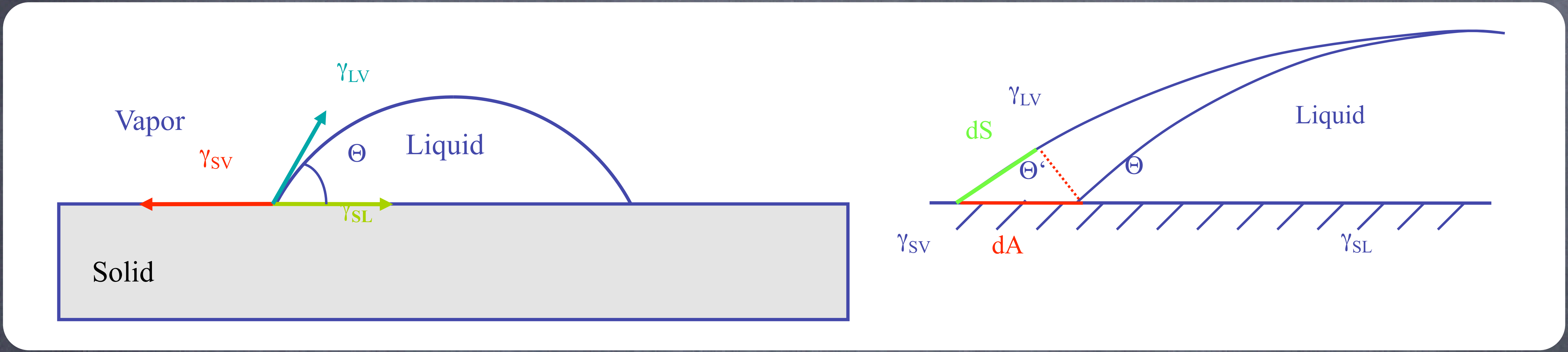
contact angle measurements

Young equation:
valid for homogeneous, smooth, rigid solids



Horizontal balance of forces:
Young equation

$$\boxed{\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \Theta}$$

$dG^S = (dG^S)_{SV} + (dG^S)_{SL} + (dG^S)_{LV}$

$dG^S = dA\,(\gamma_{SL} - \gamma_{SV}) + dA\,\gamma_{LV} \cos(\Theta')$

At equilibrium:

$dG^S / dA = 0 \Rightarrow$

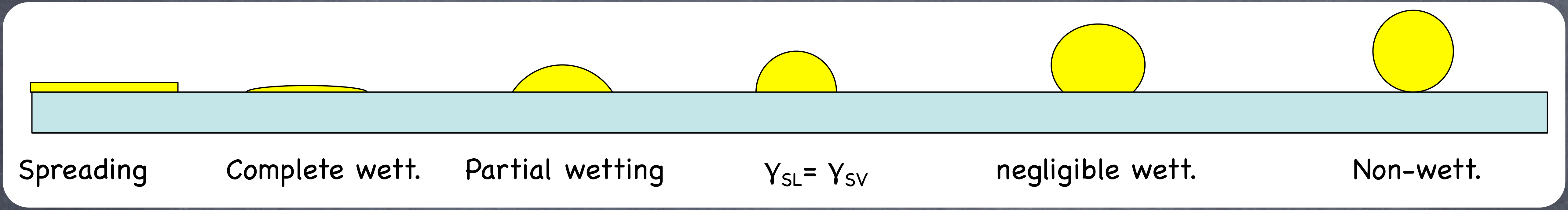
$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \Theta$

wettability

Contact angle:

Θ 0° 90° 180°

cos Θ 1 0 -1



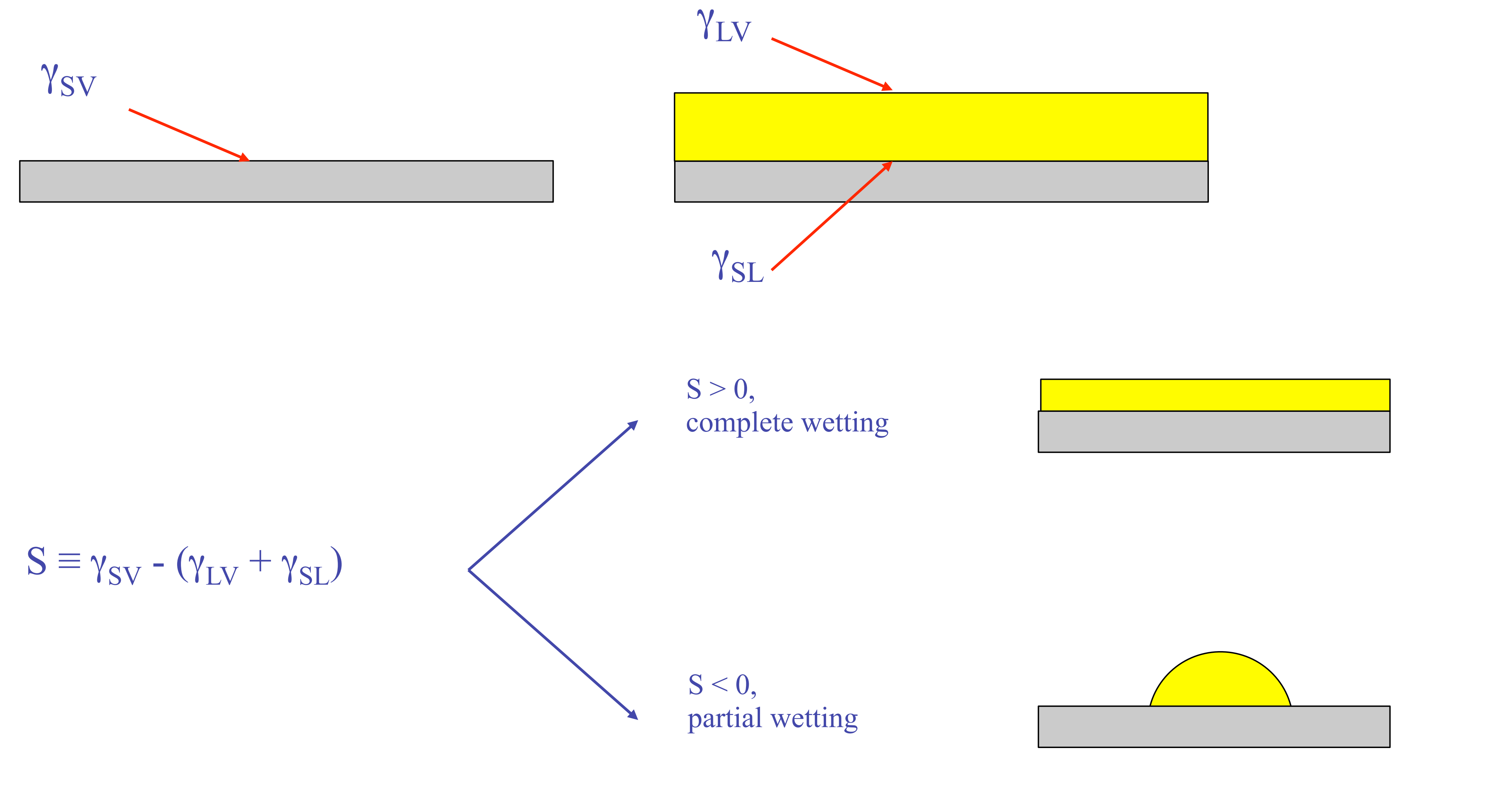
- Θ_e depends on chemical constitution of both solid and liquid

1) **hard solids** - covalent, ionic, metalic => high energy surfaces γ_{SO} ~ 500 to 5000 ergs/cm^2

2) **weak molecular crystals** - vdW, H bonds => low energy surfaces γ_{SO} ~ 50 ergs/cm^2

spreading coefficient

S = free energy difference between a bare solid, directly in contact with the vapour and a solid covered by a flat, thick liquid layer



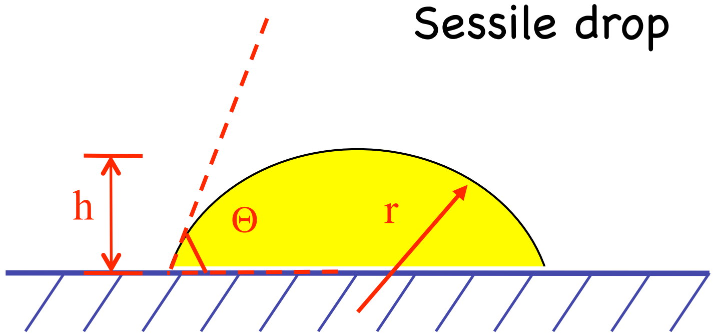
$$S \equiv \gamma_{SV} - (\gamma_{LV} + \gamma_{SL})$$

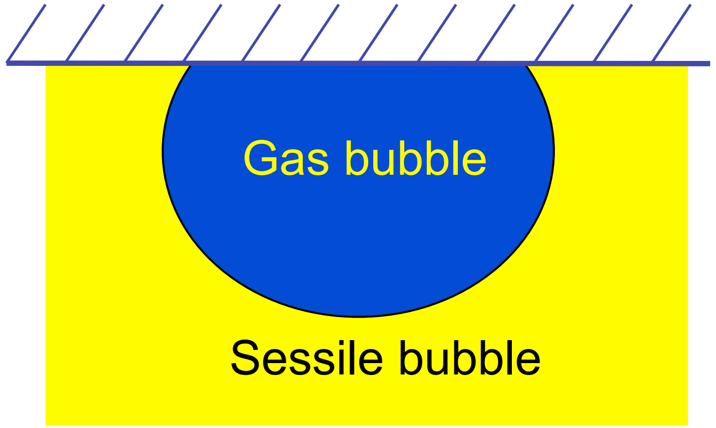
$S > 0$,
complete wetting

$S < 0$,
partial wetting

experimental methods 1

Sessile drop



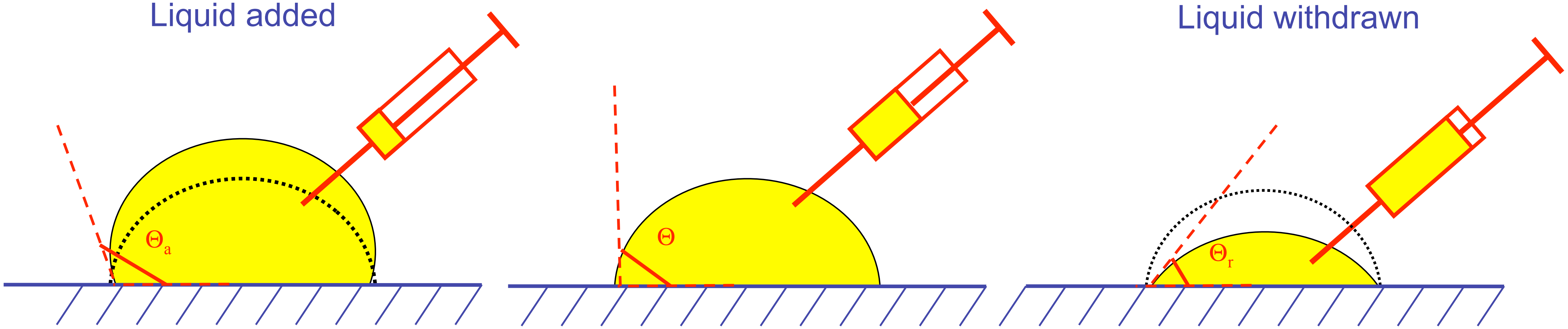


Spherical shape: $\tan \Theta/2 = h/r$

- Photograph of the drop => either by direct measurement of the contact angle or calculating it from drop profile

Liquid added

Liquid withdrawn



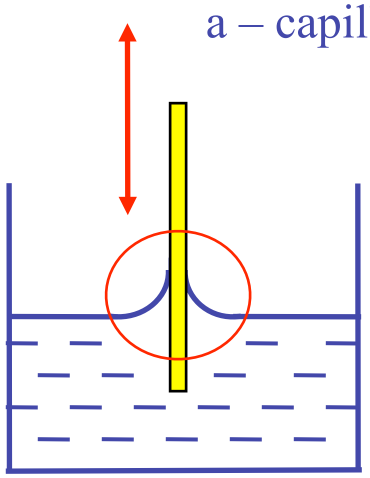
Use of a micrometer syringe: swell (shrink) the drop / bubble => receding & advancing angle

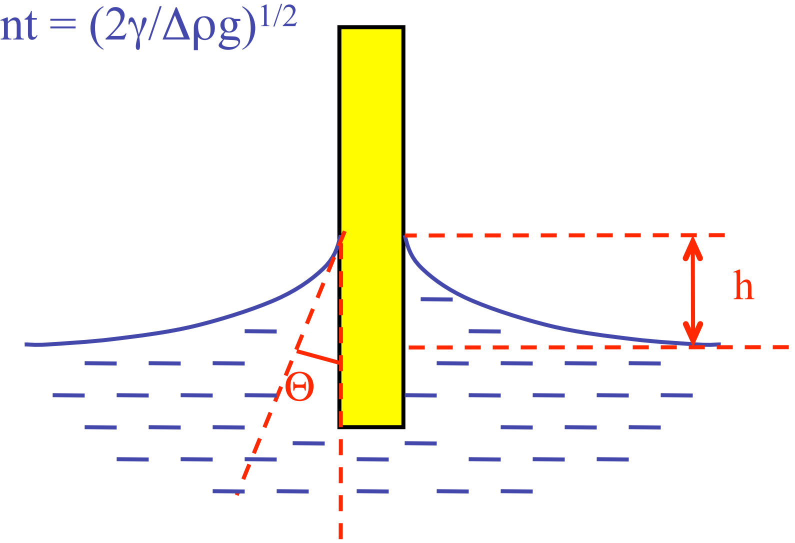
experimental methods 2

Wilhelmy slide technique:

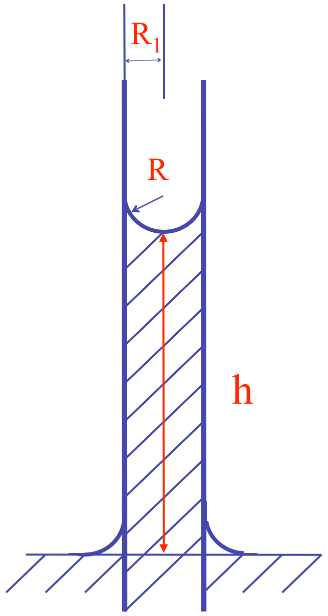
$$\sin \Theta = 1 - \rho g h^2/2\gamma = 1 - (h/a)^2$$

a – capillary constant = $(2\gamma/\Delta\rho g)^{1/2}$





Capillary rise



$\Delta\rho g h = 2\gamma/R_1$ when contact angle is 0°

$\Delta\rho g h = 2\gamma/R = (2\gamma \cos \Theta)/R_1$

contact angle hysteresis

Young eq. predicts *single* value for *intrinsic* c. a. but

Range of stable *apparent* contact angle can be measured experimentally:
=> hysteresis, $H \equiv \theta_a - \theta_r$

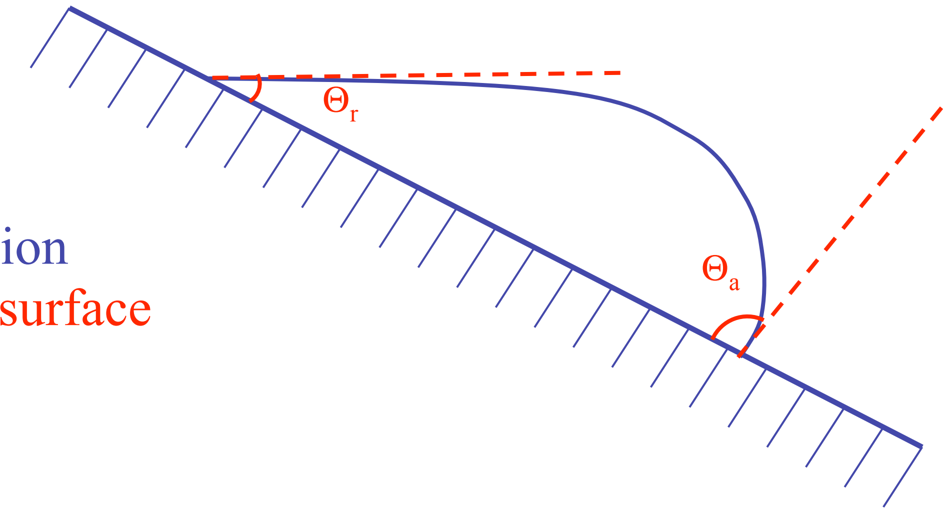
maximum - *advancing*
minimum - *receding*

Hysteresis

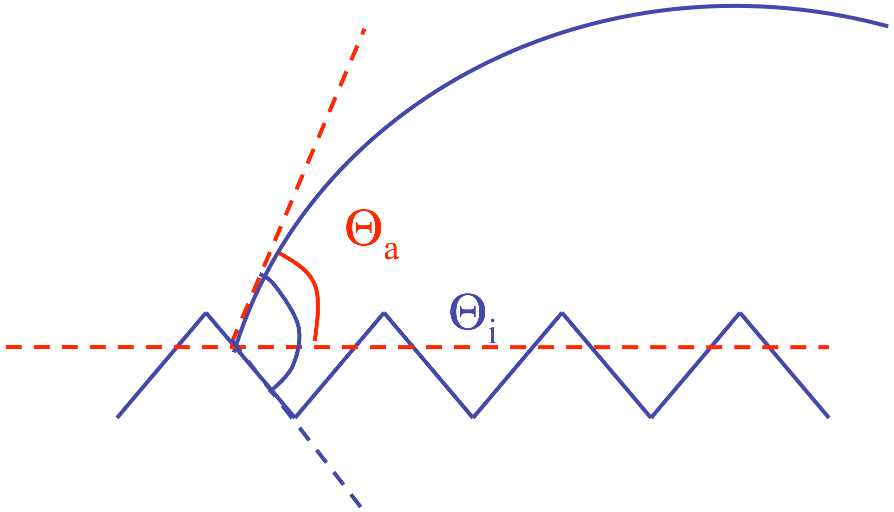
Roughness

Chemical contamination
or heterogeneity of solid surface

Solutes in the liquid
(surfactants, polymers)
may deposit a film on solid surface



roughness



Θ_a - apparent contact angle
Θi - intrinsic contact angle

Wenzel equation for wetting rough surfaces

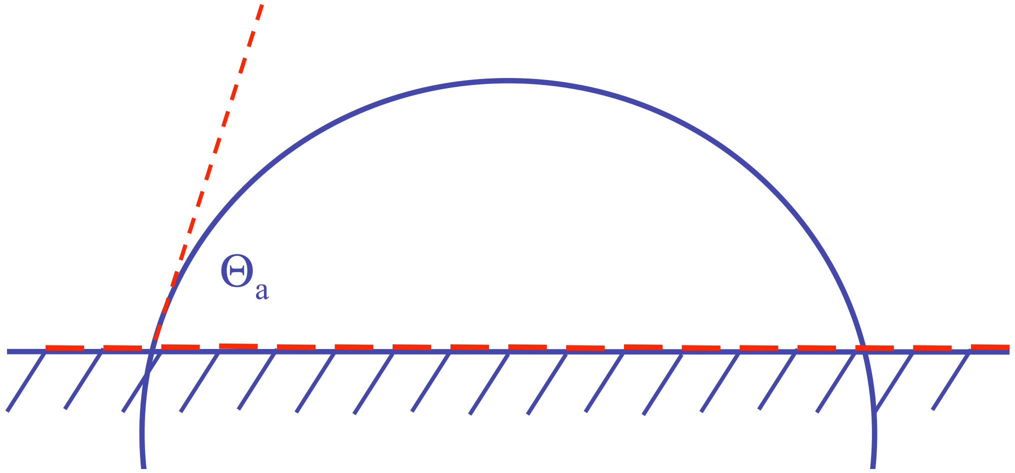
r = actual area/apparent area

γ_{SV} - γ_{SL} = γ_{LV} cosΘ - no roughness
r (γ_{SV} - γ_{SL}) = γ_{LV}cosΘ_{app} - rough surface

$$\Rightarrow \qquad \boxed{\cos\Theta_{app} = r\cos\Theta}$$

⇒ for $\Theta < 90°$, roughening the surface will reduce the contact angle!

