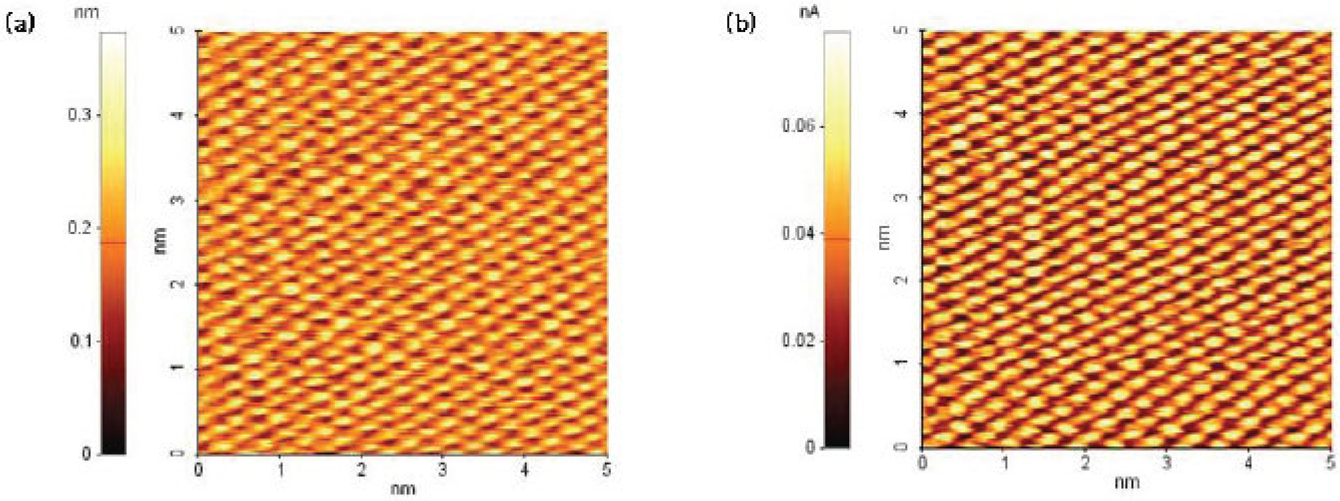


⇨ STM can be run either at constant current or at constant height.

- At constant current, the tip follows the surface topography ensuring a constant tunnelling current. The resulting image is given as a function of the tip displacement along the **z** axis which give rise, through a piezoelectric device to a tension $\mathbf{V_z}$. The function $\mathbf{V_z}$ = f (2D-tip motion) gives a 3D-map corresponding to iso-current hypersurface, the STM image.

- At constant height, the tip is maintained at a fix distance from the surface and the variation of the tunnelling current **I** is recorded. The function **I** = f (2D-tip motion) gives a 3D-map corresponding to surface topography. the STM image is built on **s** = f (2D-tip motion).

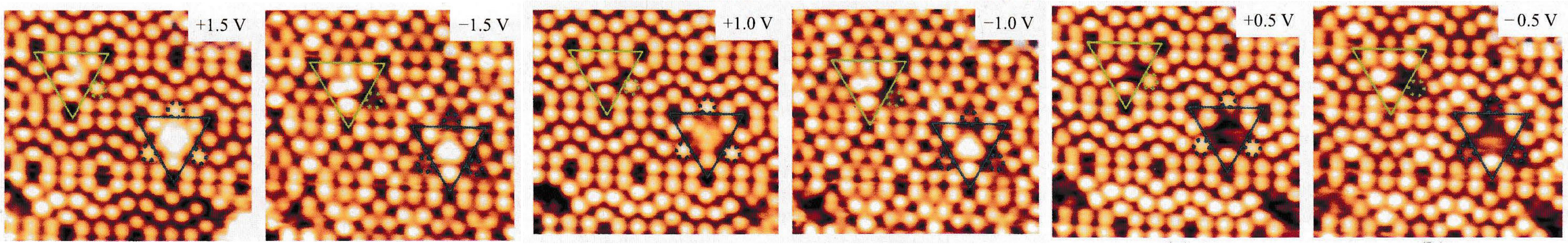
- Below, the STM topography (**a**) and STM image (**b**) of a highly ordered pyrolytic graphite (Park Systems):



Surface morphology by STM

⇨ As already mentioned, morphology can be observed by STM if morphological details provide noticeable changes in the surface profile like an inclusion, adsorption, a growing phase...