chemical heterogenity



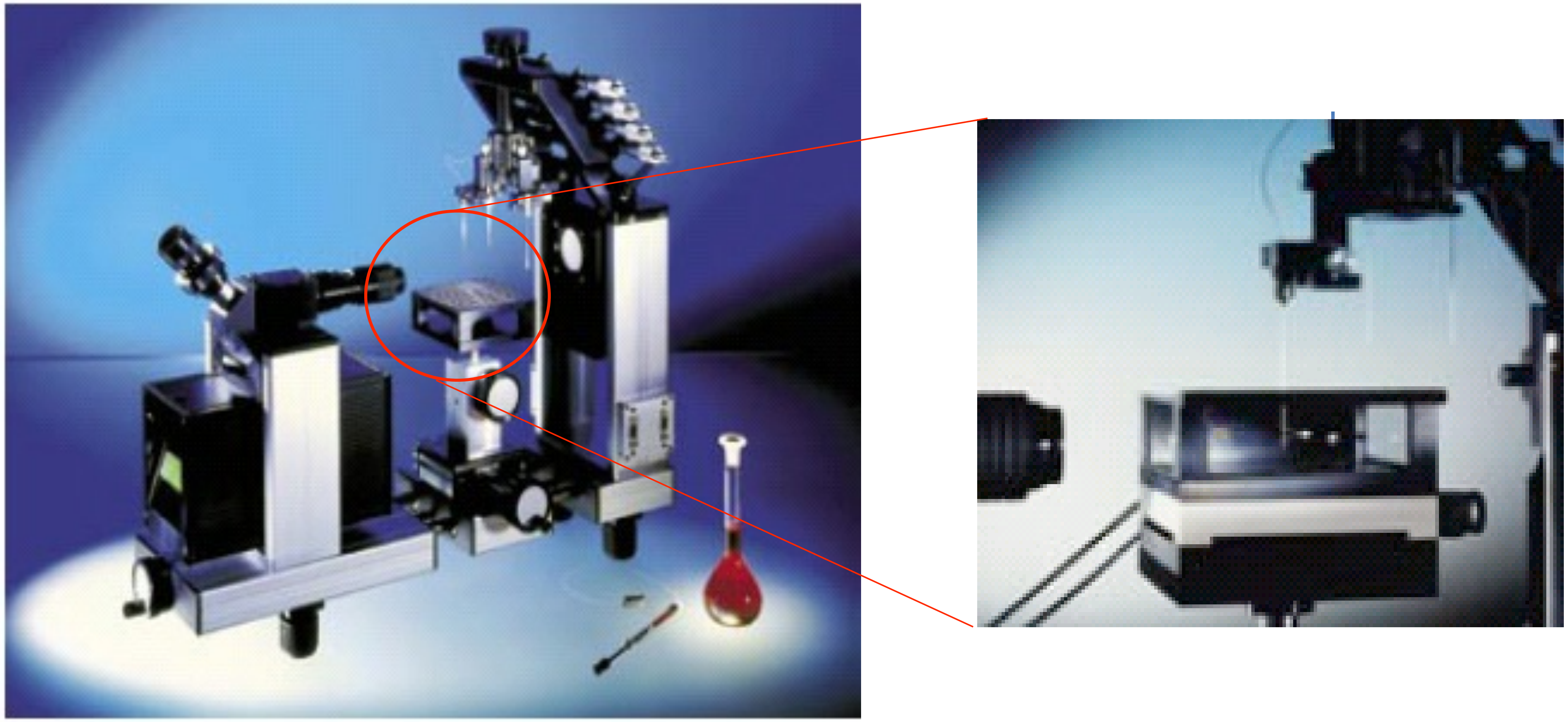
Microscopically heterogeneous surface

calculation of Θ_{app} representing the absolute minimum in the free energy of the system (Cassie equation):

$$\boxed{\cos \Theta_{composite} = f_1 \cos \Theta_1 + f_2 \cos \Theta_2}$$

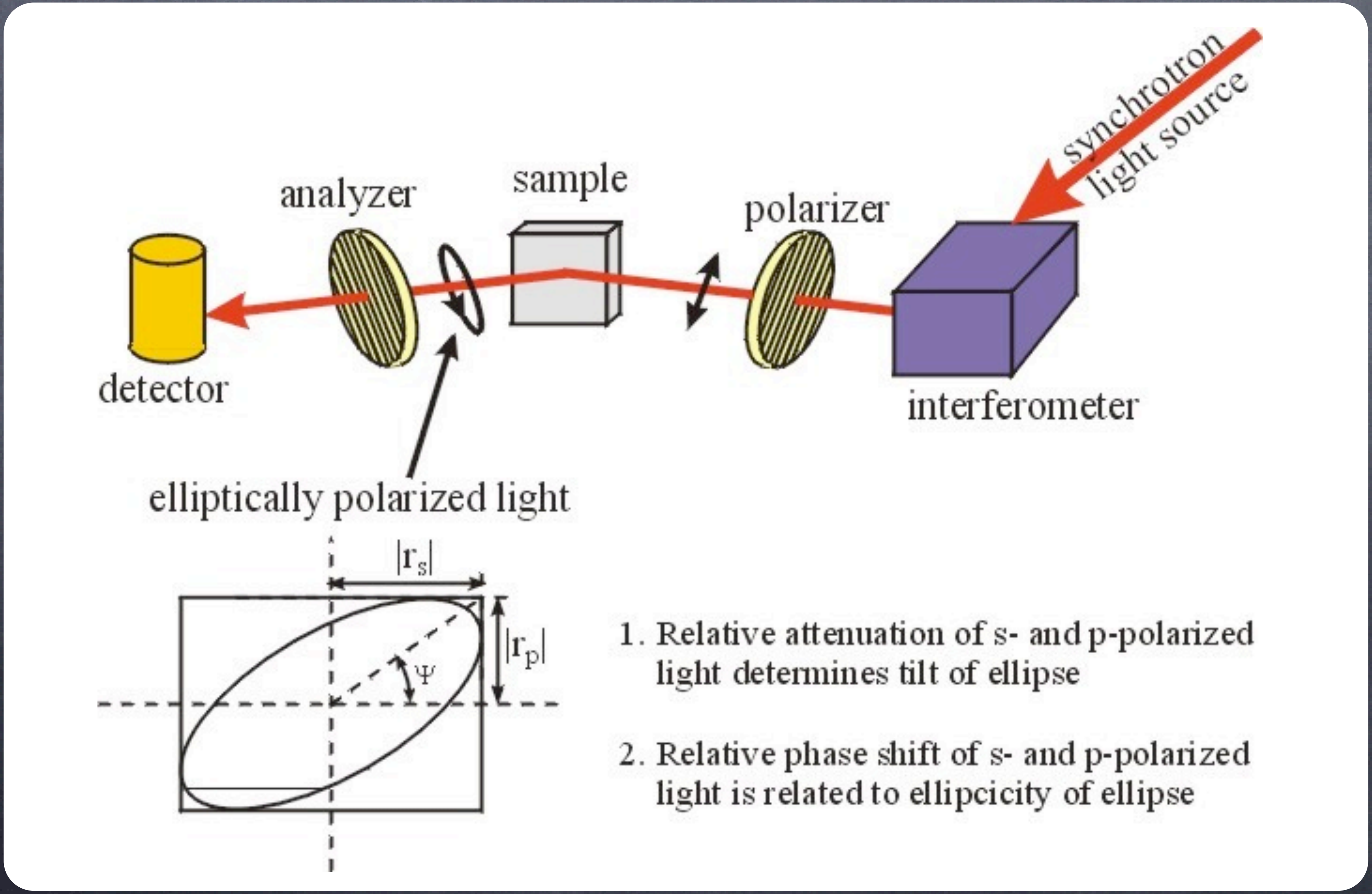
f_1 and f_2 area fractions, Θ_1 and Θ_2 corresponding intrinsic contact angle (composite - small patches of various kinds)

contact angle measurement



Ellipsometry

ellipsometry can be used to measure the **thickness** (and / or refractive index) of a **thin film / monolayer** on a solid substrate by **reflection** of **polarized light** (before and after film deposition)
-> non-contact, non-destructive method
-> it is a model based method!



1. Relative attenuation of s- and p-polarized light determines tilt of ellipse

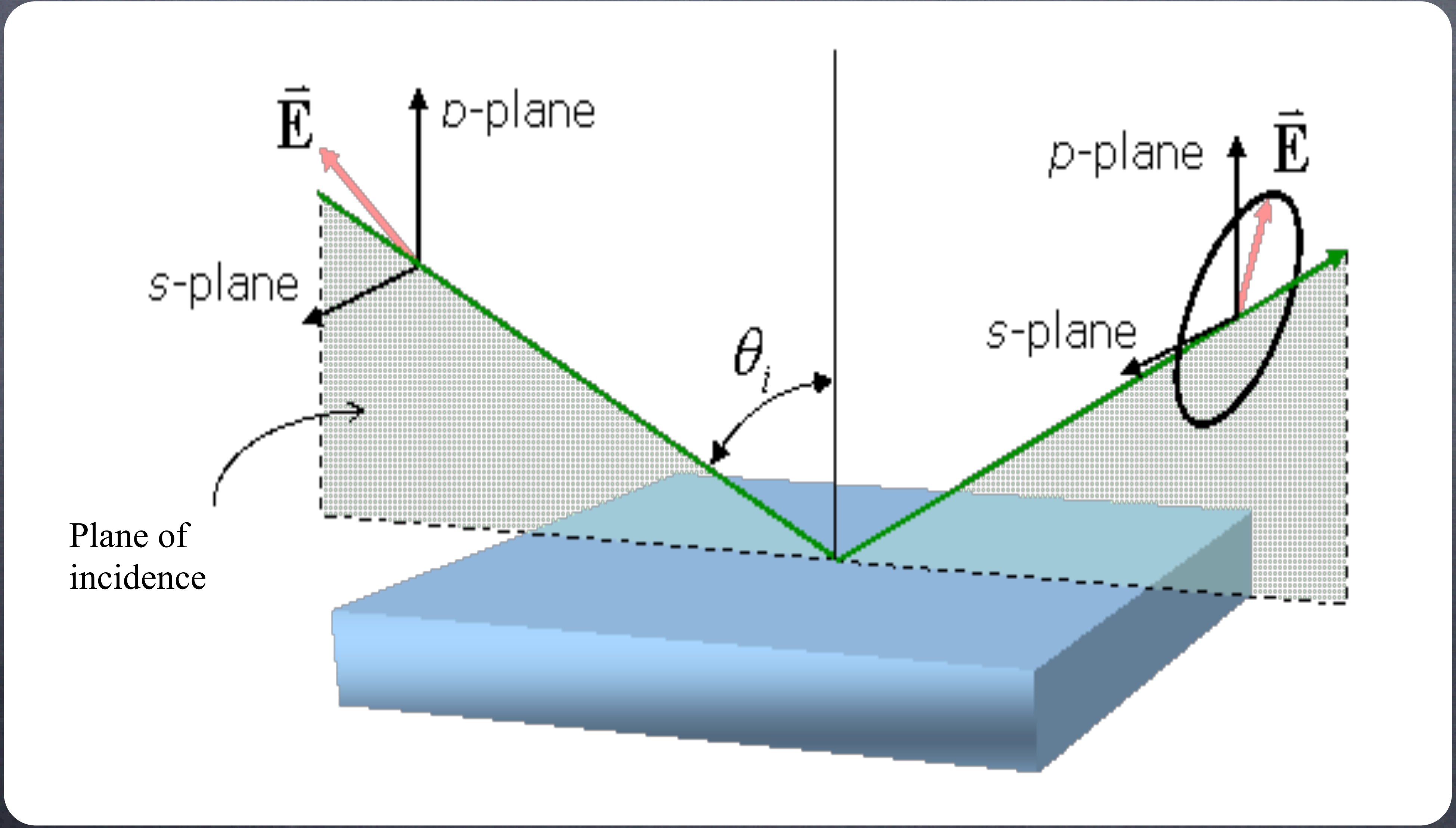
2. Relative phase shift of s- and p-polarized light is related to ellipcicity of ellipse

Ellipsometry setup

Plane of incidence of light is the plane containing the normal to the sample surface and the incident direction of light.

-> The s-plane is perpendicular to the plane of incidence.

-> The p-plane is parallel to the plane of incidence.



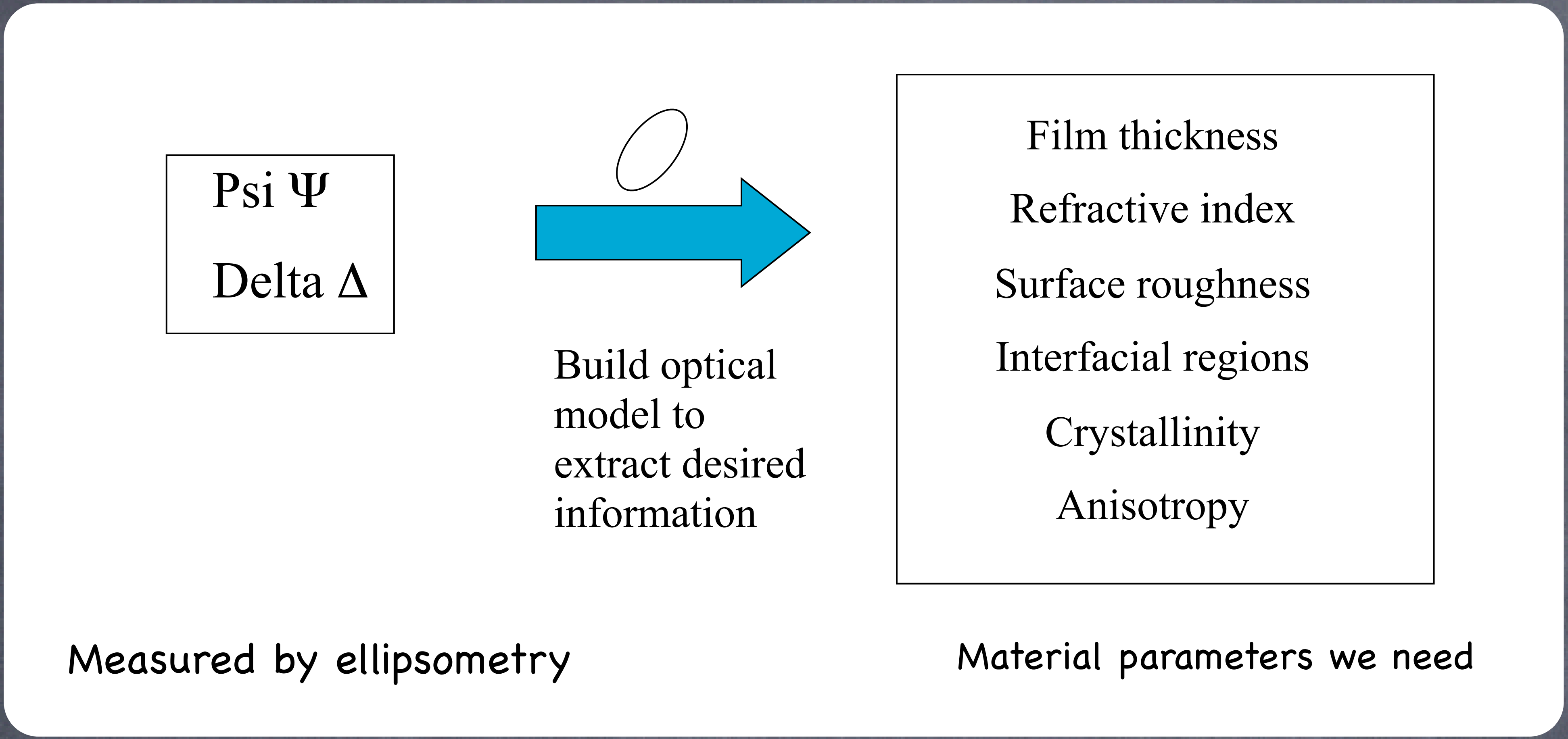
Ellipsometry setup

A linear polarized monochromatic light beam (from source & polarizer) is passing through retarder / compensator in +/– 45° orientation and then impinging on the substrate surface with equal polarization component parallel (s) and perpendicular (p) to the surface. After reflection the light is elliptically polarized due to different interaction of s– and p–component with the surface. By setting the polarizer and analyzer so that no light is passing (null ellipsometer) the relative phase change Δ and relative amplitude change ψ can be calculated. If the refractive index of the thin film (n_D =1.45 – 1.5 for hydrocarbons) is known the thickness can be calculated from Δ and ψ with angstrom resolution (→ molecular monolayers).

The two parameters Δ (sometimes $\cos\Delta$) and Ψ are related to the ratio of the Fresnel amplitude reflection coefficients for p- and s-polarised light:

$$\frac{r_p}{r_s} = \tan\Psi \exp(j\Delta)$$

Ellipsometry setup



Psi Ψ

Delta Δ

Build optical model to extract desired information

Film thickness

Refractive index

Surface roughness

Interfacial regions

Crystallinity

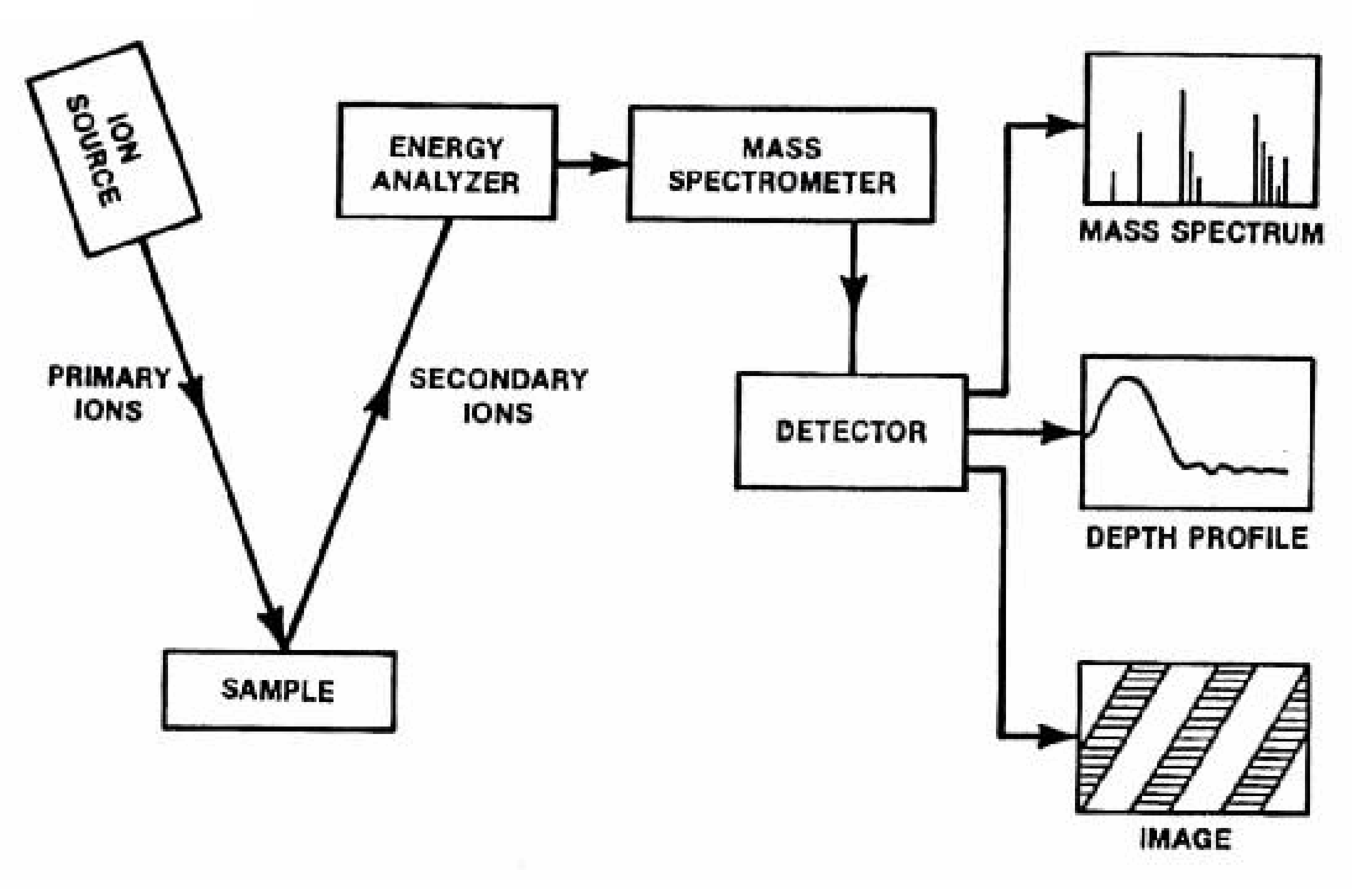
Anisotropy

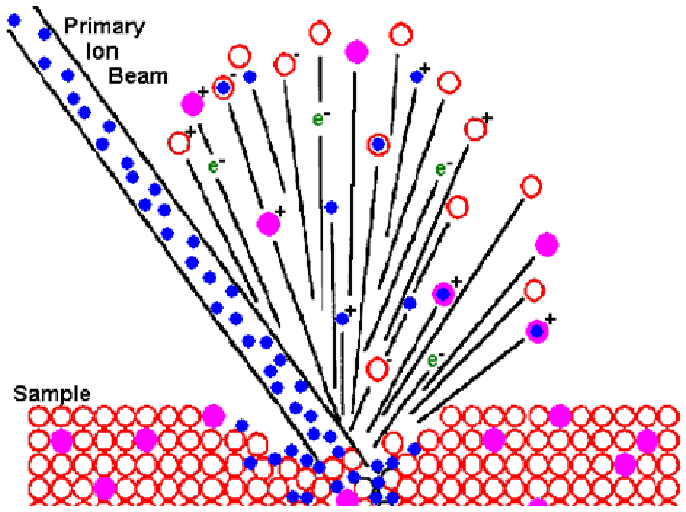
Measured by ellipsometry

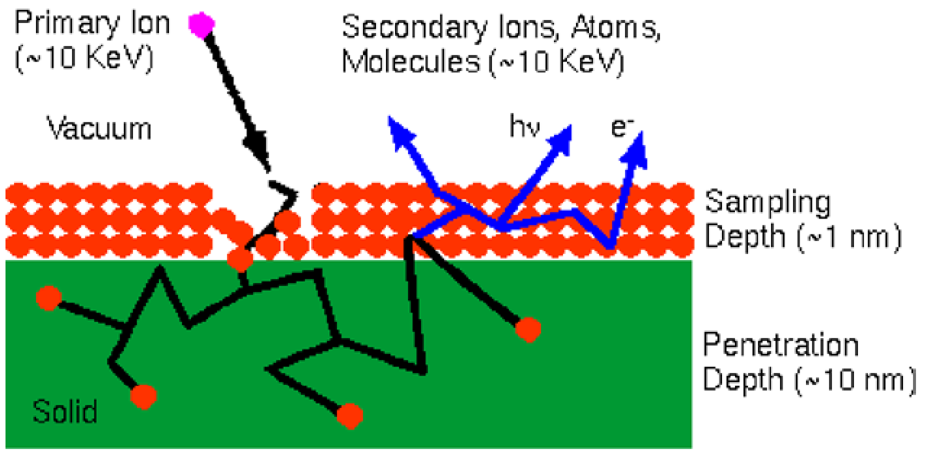
Material parameters we need

Secondary Ion Mass Spectrometry

SIMS: mass spectrometric characterization of surface and near surface regions, the sample in ultra high vacuum (10^{-9}–10^{-10} torr) is bombarded with neutral or charged ions (primary ions, Cs^+, O_2^+, O^- → reactive, Ar^+, He^+, Ne^+ → inert), which eject ions from the sample (0.5–30 keV, secondary, or sputtered ions), these ions are then analyzed with a spectrometer, which detects their mass to charge (m/z) ratios allowing identification of the elements in the material (→ depth profiling)



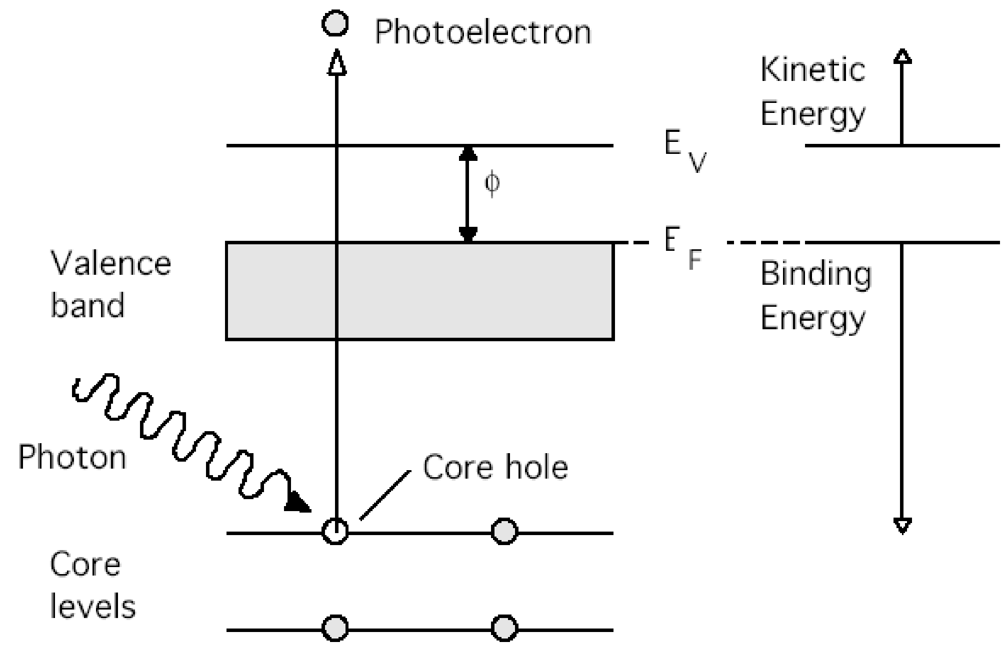




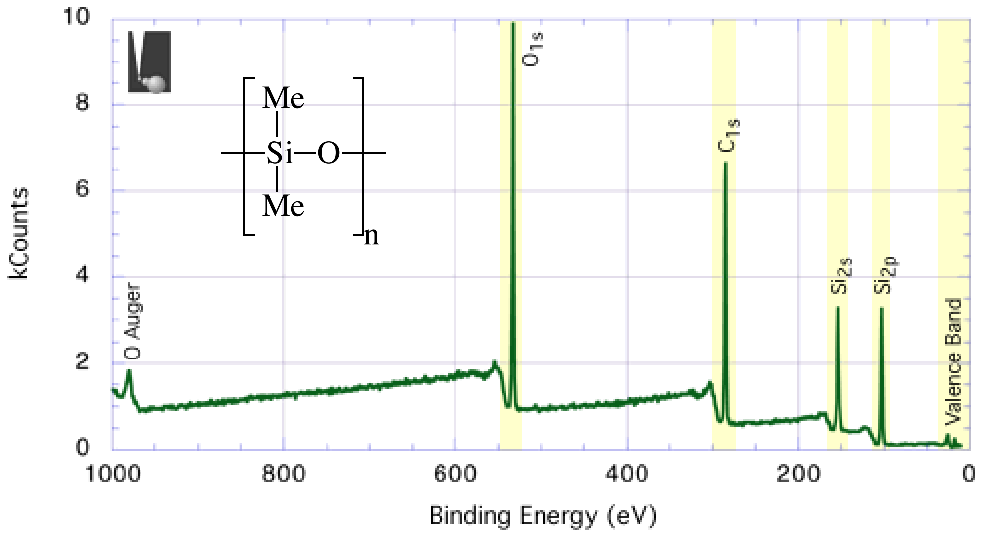
X-Ray Photoelectron Spectroscopy

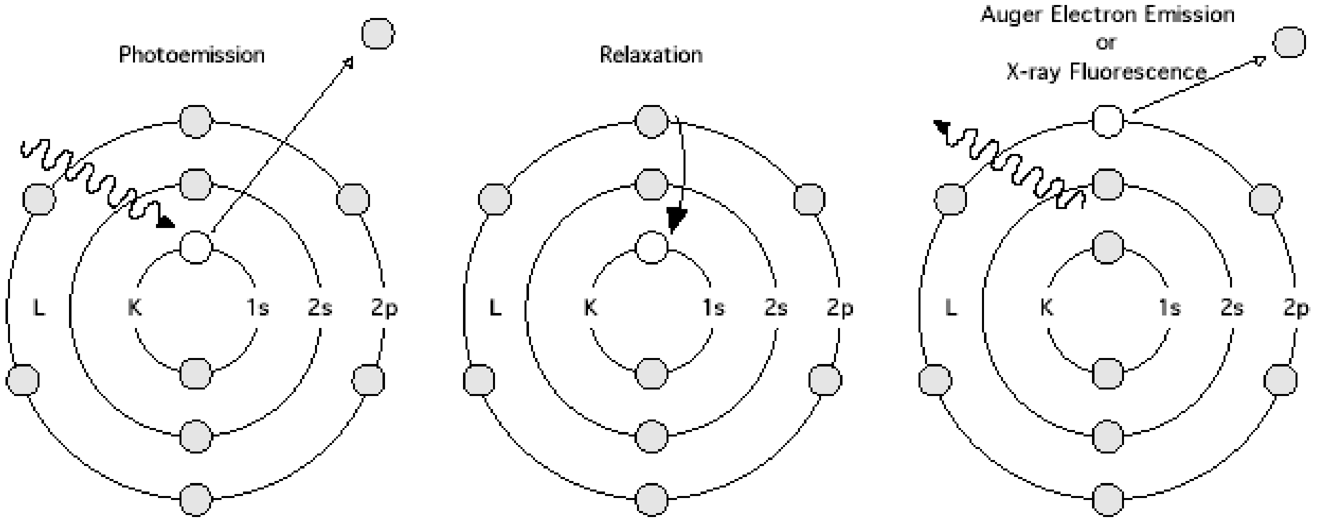
XPS: surface is irradiated with x–rays, core electrons in surface atoms are ejected and their energy is measured (element specific, often binding state specific), valence electrons can fall into core hole and emit characteristic photons (→ x–ray fluorescence) or secondary electrons of lower energy (Auger electrons)

- non destructive (...limited to organic material)
- quantitative method for elemental composition
- sensitive (0,1% ML)
- chemical shifts give information about:
  - oxidation state
  - chemical environment
- sampling depth 10–100 Å (depth profiling)
- possibility of imaging



poly(dimethyl siloxane) (PDMS) Survey Scan 0-1000 eV

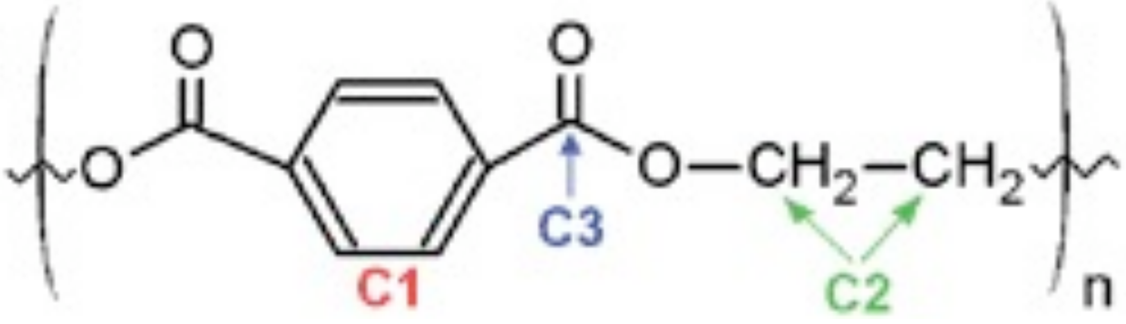




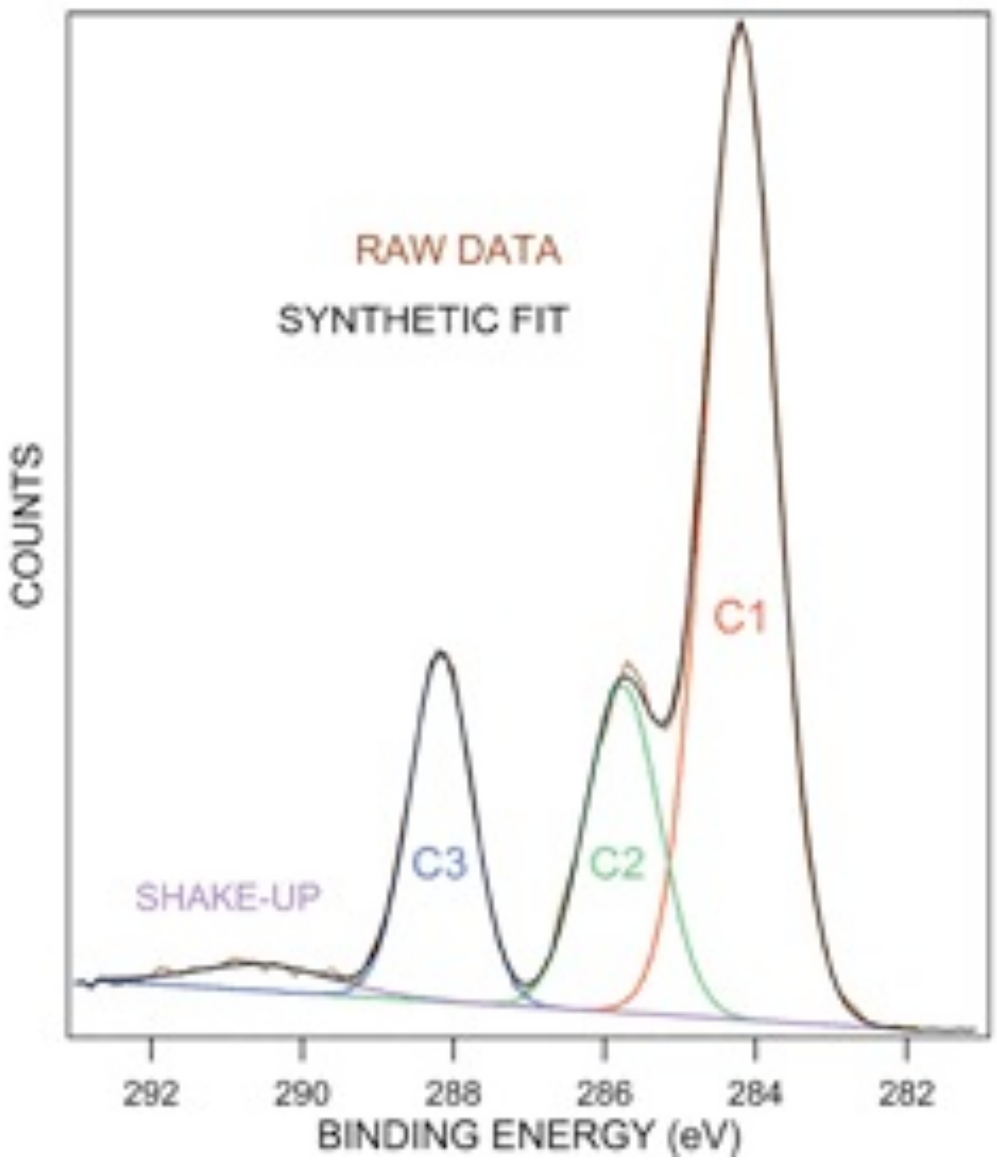
X-Ray Photoelectron Spectroscopy

Polyethylene Terephalate

Ratio of Different Carbon Atoms
C1:C2:C3 = 3:1:1



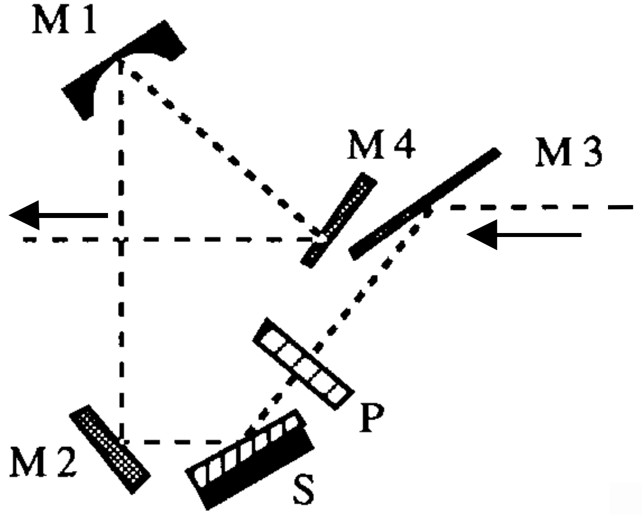
PET CARBON 1S



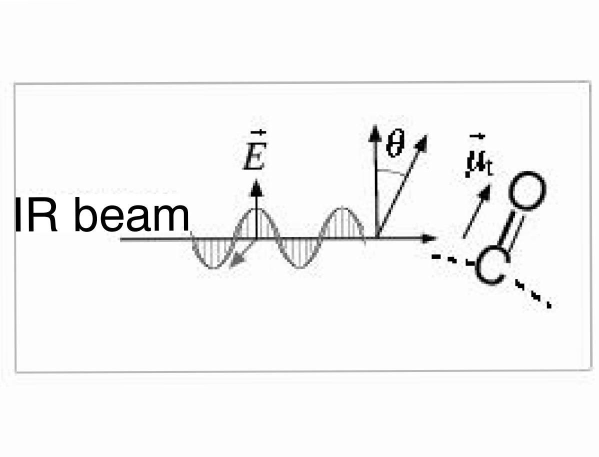
High-resolution XPS spectra of carbon 1s from polyethylene terephthalate backsheet material, showing excellent quantitative agreement between measured and predicted peak area ratios. Subtle differences in polymer functionality are assessed by deviations from stoichiometry.

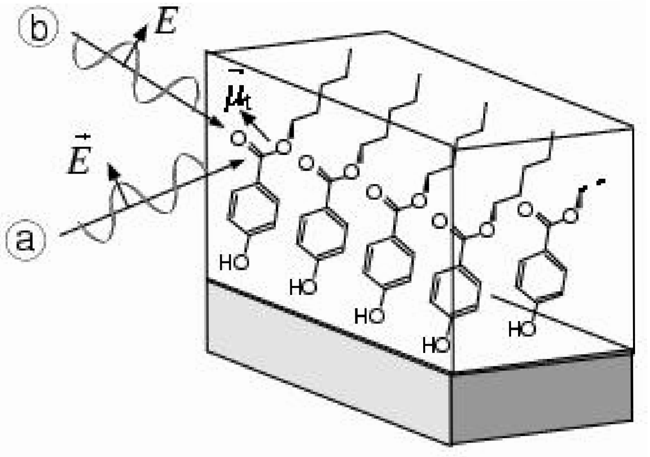
Fourier Transform Infrared Spectroscopy

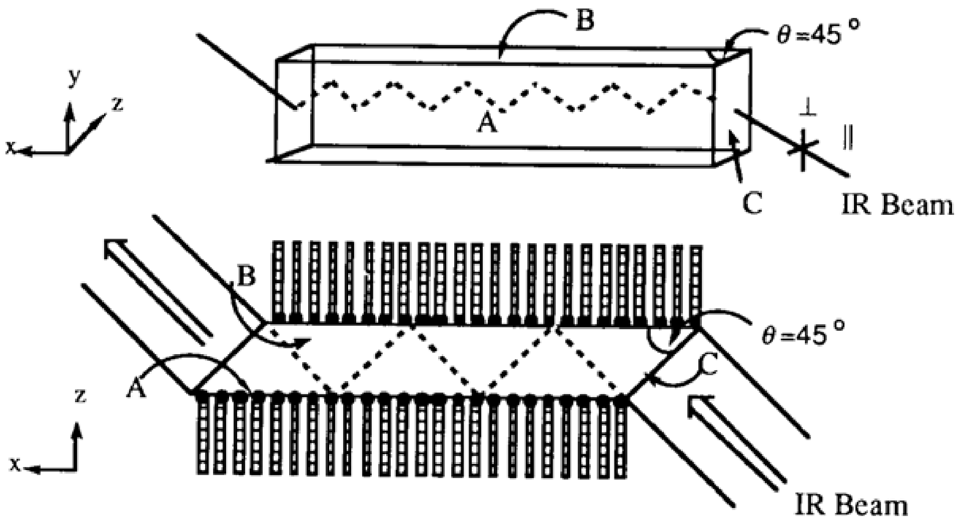
polarized IR in reflection absorption (RA) can detect **orientation** of molecules in **anisotropically** oriented **sample**, in **attenuated total reflection (ATR) higher signal-to-noise ratios can be obtained**



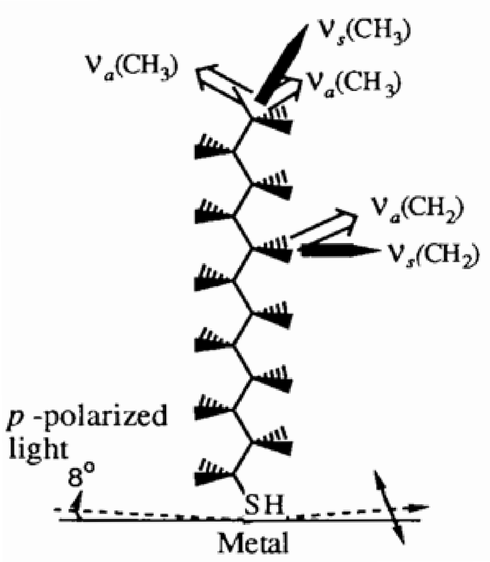
RA setup

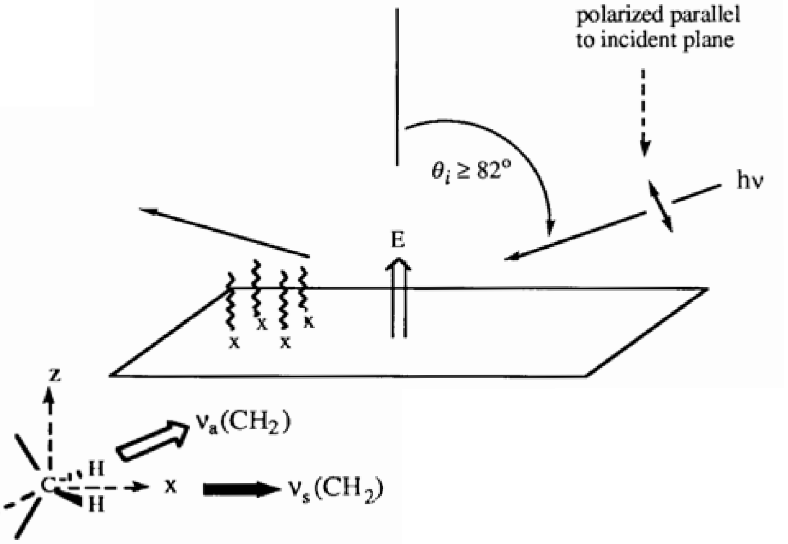






ATR setup





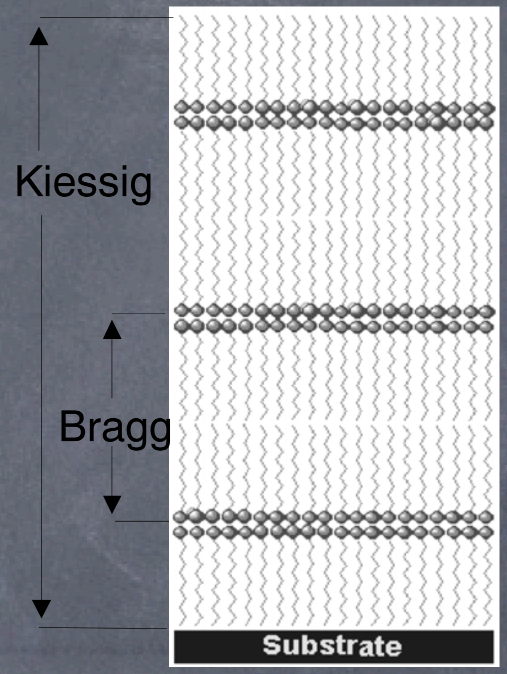
Small Angle X-Ray Scattering

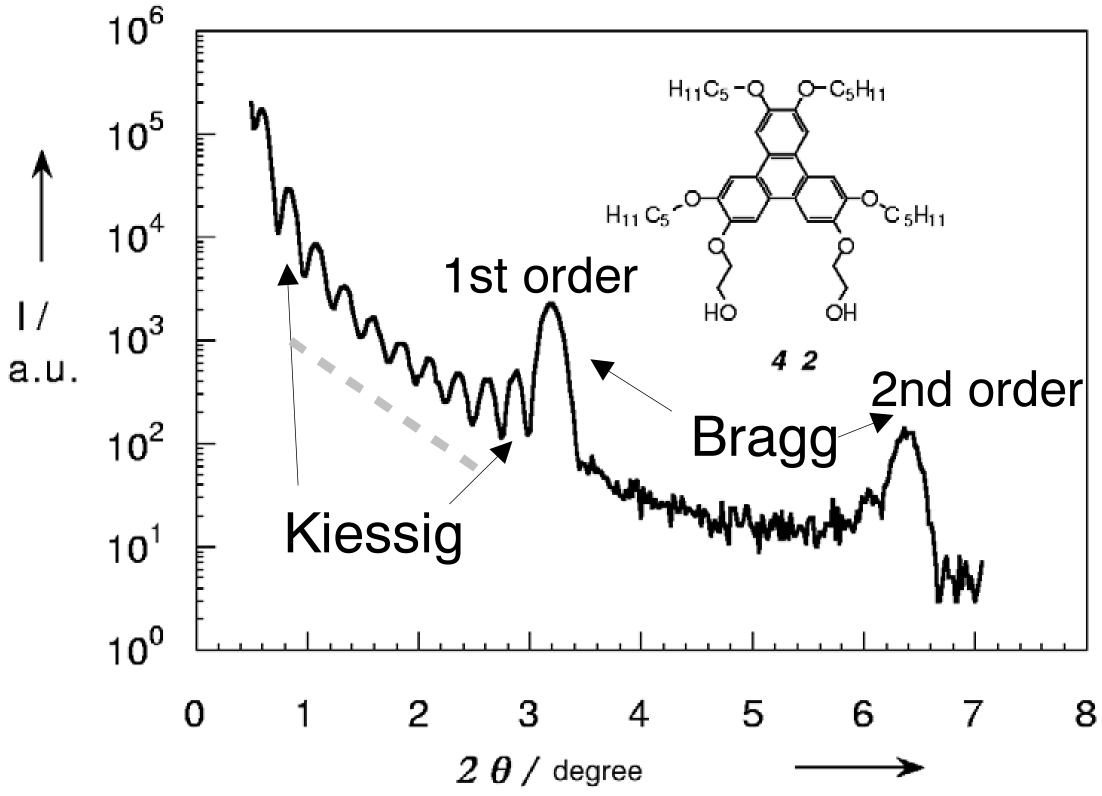
x-ray reflectivity / diffraction or small angle x-ray scattering (SAXS) provides information on film thickness / layer spacing by diffraction at the film planes / periodic layer spacings parallel to the substrate plane according to Bragg's law: $n \lambda = 2 d \sin \theta$

n: order of reflex ($n = 1, 2, 3, \ldots$); λ: wavelength of x-ray; d: layer spacing; θ: angle of x-ray to surface plane