↳ As an example, below are represented the STM images of Si(111) surfaces, recorded at a constant current of 0.05 nA using a tungsten tip (Zhou et al., *Nano-Micro letters*, **2015**, *7*, 194-202):



a **b** **a** **b** **a** **b**

empty **a** and filled **b** state STM images of Zn-induced nanocluster on an Si(111) surface. The bias voltages represent the polarisation of the sample.

↳ On these pictures, one can observe the structural features of Si(111) surfaces as well as the growing Zn nanoclusters on these surfaces which constitute a morphological study of the Si(111) surfaces.

Surface topography by AFM

⇨ AFM is the most versatile tool for surface topography as any kind of surface can be studied. AFM can be run in different modes including static and dynamic (oscillating) modes, depending on the nature of the studied surface.

↳ For robust material surfaces, a static mode, many often called the contact mode, can be operated.

↳ For softer material surfaces, a dynamic mode and especially the tapping mode is required.

⇨ In the contact mode, the tip touches the surface and the measured deflection of the cantilever reproduces the topography of the scanned surface. The image is built from the height variation **h** of the cantilever, **h** = f (2D-sample motion).

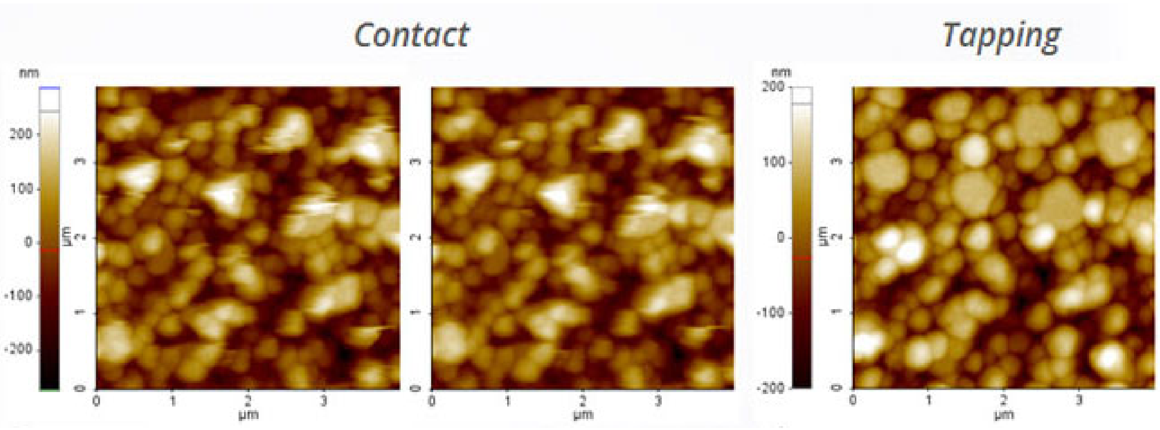
↳ This mode suffers from several drawbacks: surface injuries, tip sticking at the surface due the attractive forces established with the surface during the tip approach, strong effect of the lateral forces that distort the cantilever and thus degrade the lateral resolution.

↳ This mode needs a highly flexible cantilever (0.01 to 5 $N \cdot m^{-1}$) and provides an easy and rapid surface mapping.

⇨ In the tapping mode, the tip oscillates at or near its resonant frequency with an amplitude from a few nanometres to 200 nm. The oscillations of the cantilever are maintained constant by the tuning of the height of the tip during the scan. The image is built from the height variation **h** of the cantilever, **h** = f (2D-sample motion).

↳ Due to the intermittent contact of the tip with the scanned surface, the drawbacks described for the contact mode are ruled out.

↳ Below is shown the AFM contact mode and the AFM tapping mode images of the same ZnO nanorods (Park Systems):



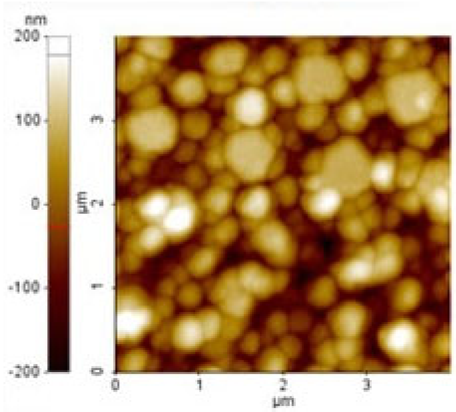
↳ This series of pictures highlights the strong effect of the lateral forces that distort the cantilever and thus degrade the lateral resolution when running the AFM analysis in contact mode.

Surface morphology by AFM

⇨ AFM is not the best apparatus to provide a morphological study of materials as it does not lead to an image based on an interaction between an electromagnetic beam and the material.