Bragg peaks (large angle): periodic layer spacing

Kiessig peaks (small angle): overall film thickness





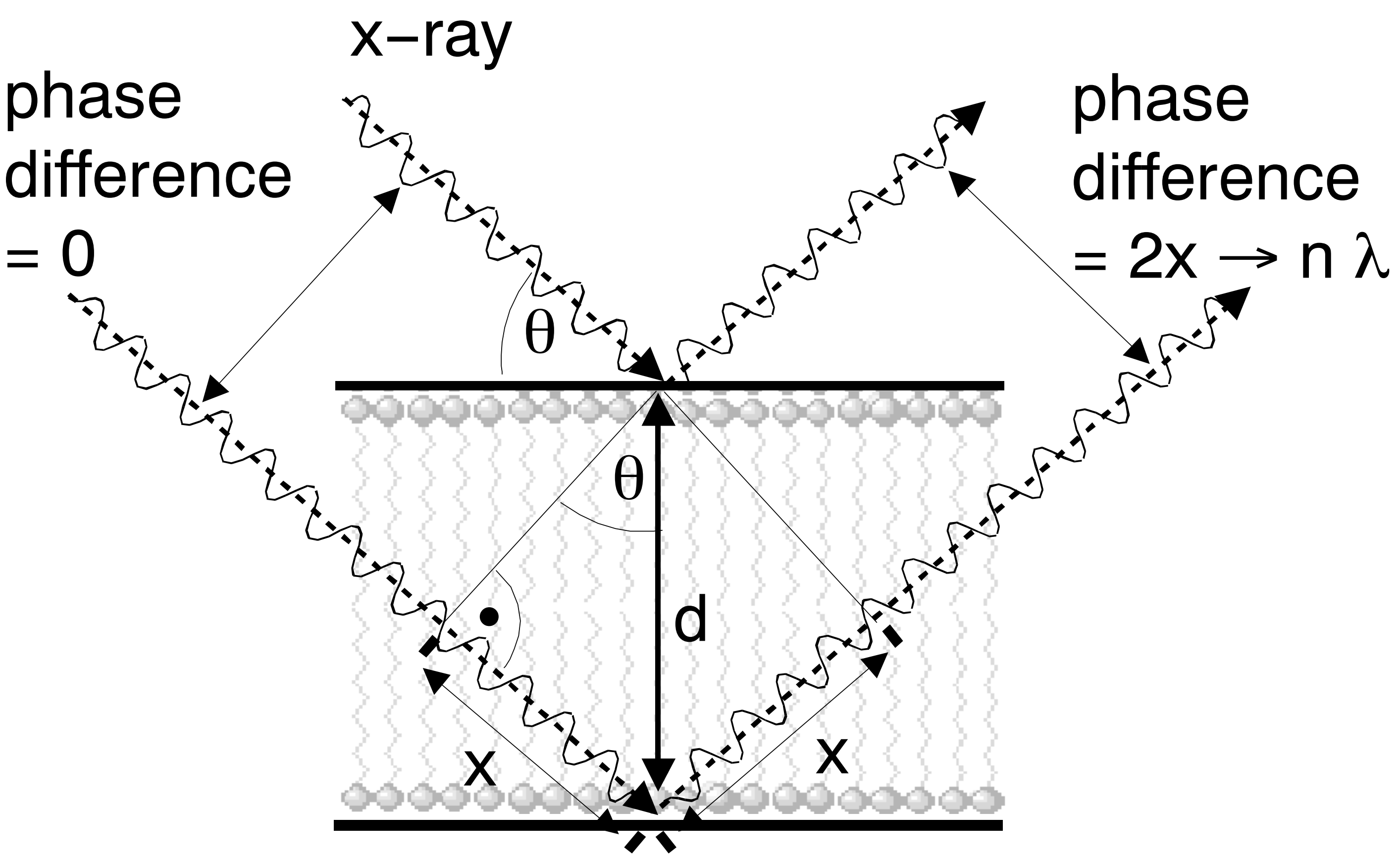
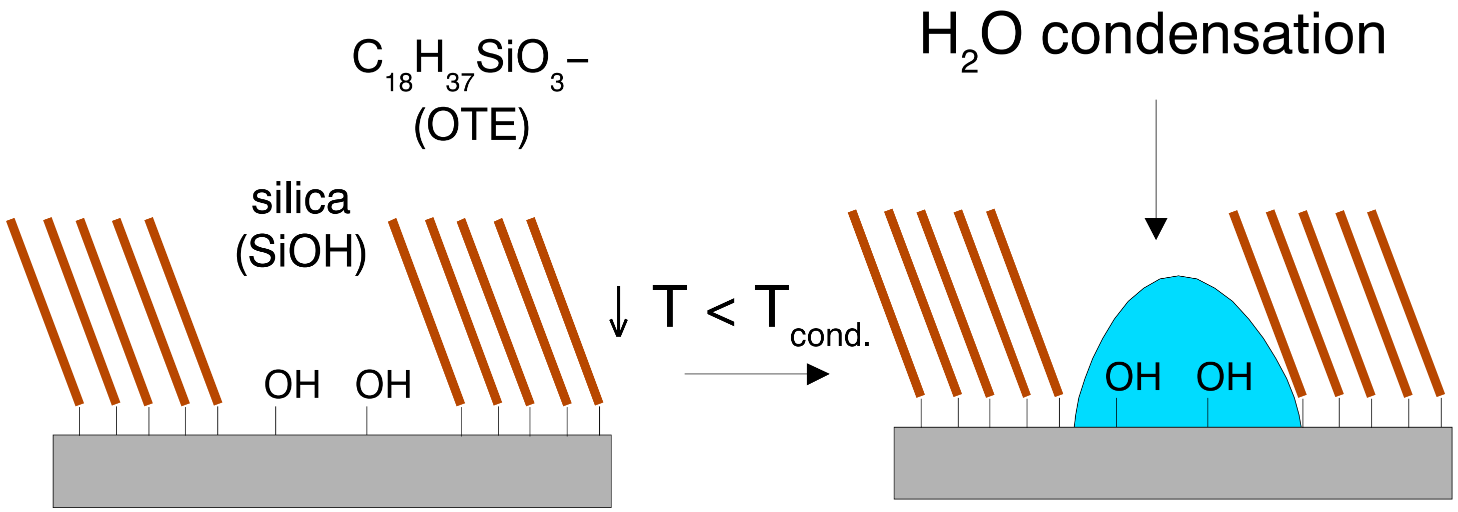
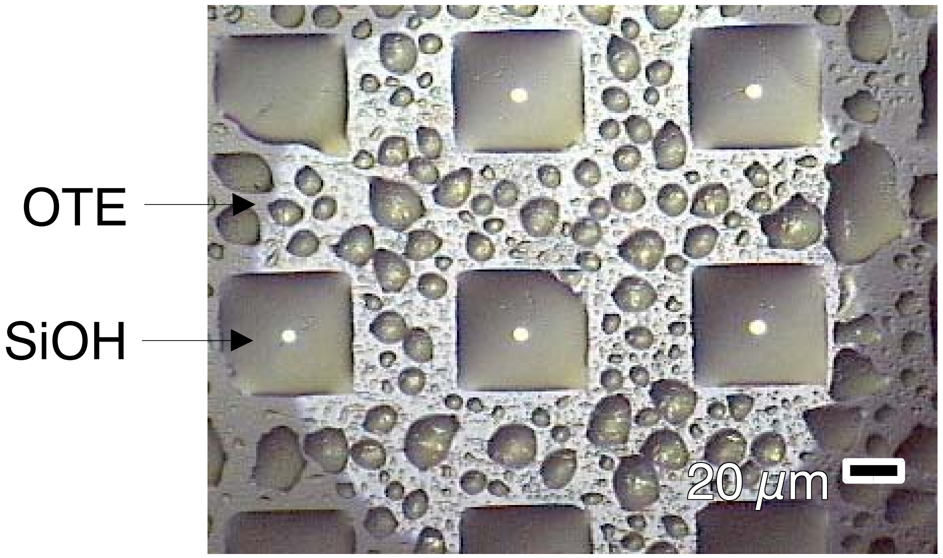


Image Methods: Breath Patterns

Breath / condensation pattern: By cooling a substrate below the condensation temperature H_2O will condense in different rates on the substrate with the nucleation rate of condensation depending on the surface topography and chemical composition / materials properties.

The resulting condensation pattern (with lateral dimensions above the wavelength of light) allows observation of differences in chemical surface composition (often vertically in molecular dimensions) by optical microscopy or even with the unequipped eye.



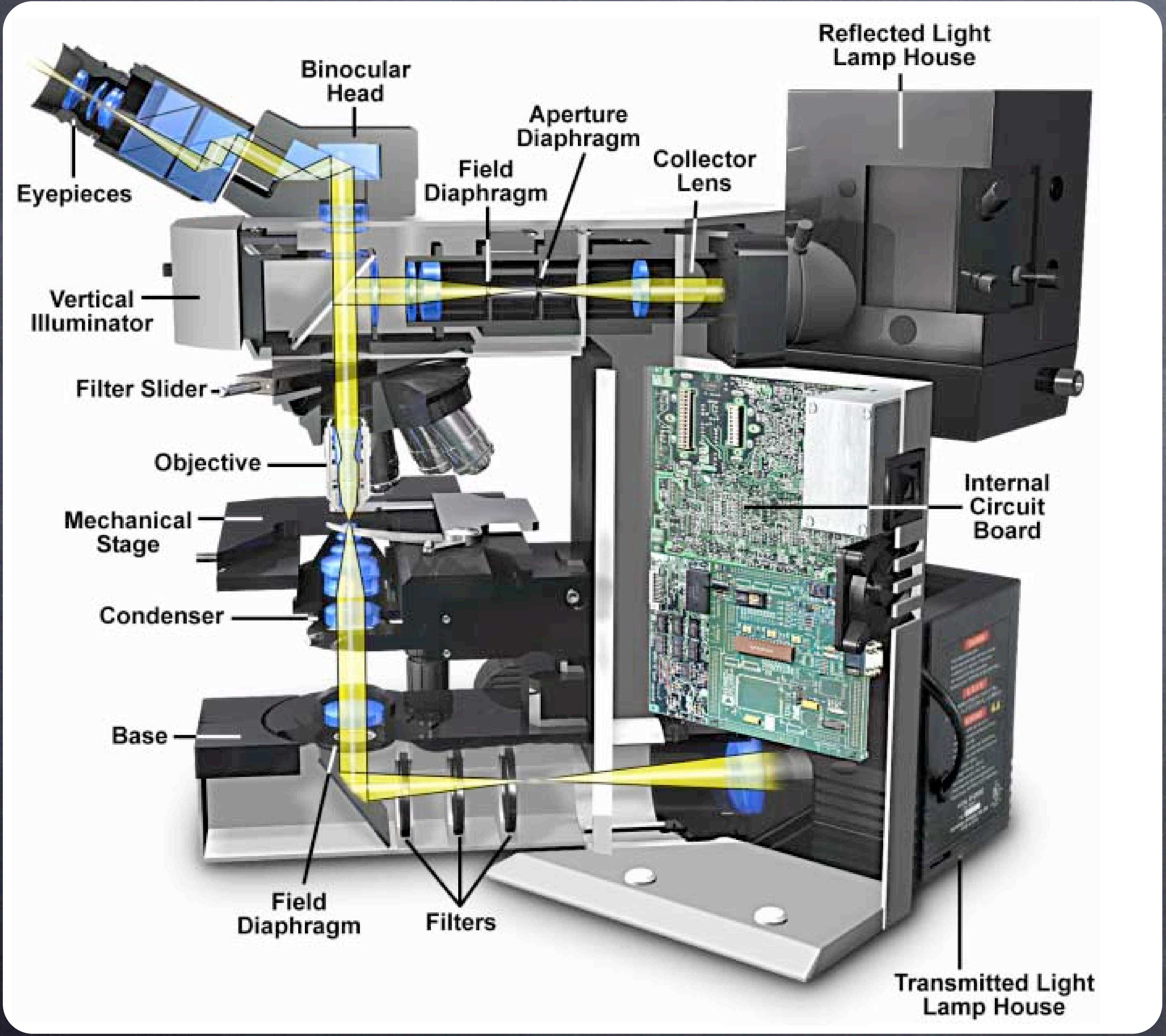


optical microscope image after H_2O condensation (octadecylsilane surface with silica squares)

The contrast can often be increased by temperature cycling above and below the condensation temperature.

Optical Microscopy

visual inspection / magnification of an object by the use of light, resolution around half the wavelength of light (practically around 0.5 μm for separated points)



two modes of illumination:

1) transmission: light source is on opposite side of specimen with respect to eyepieces (partially transparent samples required)

2) reflection: illumination from the same side as eyepieces, reflected light is observed (non–transparent samples can be investigated)

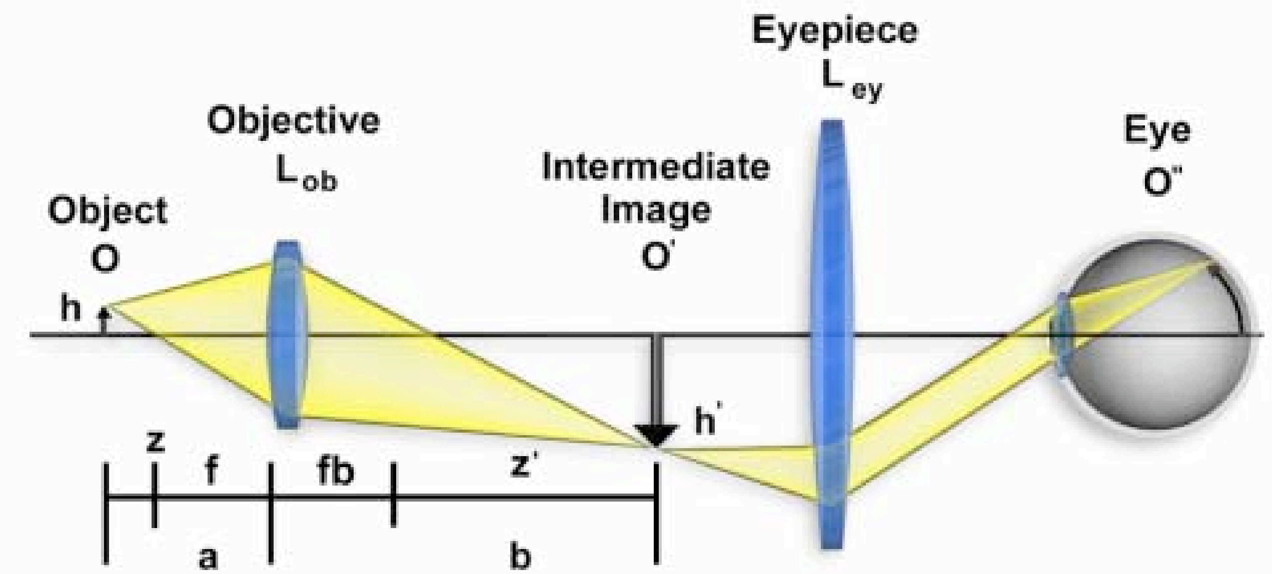
numerical aperture (NA):

NA = r / f → radius of objective r divided by the distance objective–specimen f (~ focal distance of objective)

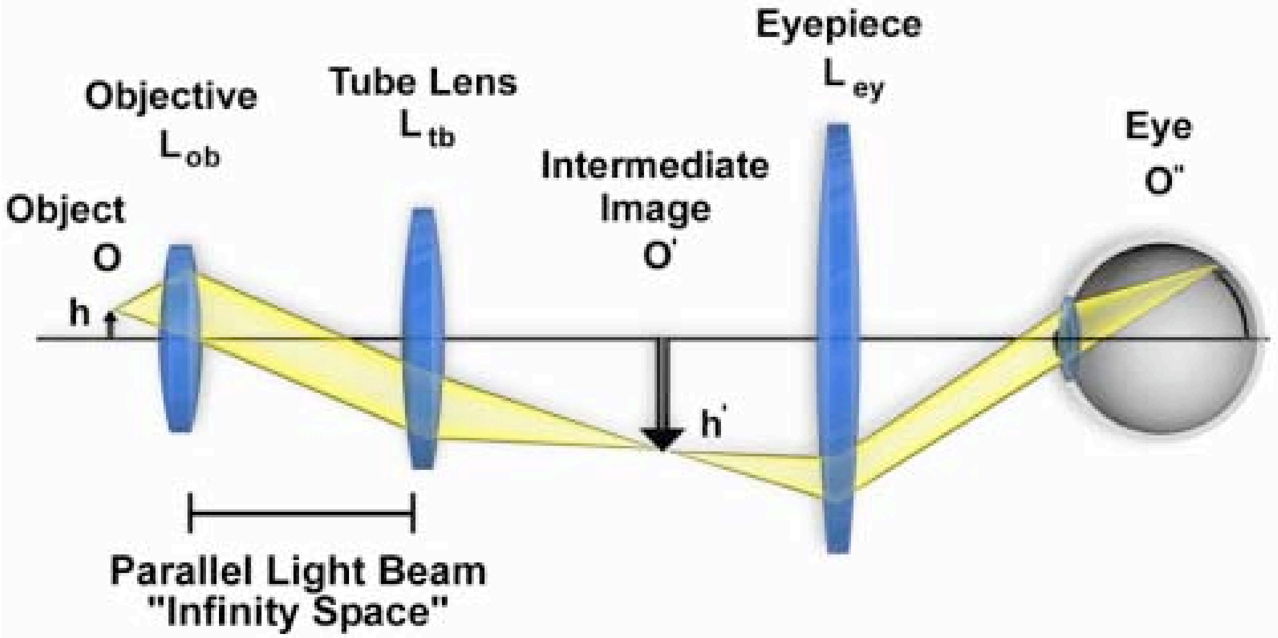
Michael W. Davidson and Mortimer Abramowitz "Optical Microscopy": http://micro.magnet.fsu.edu/primer/opticalmicroscopy.html

Light Paths in Optical Microscopy

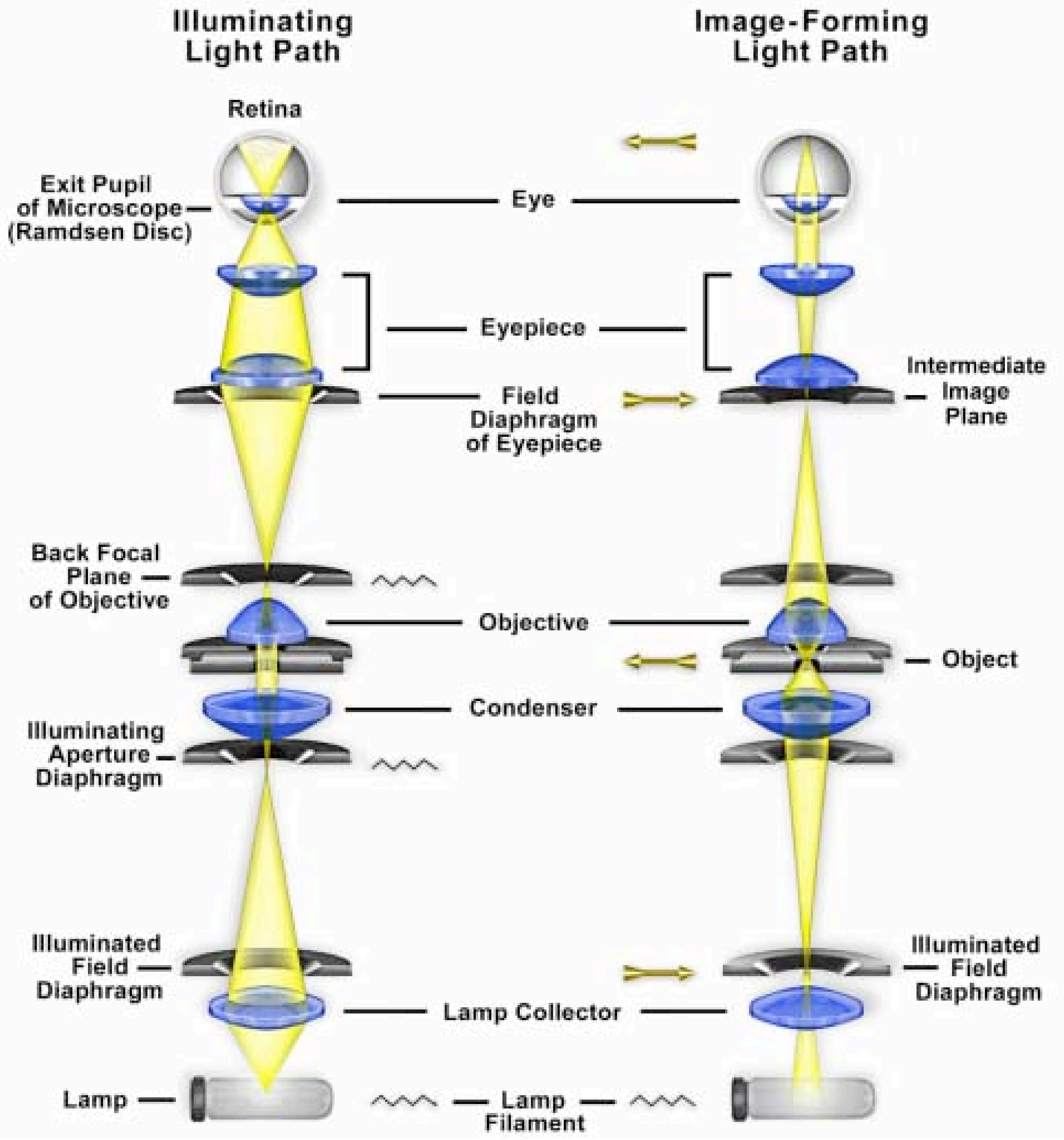
Finite-Tube Length Microscope Ray Paths



Infinity-Corrected Microscope Ray Paths



Light Paths in Köhler Illumination



Michael W. Davidson and Mortimer Abramowitz "Optical Microscopy": http://micro.magnet.fsu.edu/primer/opticalmicroscopy.html

Objective Specifications

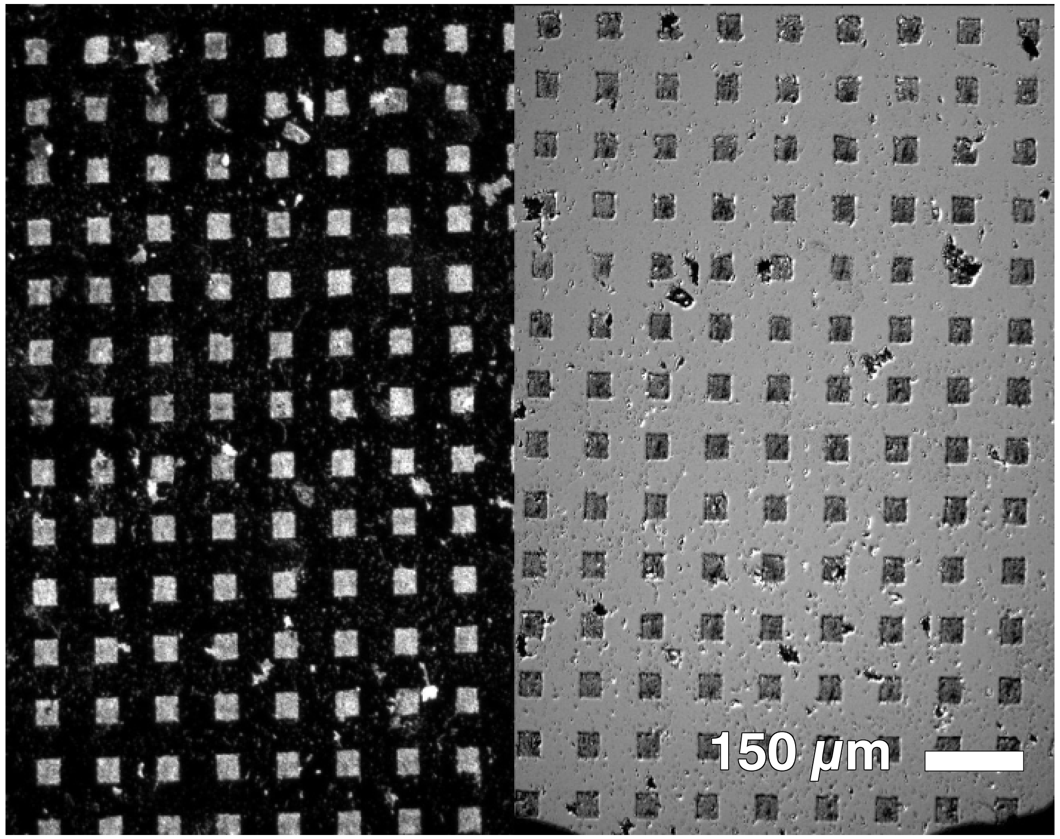
Michael W. Davidson and Mortimer Abramowitz "Optical Microscopy": http://micro.magnet.fsu.edu/primer/opticalmicroscopy.html

Bright- and Darkfield

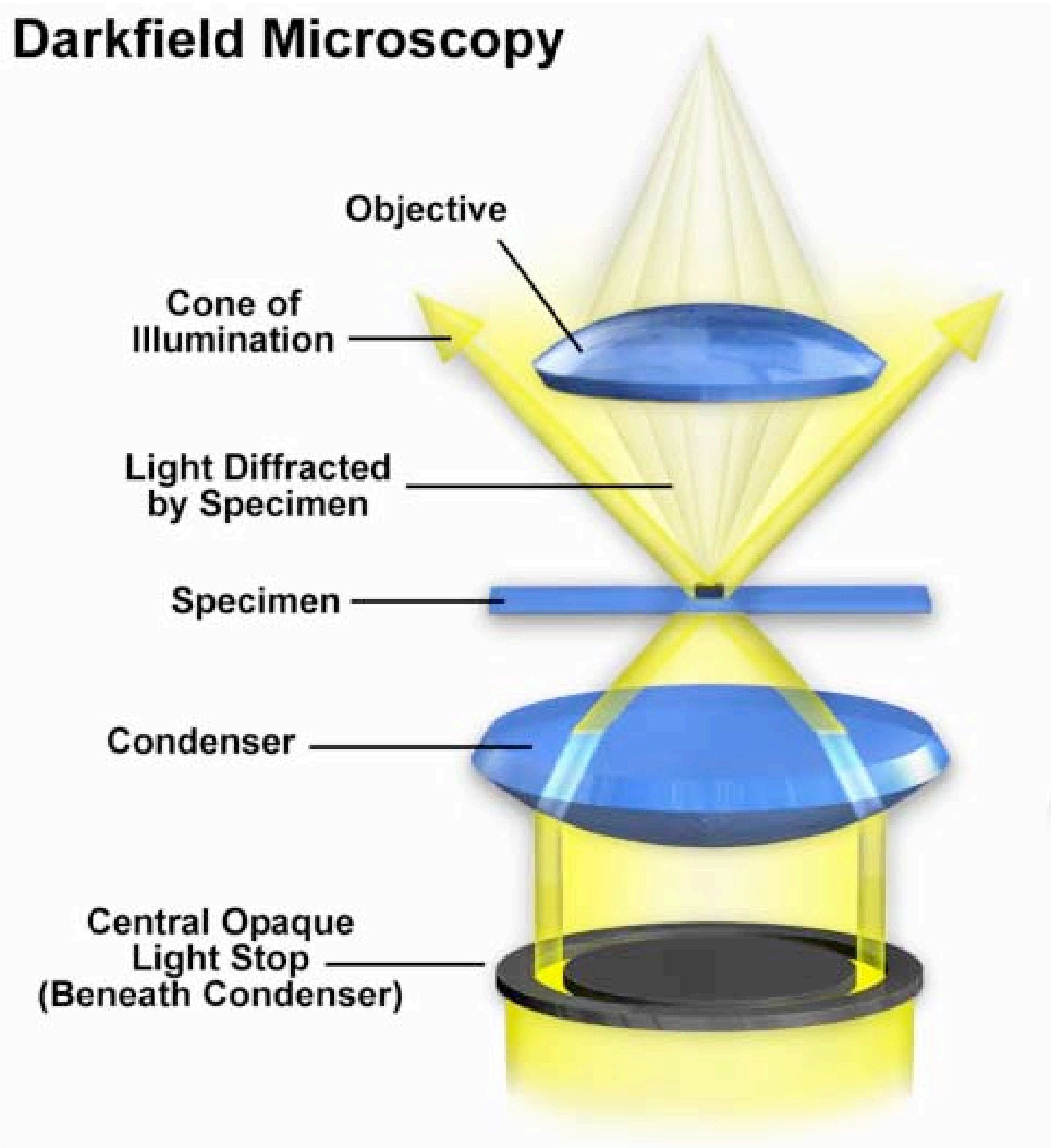
brightfield: conventional illumination with direct observation of light absorption / diffraction / reflection variations in specimen; often requires staining of sample

darkfield: striking illumination of specimen under oblique angle and observation of diffracted / reflected / refracted (scattered) light by specimen

thin film of polymer colloid particles (in squares) on OTE / SiOH (squares) pattern



darkfield brightfield (DIC)



Michael W. Davidson and Mortimer Abramowitz "Optical Microscopy": http://micro.magnet.fsu.edu/primer/opticalmicroscopy.html

Rheinberg Illumination

This technique is a striking variation of low to medium power darkfield illumination using colored gelatin or glass filters to provide rich color to both the specimen and background. The central opaque darkfield stop is replaced with a transparent, colored, circular stop inserted into a transparent ring of a contrasting color.

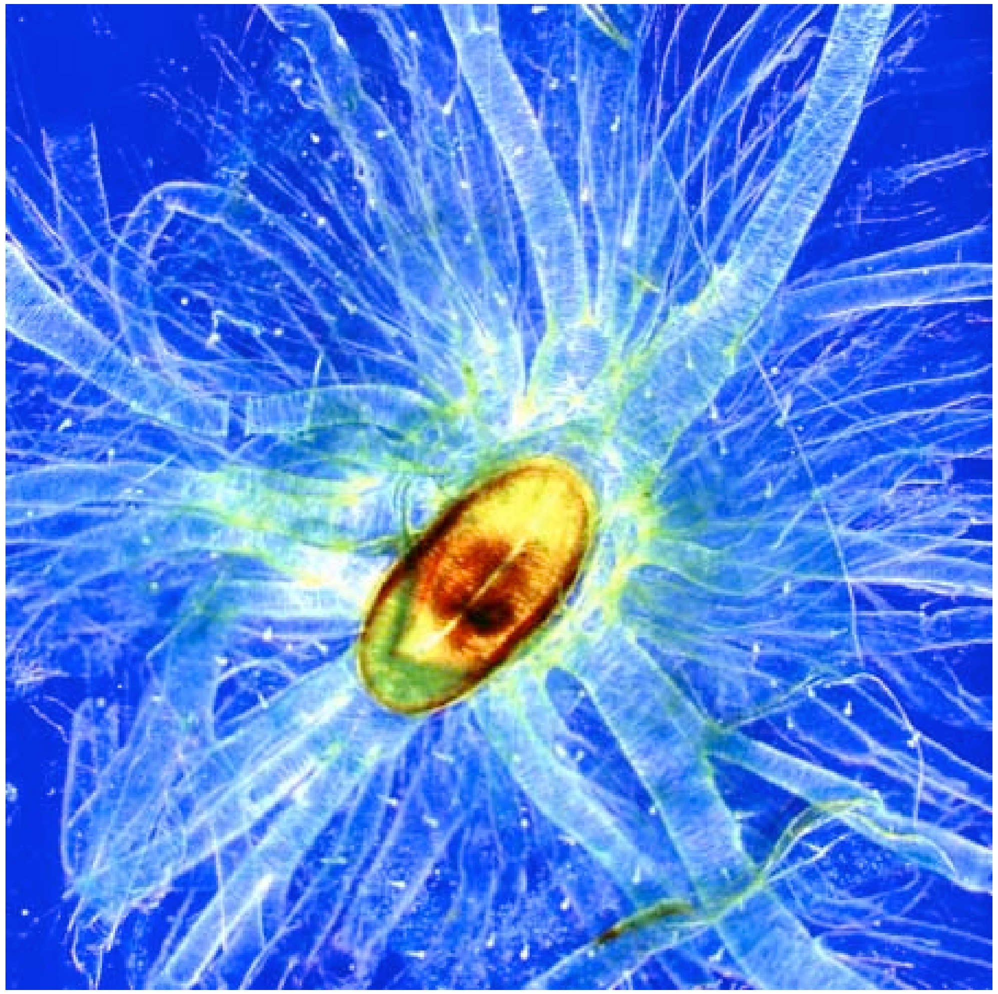
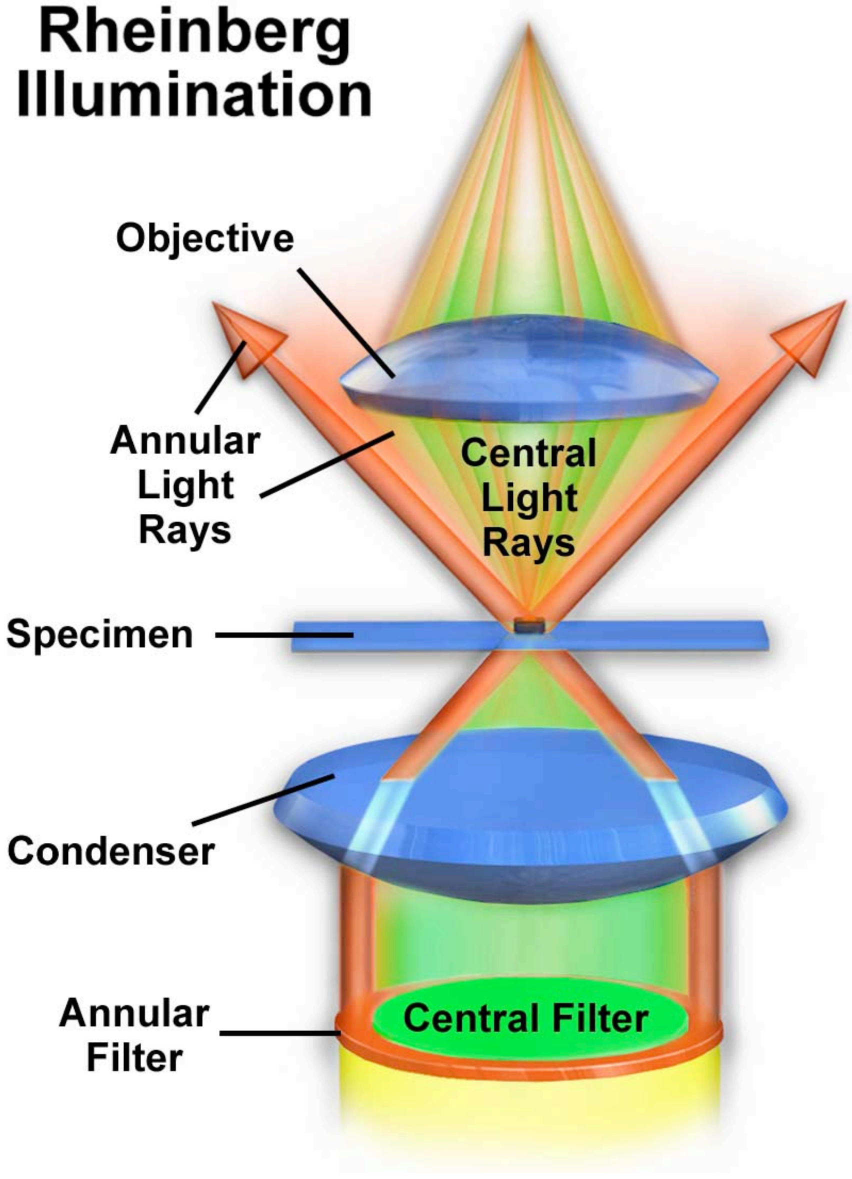


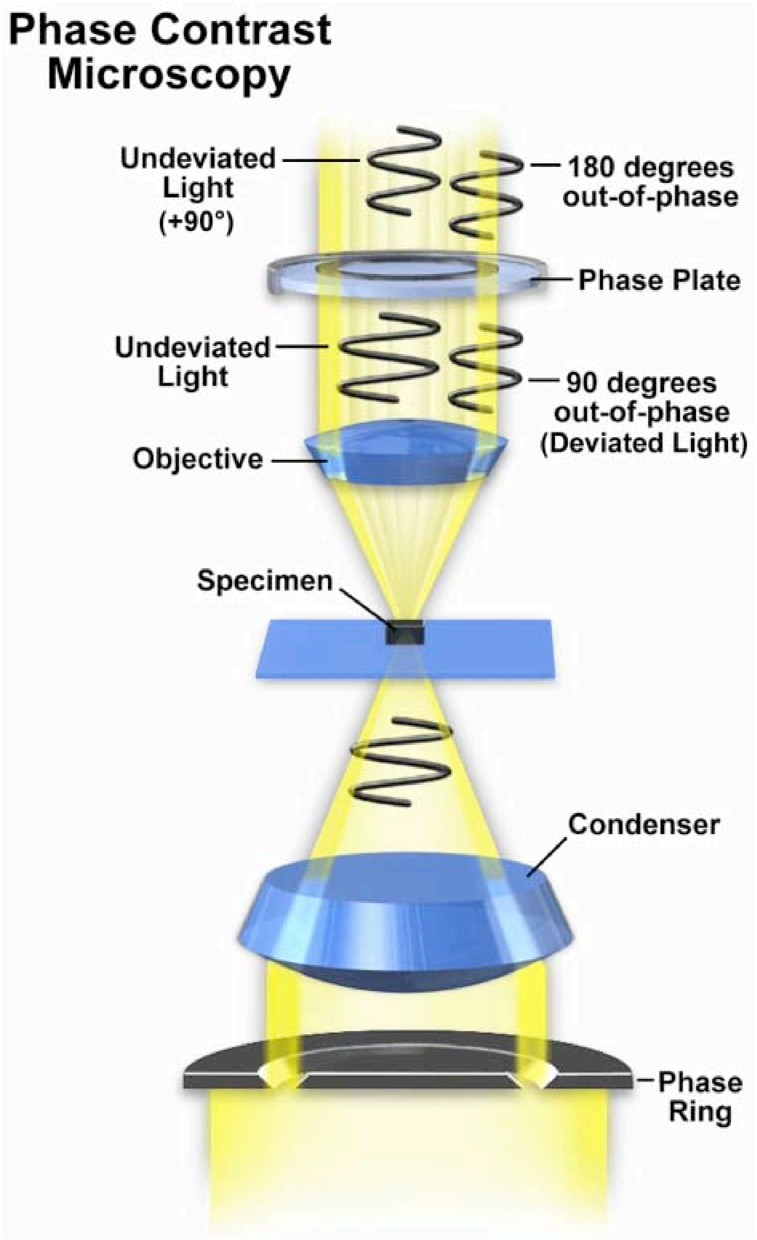
Figure 17. Spiracle and trachea from silkworm larva photographed at low magnification under Rheinberg illumination using a blue central and yellow annulus filters and a 2x objective.



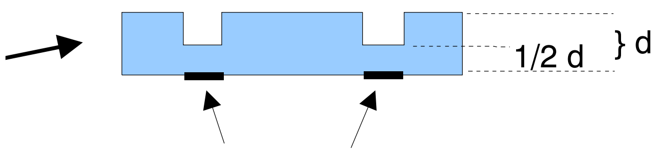
Michael W. Davidson and Mortimer Abramowitz "Optical Microscopy": http://micro.magnet.fsu.edu/primer/opticalmicroscopy.html

Phase Contrast

Variations of refractive index (or thickness) in the specimen cause different light velocities and phase differences compared to undeviated (zeroth order) light around the sample. Image contrast is obtained by interference of deviated and zeroth order light (phase lag 1/2 λ) at the eyepiece.



cross section through
phase plate (transparent !)



semitransparent metal film

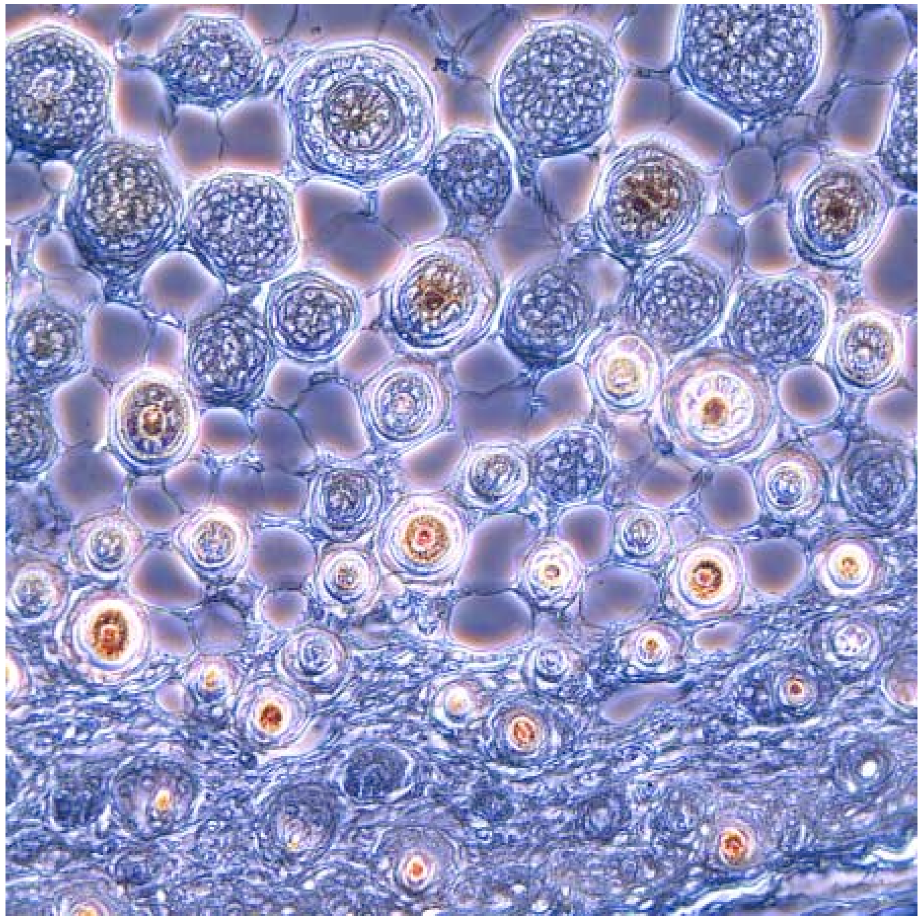
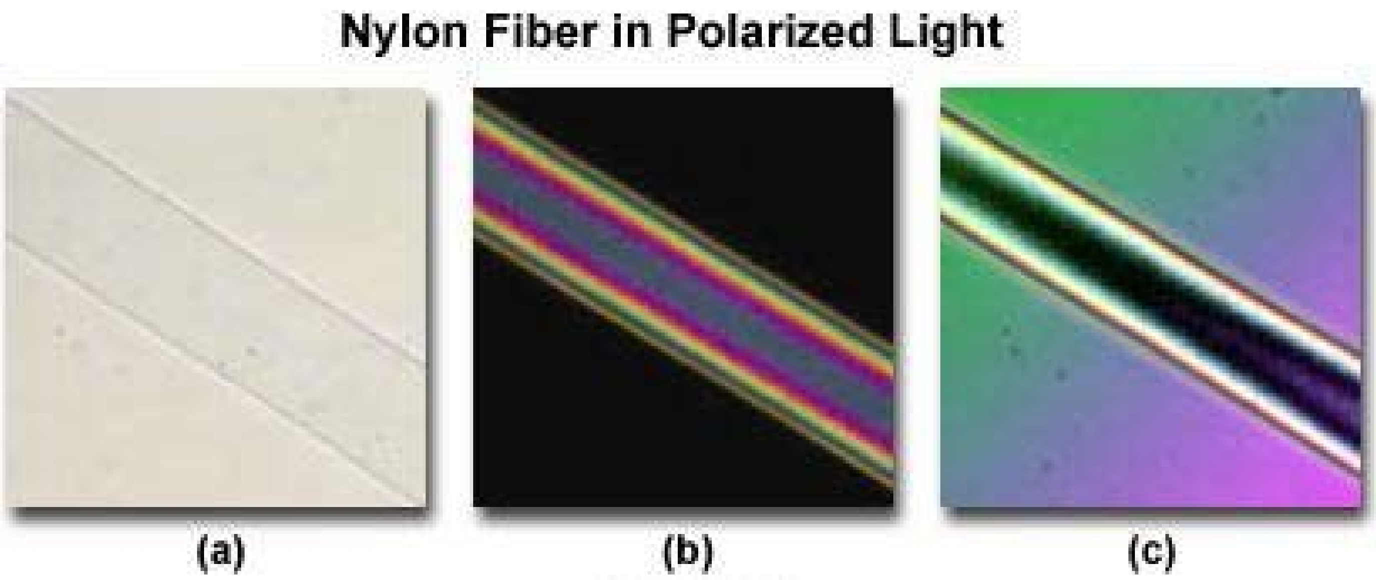


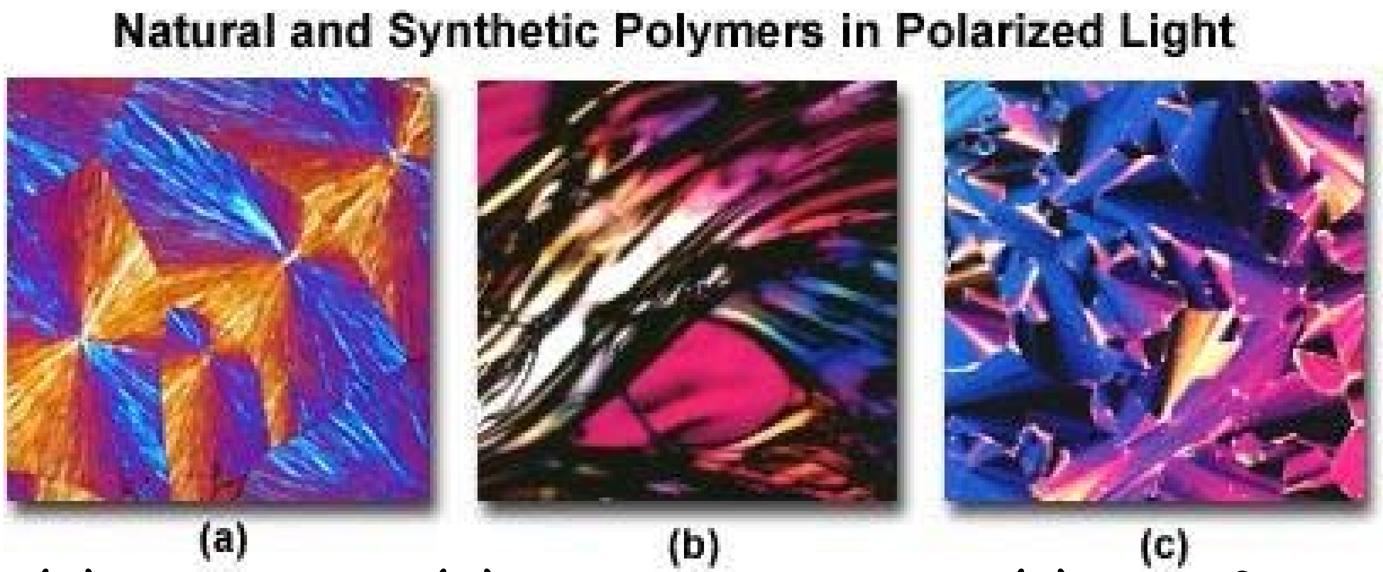
Figure 19. Photomicrograph of hair cross sections from a fetal mouse taken using phase contrast optics and a 20x objective.