⇨ Nevertheless, as for STM, it is possible to obtain morphological information when the resolution is not hindered by lateral forces that blur the AFM image.

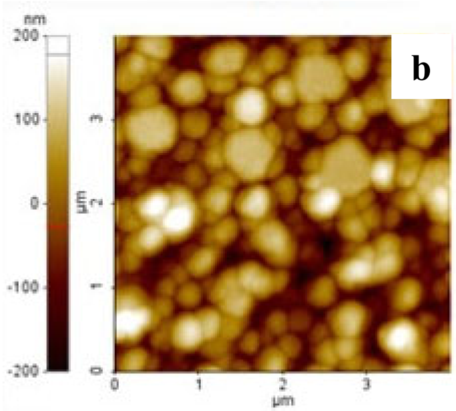
↳ Below is shown the AFM tapping mode image of ZnO nanorods (Park Systems):



↳ On this picture one can observe the morphological details of the nanorods.

Comparisons between SEM and AFM

⇨ Below are shown the SEM picture (**a**, X. Y. Chen et al., *J. Am. Chem. Soc.*, **2007**, *129*, 13305) of a Zeolite nanorods and the AFM tapping mode image of ZnO nanorods (**b**, Park Systems):

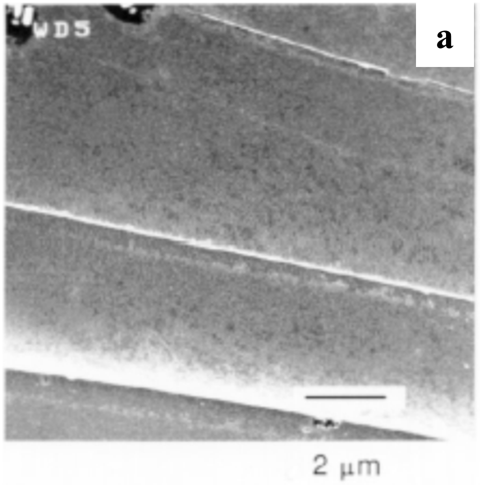


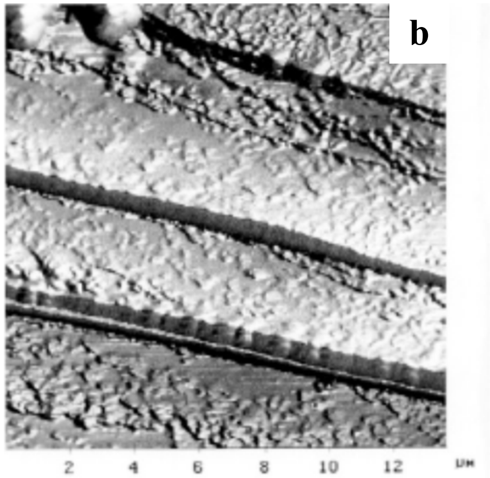
↳ Taken at the same scale, the AFM picture shows a blurred contour compared to the SEM picture.

↳ AFM exhibits less morphological details than SEM.

↳ These two pictures show that SEM is more dedicated to morphological studies than AFM.

⇨ Below are shown the SEM pictures (**a**) and the AFM contact mode image (**b**) of highly ordered pyrolytic graphite (J. E. Castle et al., *J. Phys. D: Appl. Phys.*, **1997**, *30*, 722):





↳ These two pictures at a comparable scale show that SEM is less sensitive than AFM to surface topography.

↳ To assess to surface topography by SEM, one has to collect several images using the tilting method.

↳ These two pictures show that AFM is more dedicated to topographical studies than SEM.

Surface studied by profilometry

Introduction

⇨ Surface topography can be studied by profilometry. Profilometry is explored either by contact profilometers or by optical profilometers.

⇨ Profilometry gives mainly rise to topographical analyses while scanning a surface. Some morphological details can be obtained when these details provide noticeable changes in the surface profile like an inclusion, adsorptions, a growing phase...

⇨ These details are only accessible if the vertical resolution of the apparatus is comparable with the size of the details.

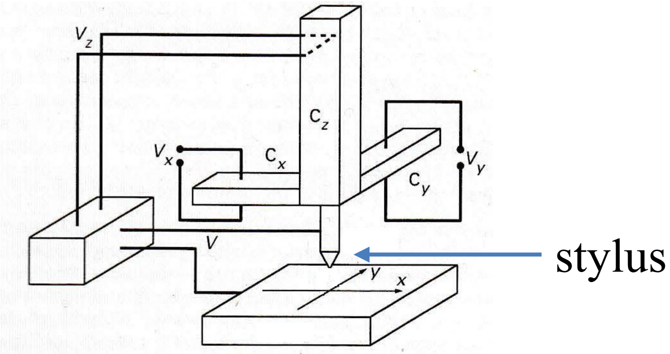
⇨ Profilometry is more dedicated to industrial quality assurance than to research purposes.