Michael W. Davidson and Mortimer Abramowitz "Optical Microscopy": http://micro.magnet.fsu.edu/primer/opticalmicroscopy.html

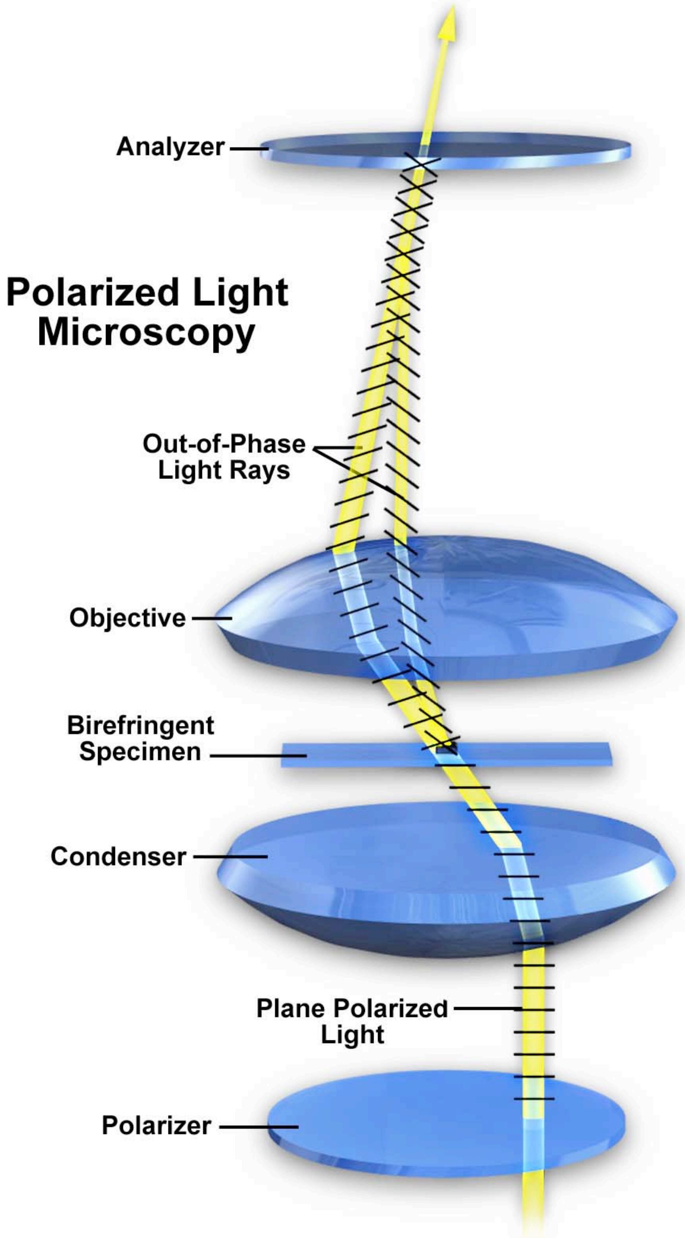
Polarized Light

Birefringent or optically anisotropic samples (e.g. minerals, liquid crystals, oriented polymers) can be observed between two crossed plane polarizers. Variation in intensity and color occur due to different light velocities for differently oriented polarization vectors in the specimen plane, leading to the rotation of the polarization axes. (birefringence → correlates to orientation of anisotropic crystal axes)


Nylon Fiber in Polarized Light


Natural and Synthetic Polymers in Polarized Light

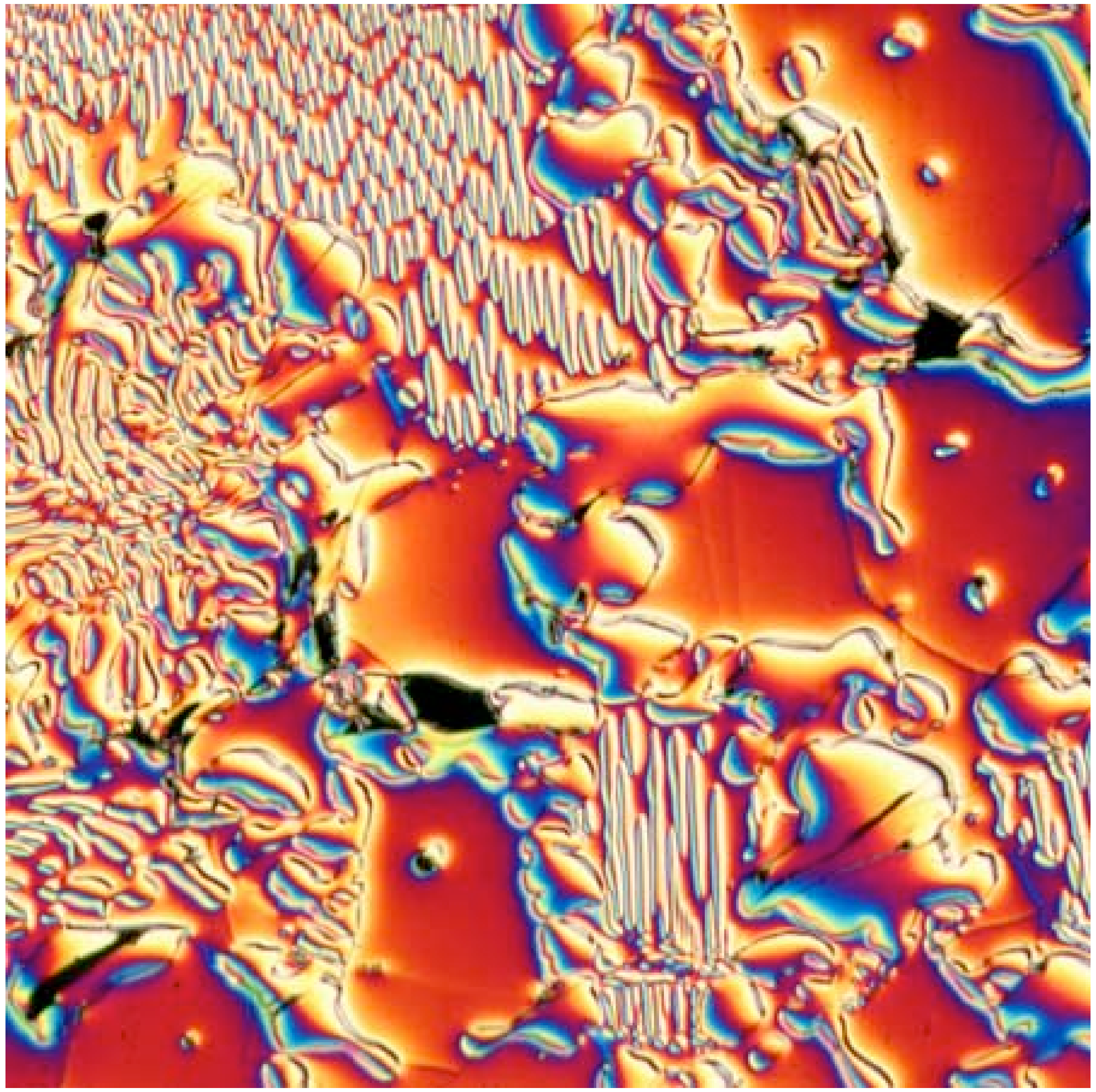
(a) spherolite (b) amorphous PC (c) LC of DNA


Polarized Light Microscopy

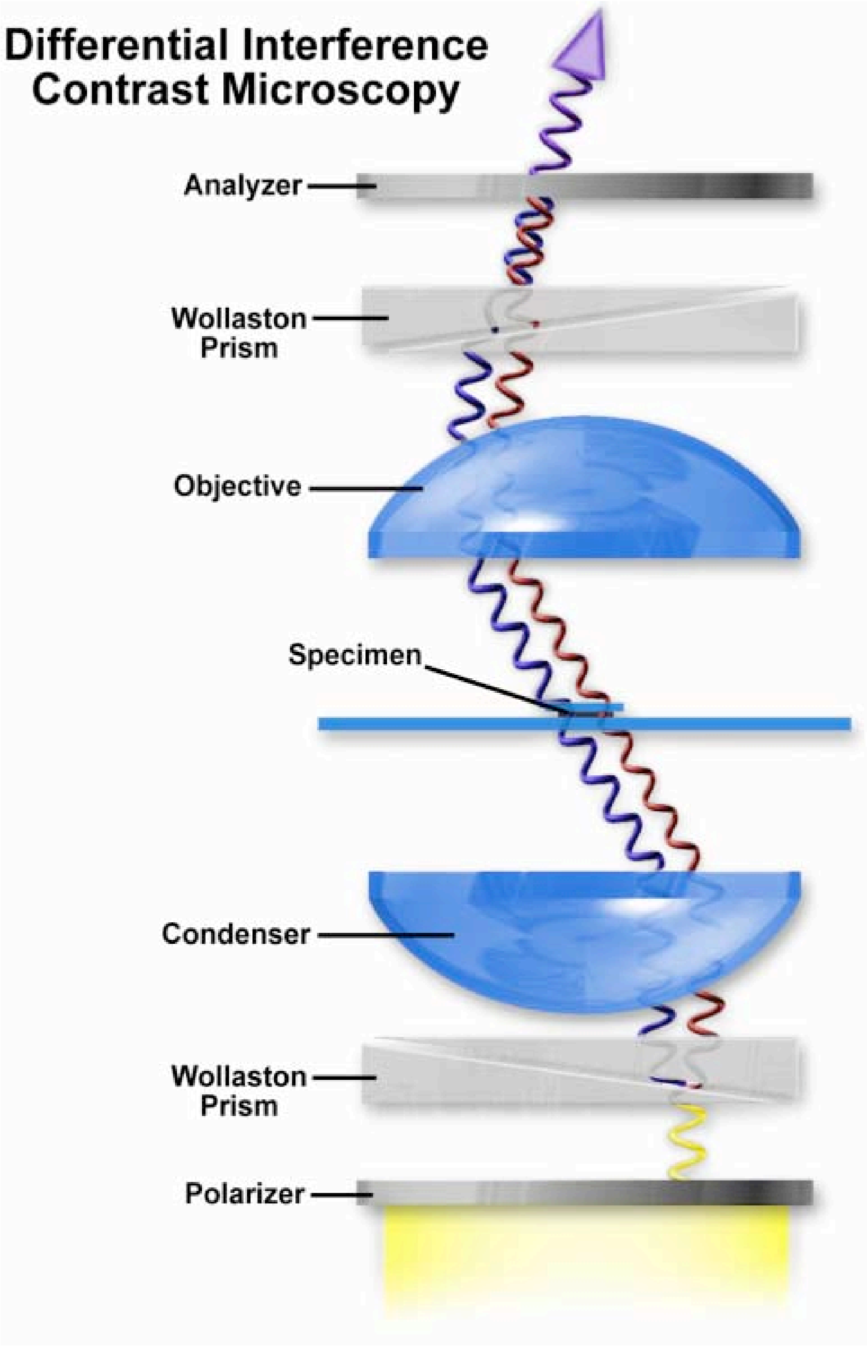
Differential Interference Contrast (DIC)

contrast enhancement of non–absorbing specimen due to variations in thickness / slope / refractive index

→ light is split into two perpendicular polarizations with minute horizontal separation (below resolution limit) and recombined (interference) after sample



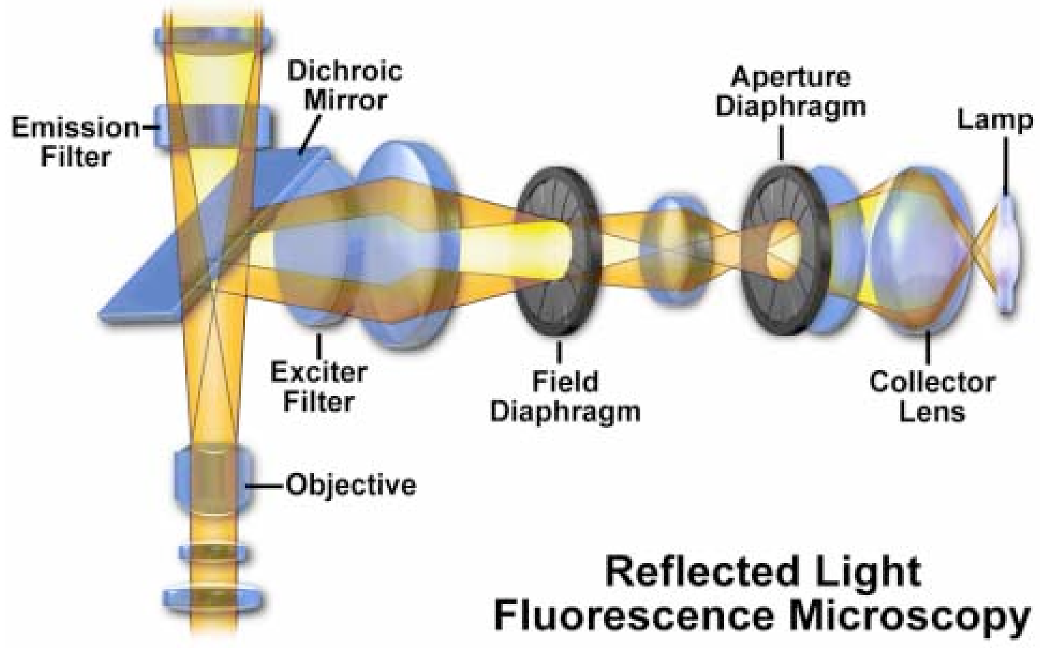
reflected light DIC of defects on the surface of a ferro–silicon alloy

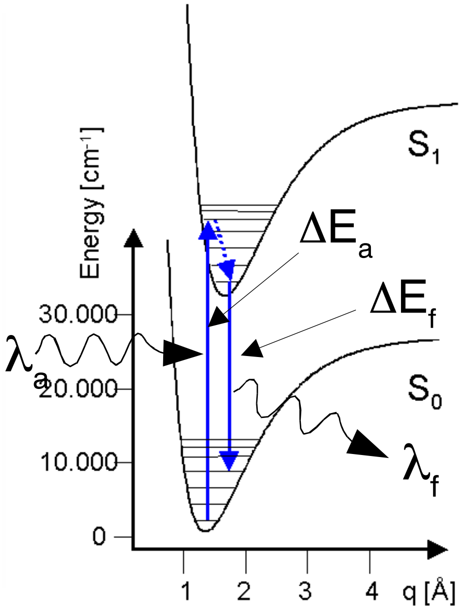


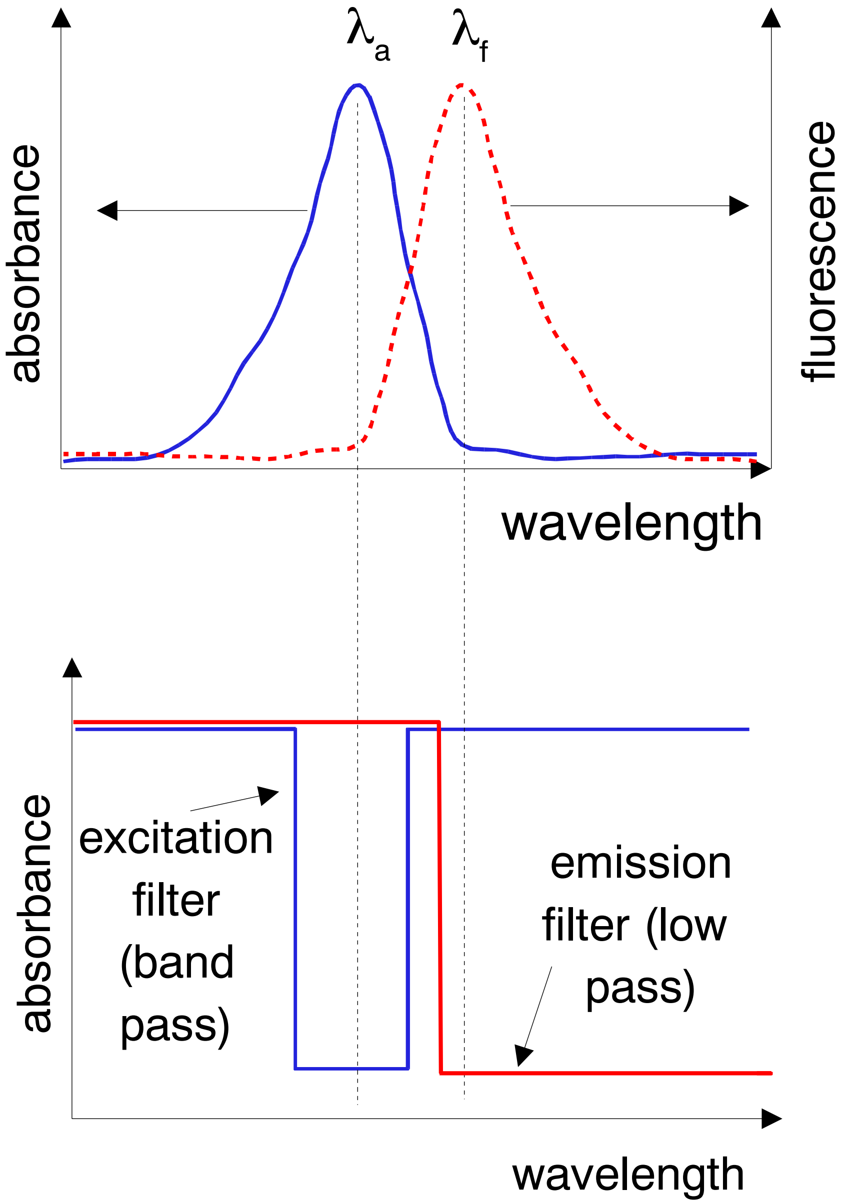
Fluorescence

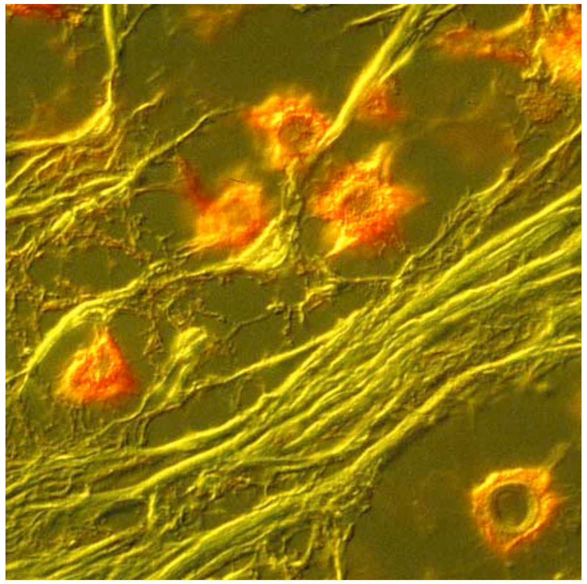
chemical surface functions (like $-NH_2$) can be specifically decorated with fluorescent labels

→ bleaching with high intensity light provides contrast to unbleached regions at low fluorescence intensity









Fluorescence/DIC combination of brain tissue. Infected neurons
are stained with dye.
-> pseudo 3D effect.

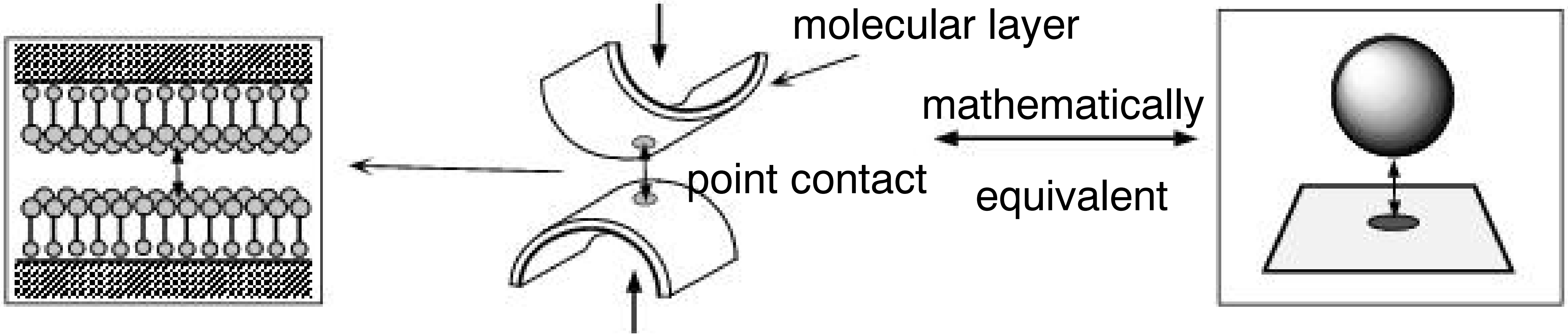
$$\Delta E_a > \Delta E_f$$

$$h\nu_a > h\nu_f$$

$$\nu = c / \lambda$$

$$\rightarrow \lambda_a < \lambda_f$$

Surface Force Apparatus



molecular layer

point contact

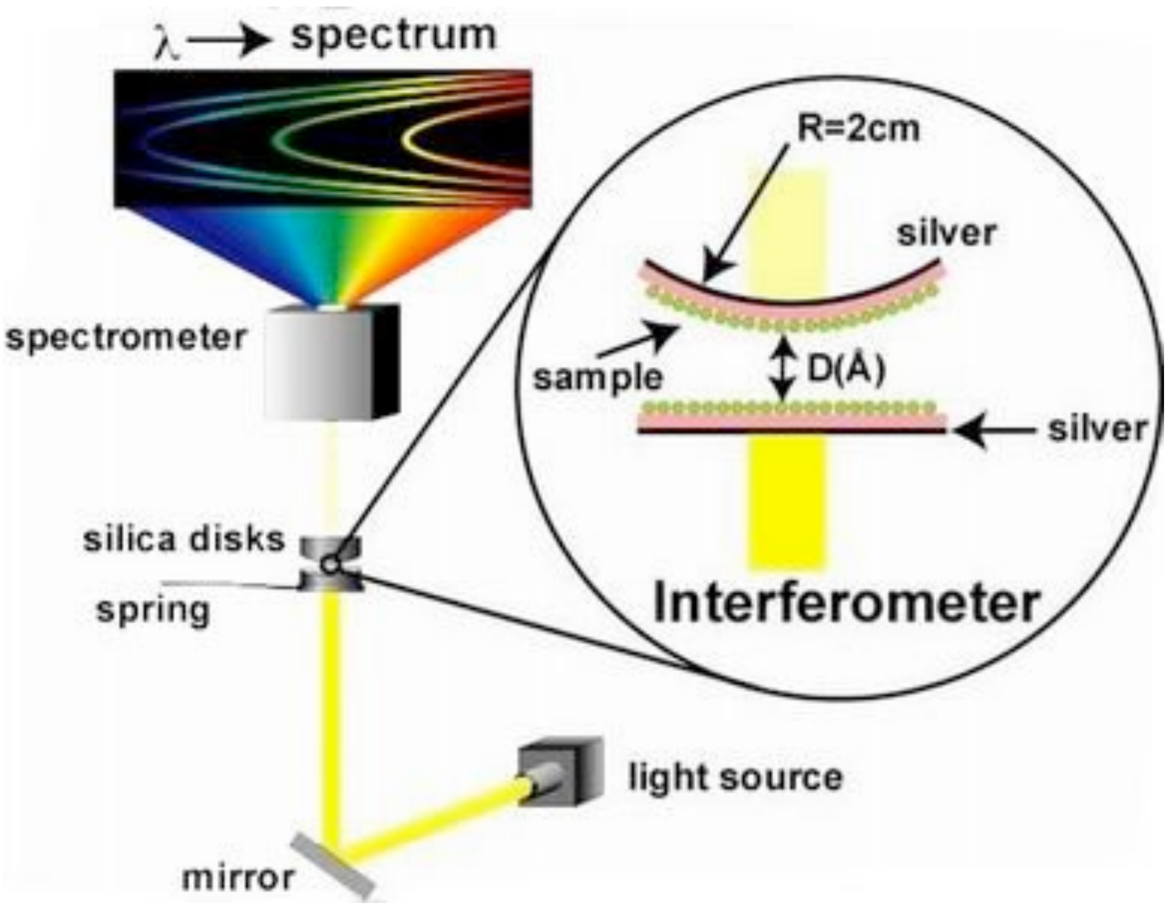
mathematically

equivalent

surface force apparatus measures the force acting between two surfaces coming into contact crossed cylinder geometry of mica sheets used in SFA is mathematically equivalent to sphere on flat surface contact measurement of adhesion forces and interfacial energy can be analyzed by JKR (Johnson, Kendal, Roberts) theory for large soft objects, or DMT (Derjaguin, Muller, Toporov) for small hard objects

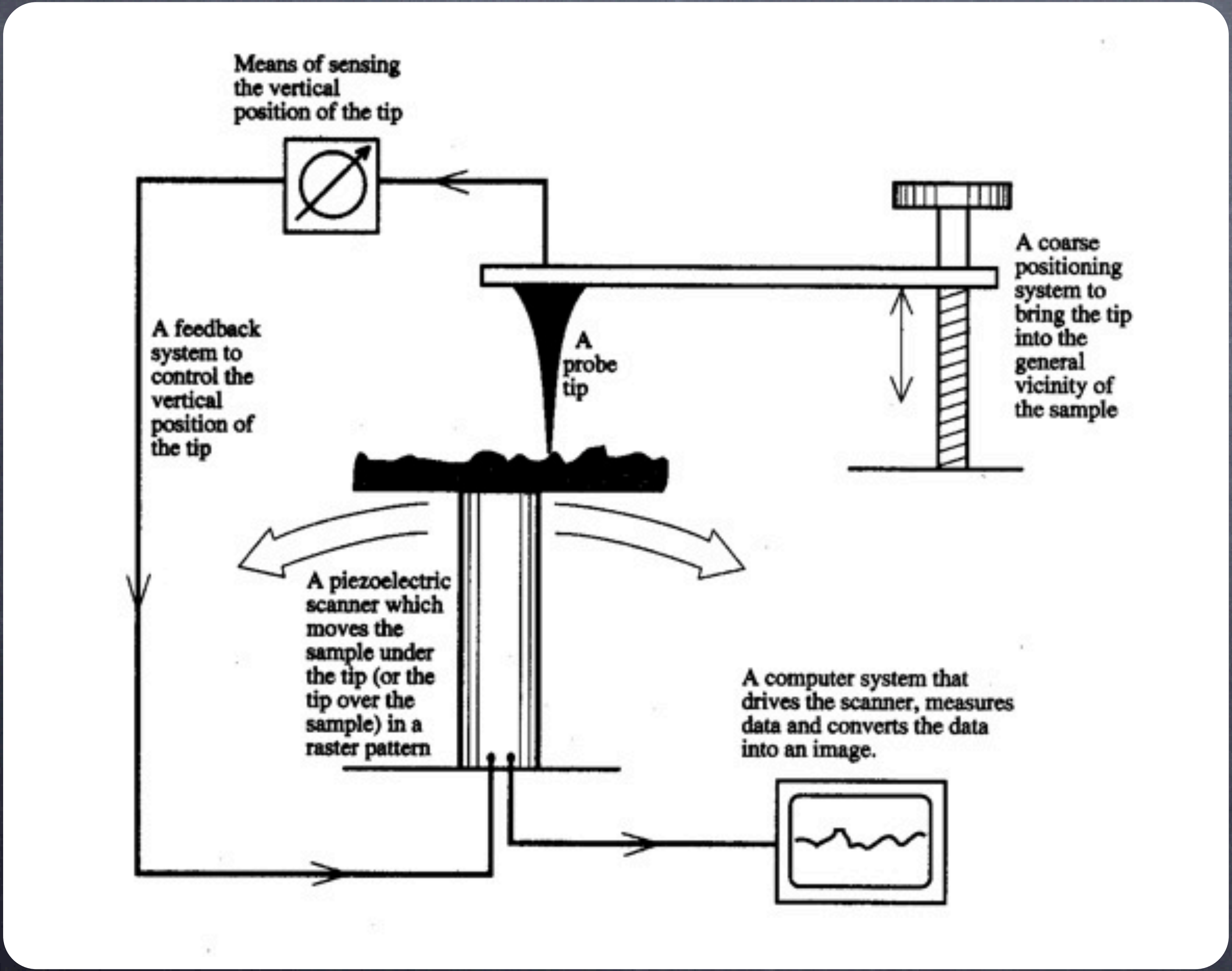
JKR: $F_{adhesion} = 3\pi\gamma R$

DMT: $F_{adhesion} = 4\pi\gamma R$



Scanning Probe Microscopy (SXM)

[...The scanning probe microscope is an imaging tool with a vast dynamic range, spanning the realms of optical and electron microscopes. It's also a profiler with unprecedented 3-D resolution. In some cases, scanning probe microscopes can measure physical properties such as surface conductivity, static charge distribution, localized friction, magnetic fields, and elastic moduli. As a result, applications of SPMs are very diverse. ...]



fundamental principle:
A probe tip is brought into close proximity / contact with a specimen which is scanned in the x–y–plane. The interaction of the probe tip with the surface is recorded with respect to the x–y–position of the sample and converted into a 3 D map of the measured surface property (e.g. topography, conductivity, friction, mechanical module).

STM tunneling

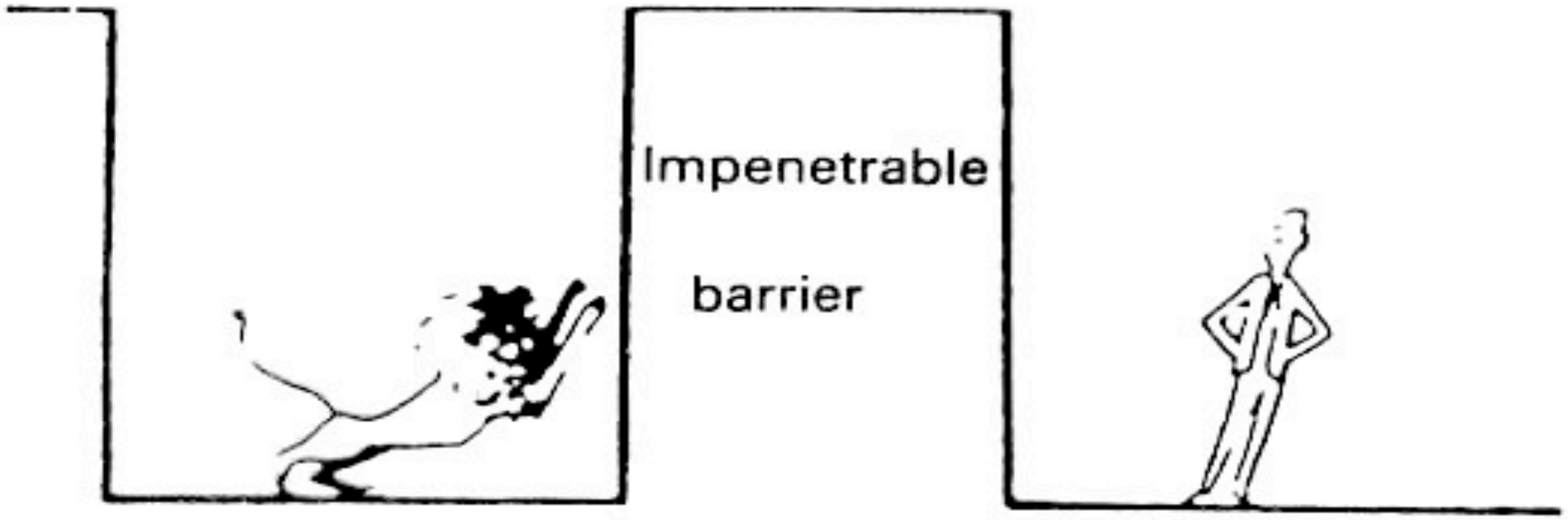
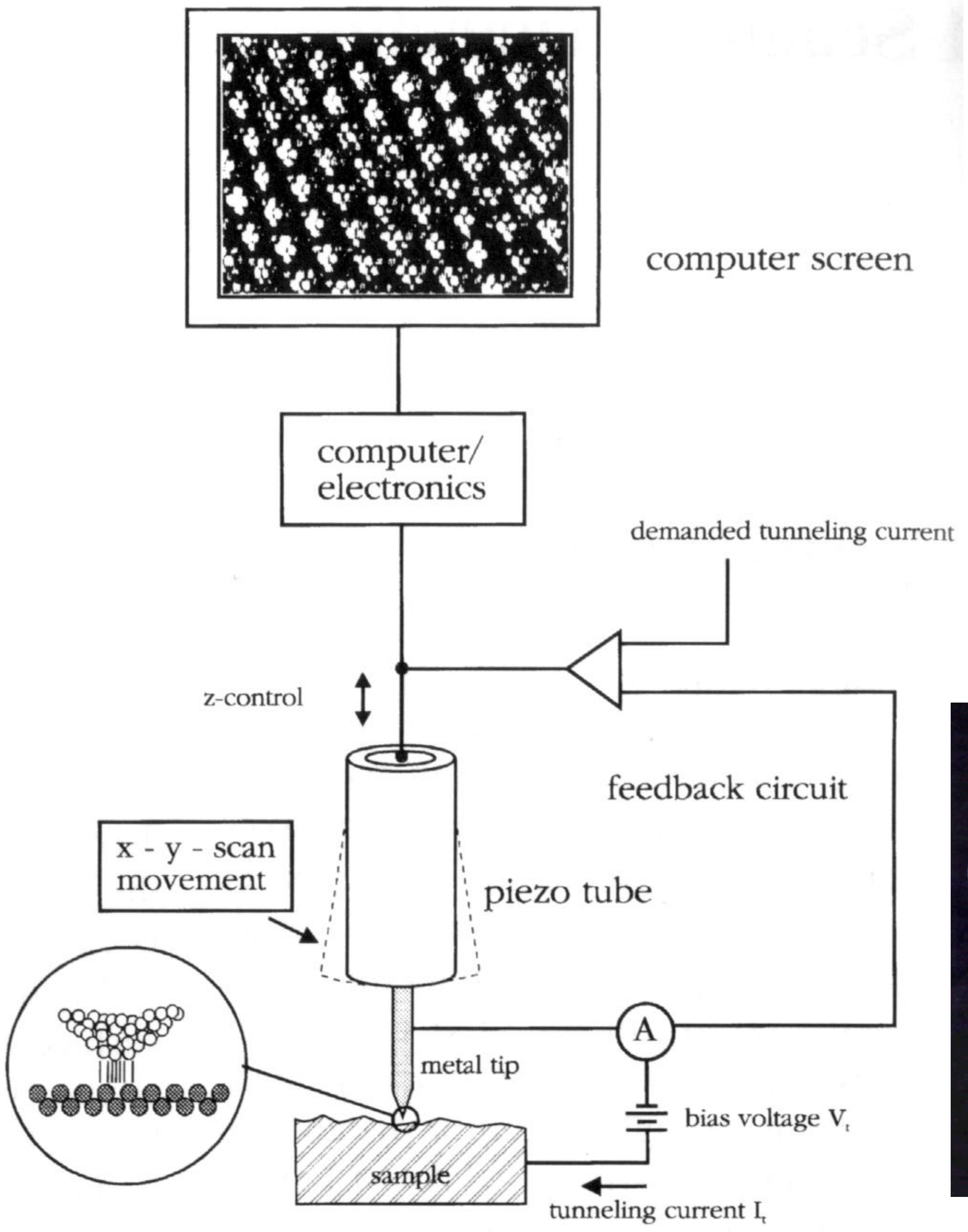
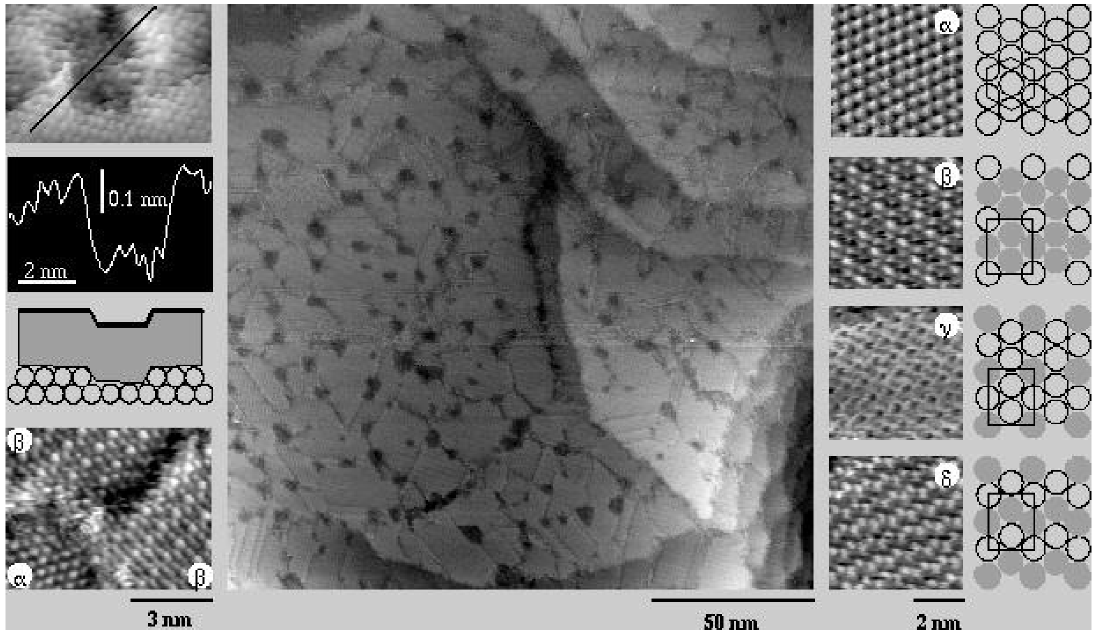


Fig. 1.1. The difference between classical theory and quantum theory, illustrating tunneling through a potential barrier (Bleaney, 1984).

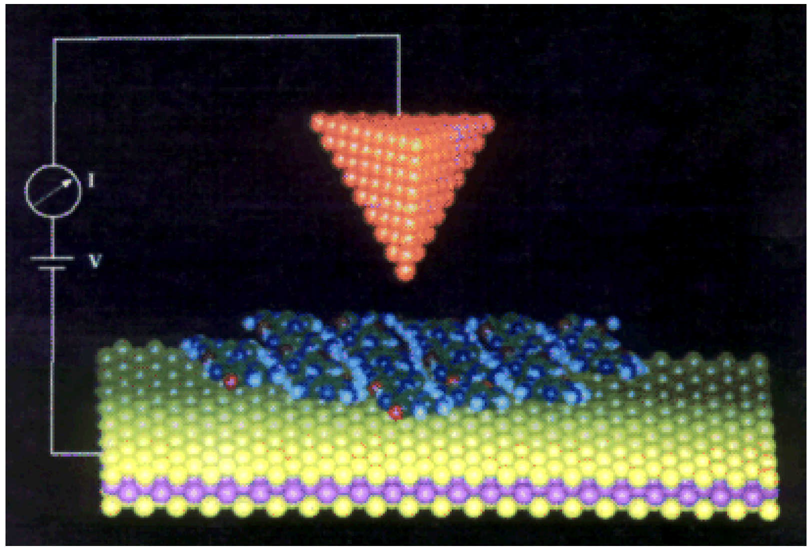
STM:

sharp conducting tip is scanned over conducting surface and electrons tunneling between tip and surface (depends on bias voltage) at a separation below ~10 angstroms are measured with respect to tip position





monolayers of dodecanethiol $C_{12}H_{25}SH$ on gold (111)



tunneling principle of STM:

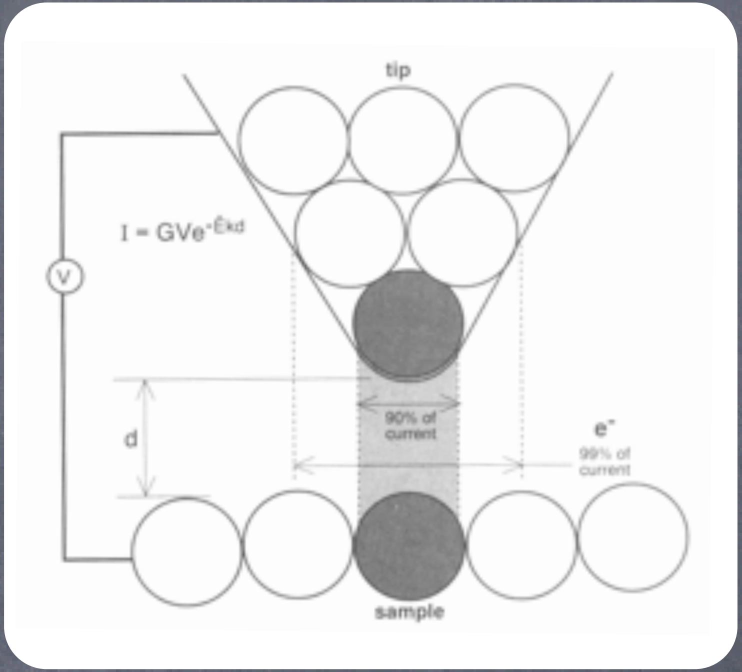
$$I_{tunnel} \rightarrow U \frac{k}{s} e^{(-2ks)}$$

I: tunnel current
U tunneling voltage
1/k: range of WF over surf.
s: distance tip–surface

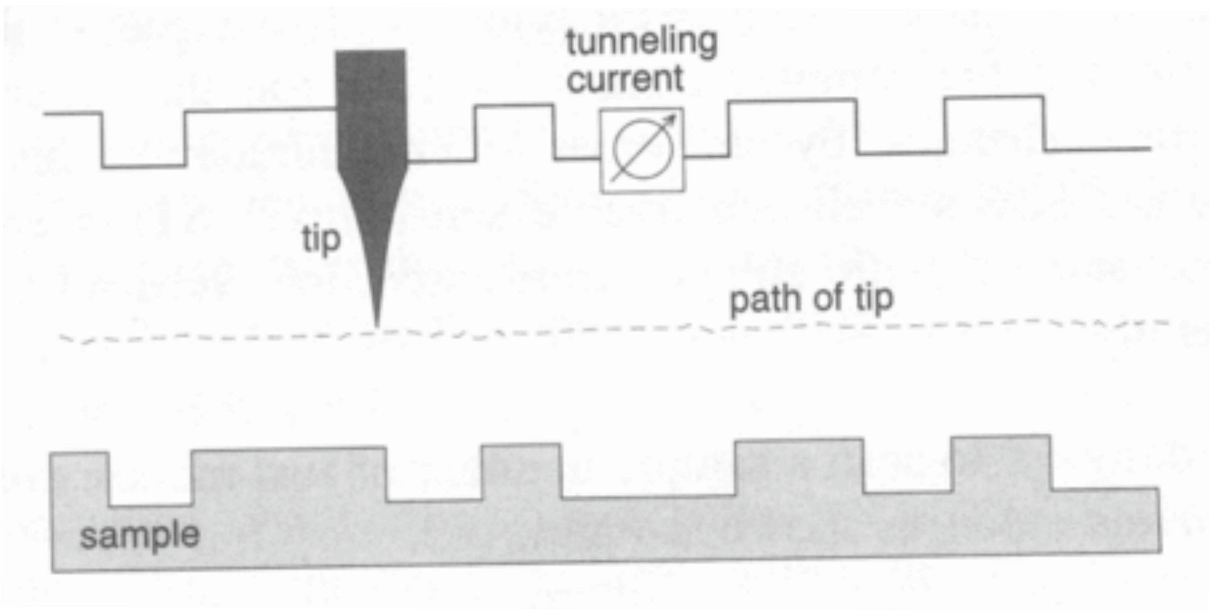
STM: constant height/constant current

constant height mode: the tip is scanned over the surface keeping the vertical tip position constant, topography / conductivity differences are mapped by recording variations in tunnel current with respect to x–y–position of tip

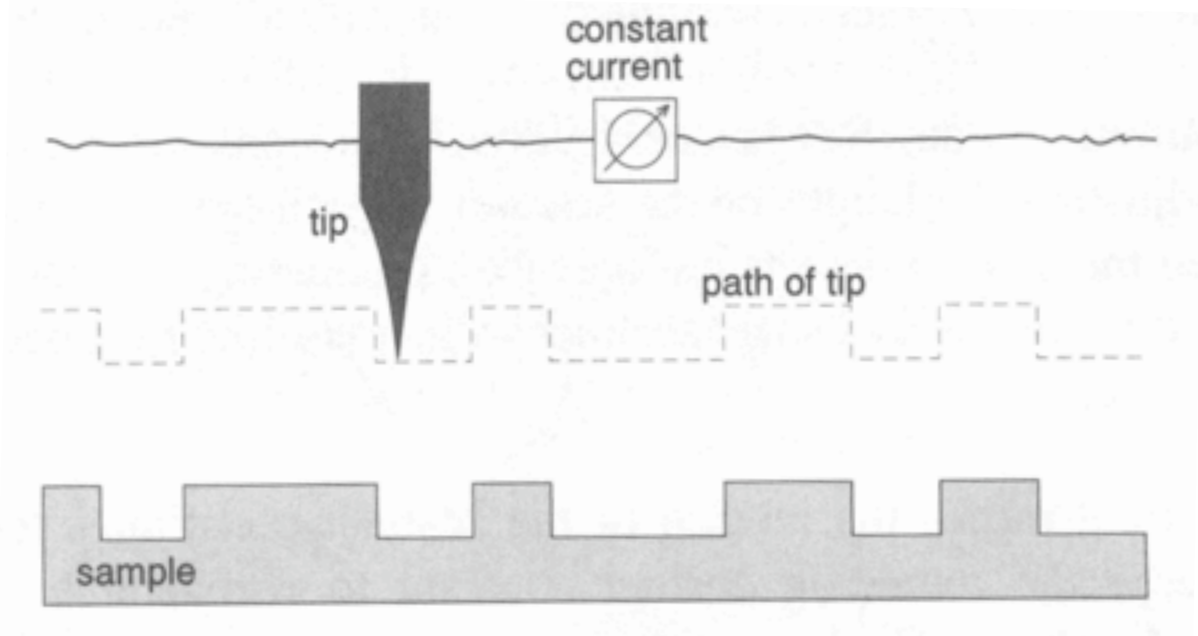
constant current mode: the vertical tip position is adjusted during scanning to keep tunnel current constant, topography / conductivity map is constructed from vertical tip position with respect to x–y–position



high resolution possible since most of the tunnel current (~90 %) flows within the shortest tip–surface separation (exponential distance dependence of tunnel current)