Contact profilometer

⇨ A contact profilometer is a apparatus similar to an AFM microscope. The cantilever of the AFM is replaced by a stylus ended by a tip many often made of diamond. Some tips made of ruby are also available. The choice depends on the brittleness of the studied surface.

⇨ The stylus is a cone of angle from 20 - 100° (60 to 90° are the most commons), terminated by a spherical tip of radius from 20 nm to 50 µm.

⇨ The displacement of the stylus over the surface gives an image corresponding to the variation of the stylus position along the **z** axis.



stylus

object

⇨ The method is neither sensitive to the optical properties of the material nor to the cleanliness of the scanned surface (presence of lubricant for example).

⇨ The surface scanned ranges from 5 mm^2 up to 25 cm^2.

⇨ The lateral resolution depends on the tip size, it can be below 1 µm.

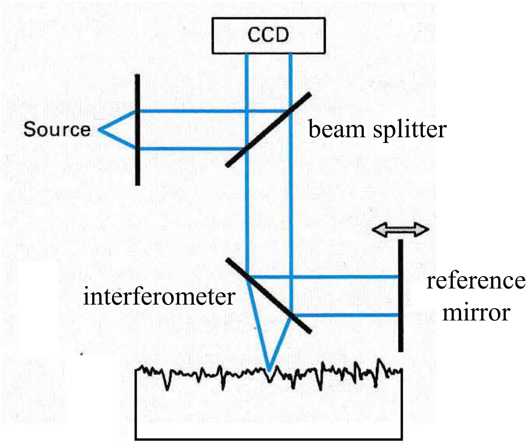
⇨ The vertical resolution spans from 3 to 6 nm, recent apparatus claim a vertical resolution of 1 Å.

⇨ The range of the vertical measurements is from 1 to 6 mm.

Non-contact profilometer

⇨ Non-contact profilometers are base on optical microscopy: coaxial laser and triangulation laser profilometries, confocal and interferometry microscopy.

⇨ For accurate measurements, interferometry microscopy is the most widely used:



↳ The white light source is split by a mirror, one part of the beam being directed on the sample and the other part being shone on a reference mirror.

↳ After reflexion, the two beams will superimpose on the interferometer thus generating an interference pattern recorded by a CCD camera.

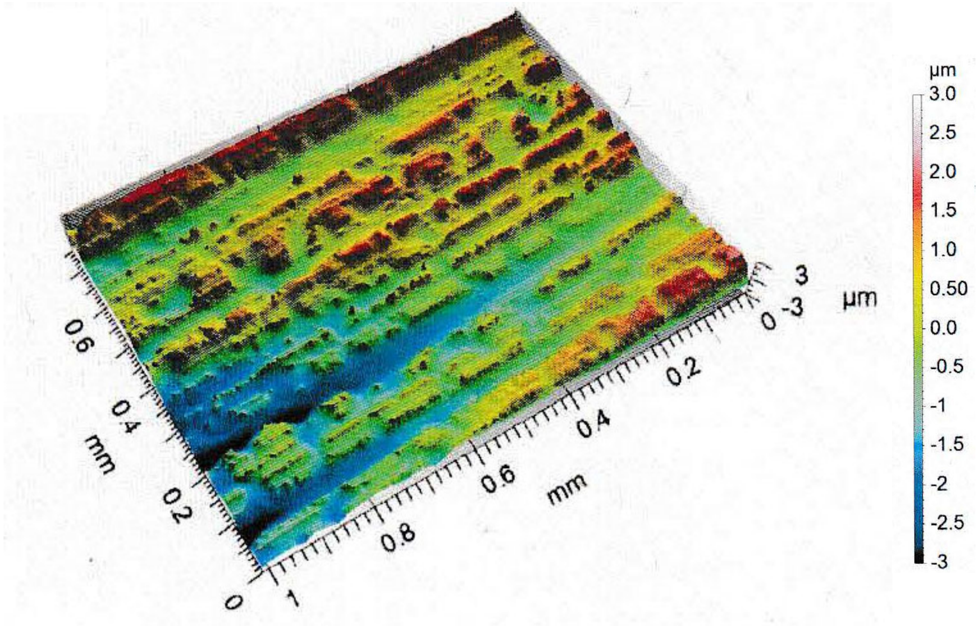
↳ The difference of the two optical paths gives the surface topography when moving the sample along the **x** and **y** axes.

⇨ The surface scanned ranges from 0.1 up to 100 mm^2.

⇨ The lateral resolution depends on the diffraction limit (**0.47 λ / α**) and is about 350 - 400 nm. The vertical resolution spans from 0.1 to 5 nm.

⇨ The range of the vertical measurements is below 0.1 mm.

⇨ Below is represented the 3D-White light interferometry image of a tinplate for food cans (F. Cova Caiazzo, *EPFL PhD thesis n° 8910*, **2018**):



Specific surface area determination

Introduction

⇨ Specific surface area defines the real surface against the apparent one as it takes into account the topography of the studied surface.

⇨ This notion is of importance for adsorption, absorption, diffusion, surface modification processes, catalysis, heat exchange…

⇨ Specific surface area is usually assessed by measuring the quantity of a chemically inert gas adsorbed on a material surface.

⇨ Probe gazes are: N_2, CO_2, Ar, Kr and sometimes O_2 , He or CH_4.

↳ Nevertheless, N_2 remains the most used one.

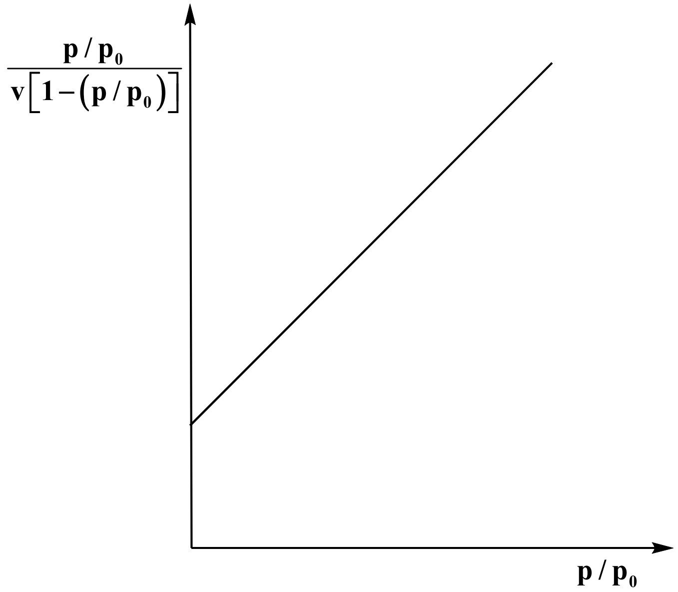
Specific surface area measurement

⇨ The Specific surface area measurement is realised by the adsorption of more often N_2 at 77 K.

⇨ The adsorption process is described by the Brunauer, Emmett, Teller model known as BET model.

⇨ The BET equation reads:

$$\frac{1}{v\left[\left(p_0/p\right)-1\right]}=\frac{C-1}{v_{ml}C}\left(\frac{p}{p_0}\right)+\frac{1}{v_{ml}C}$$



↳ In this equation, **p** and $\mathbf{p_0}$ (pressure units) are the equilibrium and the saturation pressure of the adsorbed gas respectively (at the working temperature), **v** (volume units) is the volume of adsorbed gas, $\mathbf{v_{ml}}$ (volume units) is the volume of an adsorbed gas monolayer and **C** is a constant which is related to the heat of adsorption of the different layers (dimensionless).

↳ The plot at the left side allows the determination of the BET parameters *i.e.* the slope $\boldsymbol{\alpha}$ and the y-intercept $\boldsymbol{\beta}$:

$$v_{ml}=\frac{1}{\alpha+\beta}\quad \text{and}\quad C=1+\frac{\alpha}{\beta}$$

⇨ The total surface area $\mathbf{S_{total}}$ and the BET surface area $\mathbf{S_{BET}}$ are:

$$\mathbf{S_{total} = \frac{v_{ml} N \sigma_s}{v_m} \quad \Rightarrow \quad S_{BET} = \frac{S_{total}}{m}}$$

⇨ In these equations, $\mathbf{v_{ml}}$ (volume units) is the volume of an adsorbed gas monolayer, **N** is the Avogadro number (6.022×10^{23} mol^{-1}), $\boldsymbol{\sigma_s}$ (m) is the cross section of absorption of the probe gas, $\mathbf{v_m}$ (volume units per mol) is the molar volume of the probe gas and **m** (g) is the mass of the probed material.

⇨ The BET surface area $\mathbf{S_{BET}}$ corresponds to the specific surface area.