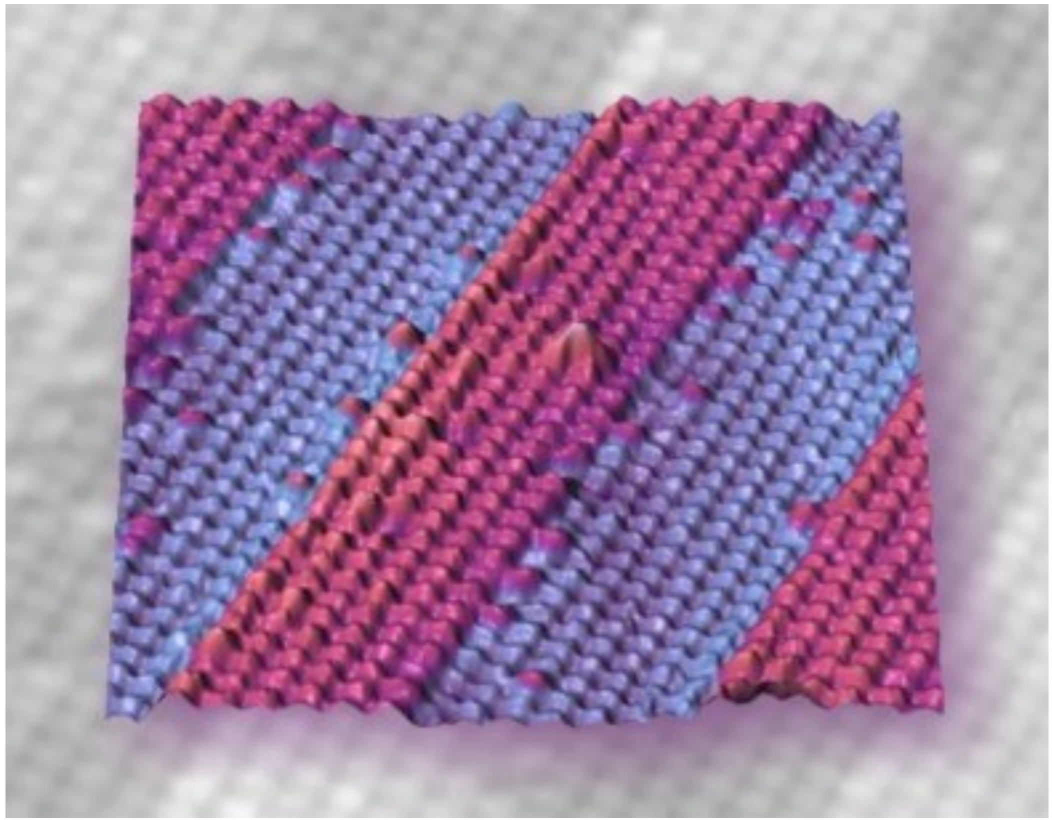


constant height mode
(flat surface, high resolution, fast scanning)

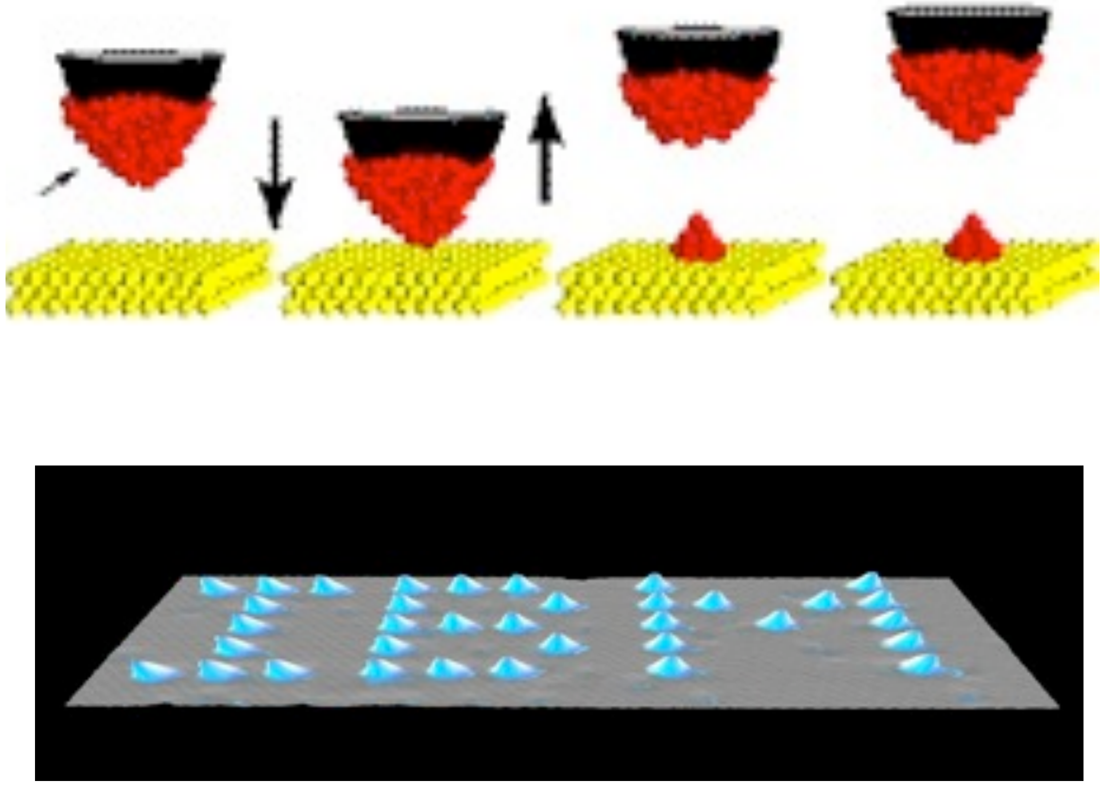


constant current mode
(rich topography, lower resolution)

STM: examples



Only every-other lattice plane is exposed on the (110) surface, where only the Sb (reddish) and As (blueish) atoms can be seen.

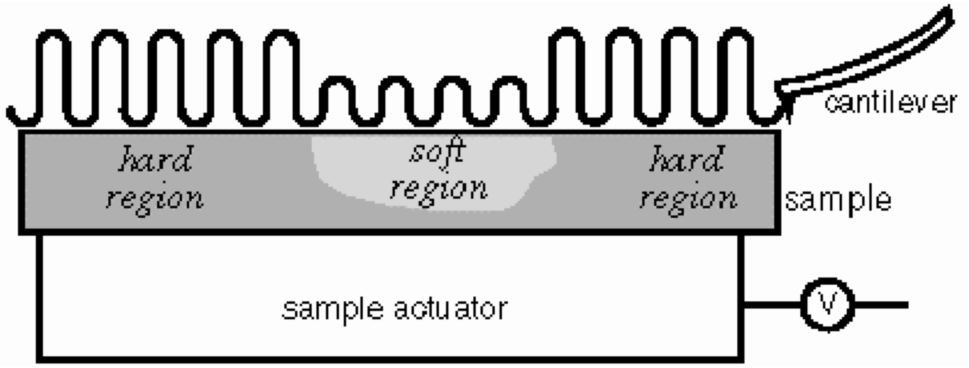


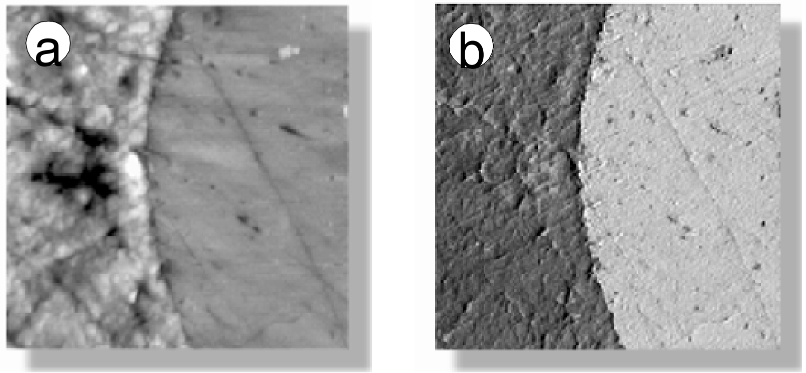
Nanolithography STM

SFM / AFM

force modulation microscopy: damping of cantilever oscillation due to energy dissipation in sample surface is correlated to elastic properties of surface (compare also phase modulation)

→ hard surface: weak damping, soft surface: strong damping



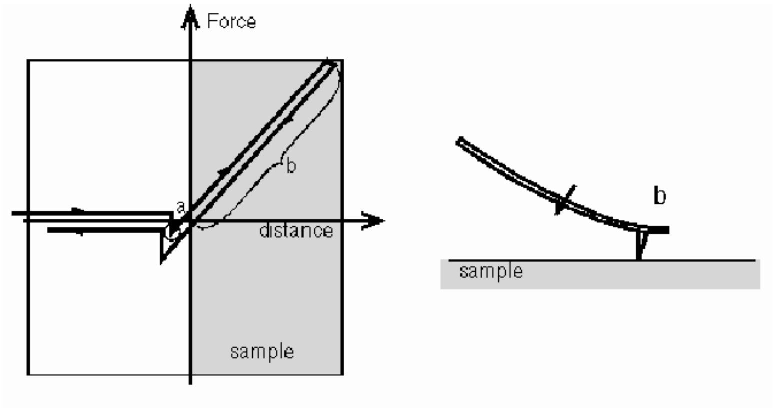


a) contact mode AFM of carbon fiber (right half) in polymer matrix (left half)

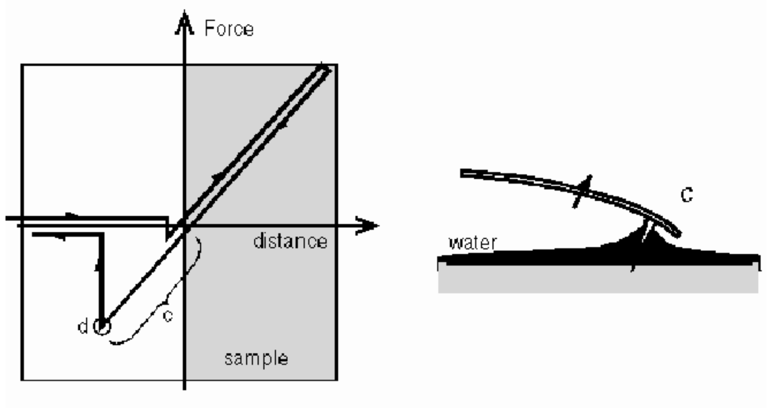
b) force modulation mode image of a)

force versus distance curves: vertical deflection of cantilever is measured with respect to acting force over a spot on the sample surface

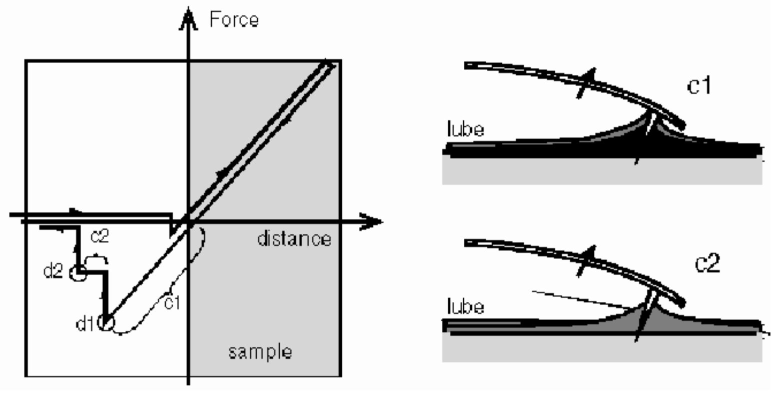
→ provides information on adhesive forces



in vacuum: primarily vdW interactions of tip and surface



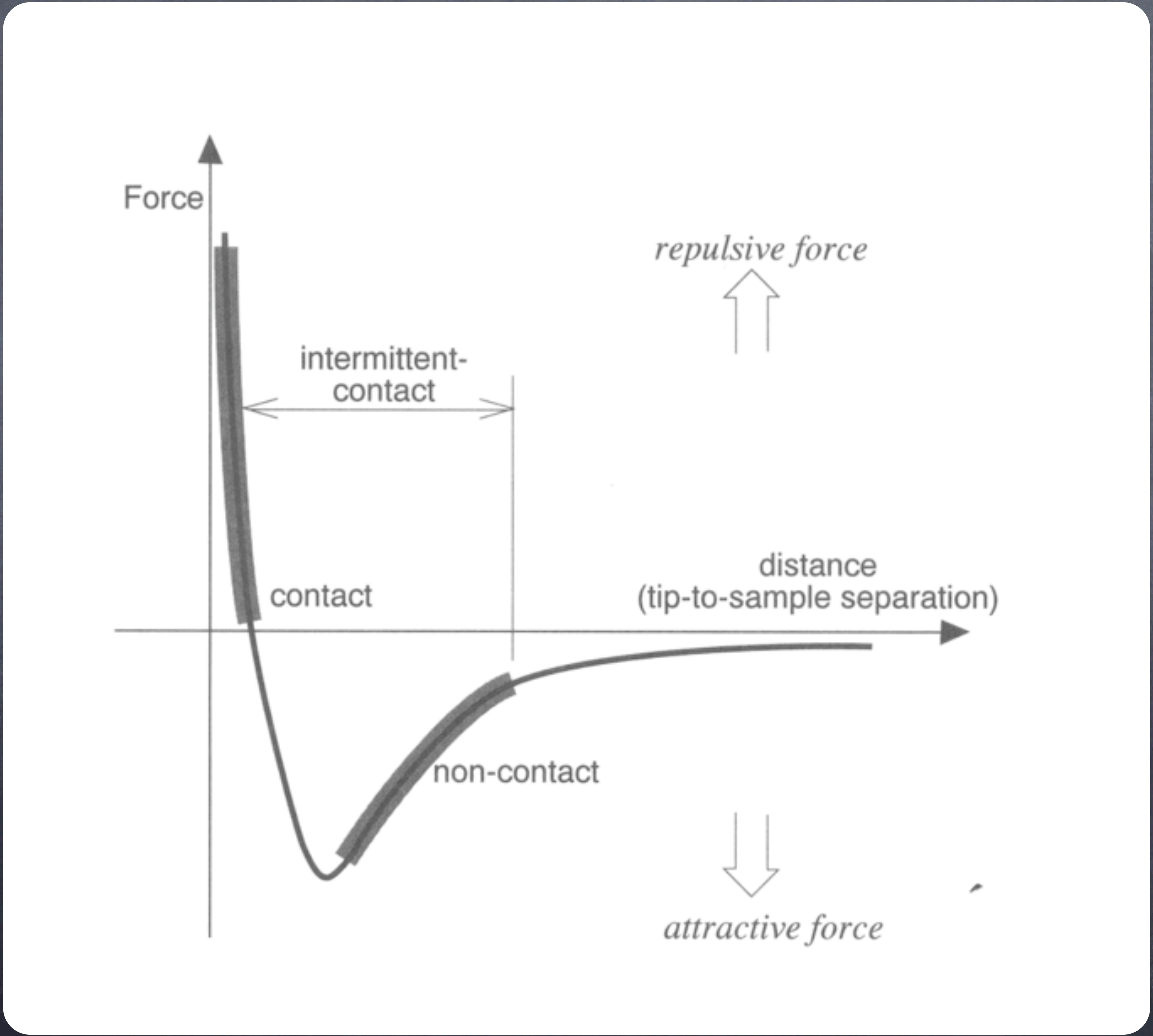
in clean air: thin water film on surface, capillary forces



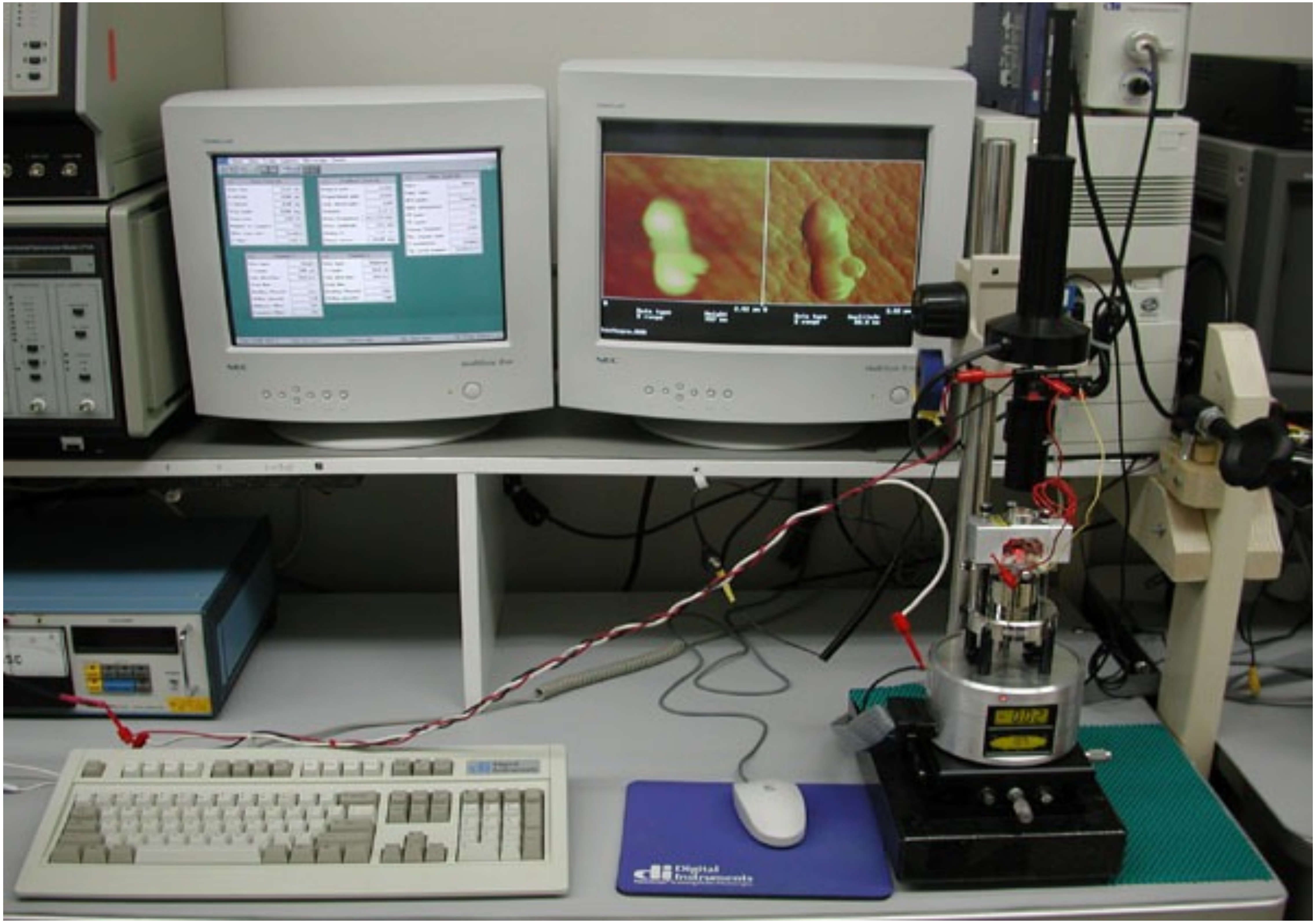
in ambient air: thin contamination / lubrication film (+/– H_2O)

Atomic Force Microscopy (AFM)

Interatomic force vs. distance curve:



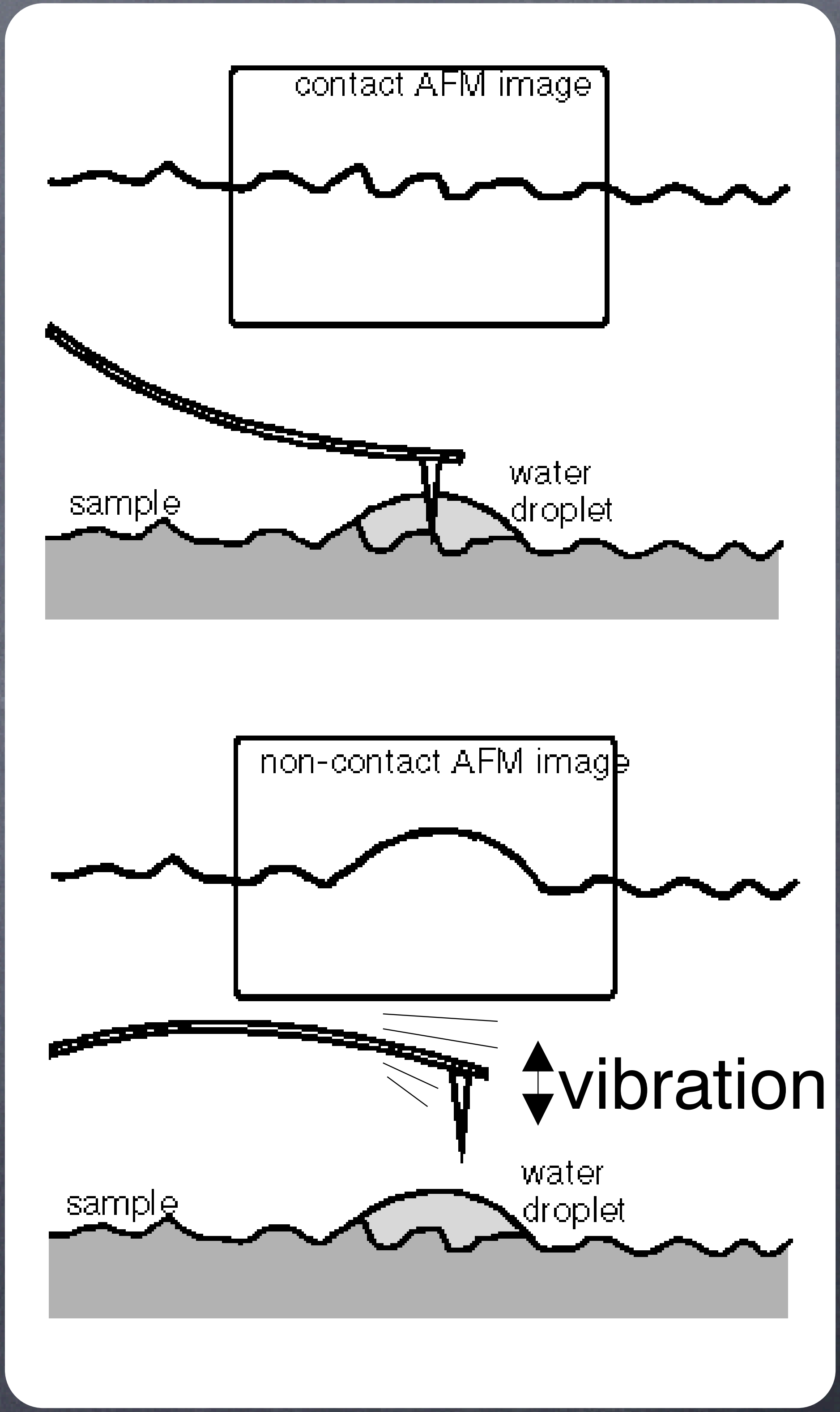
real AFM



AFM: contact / non-contact mode

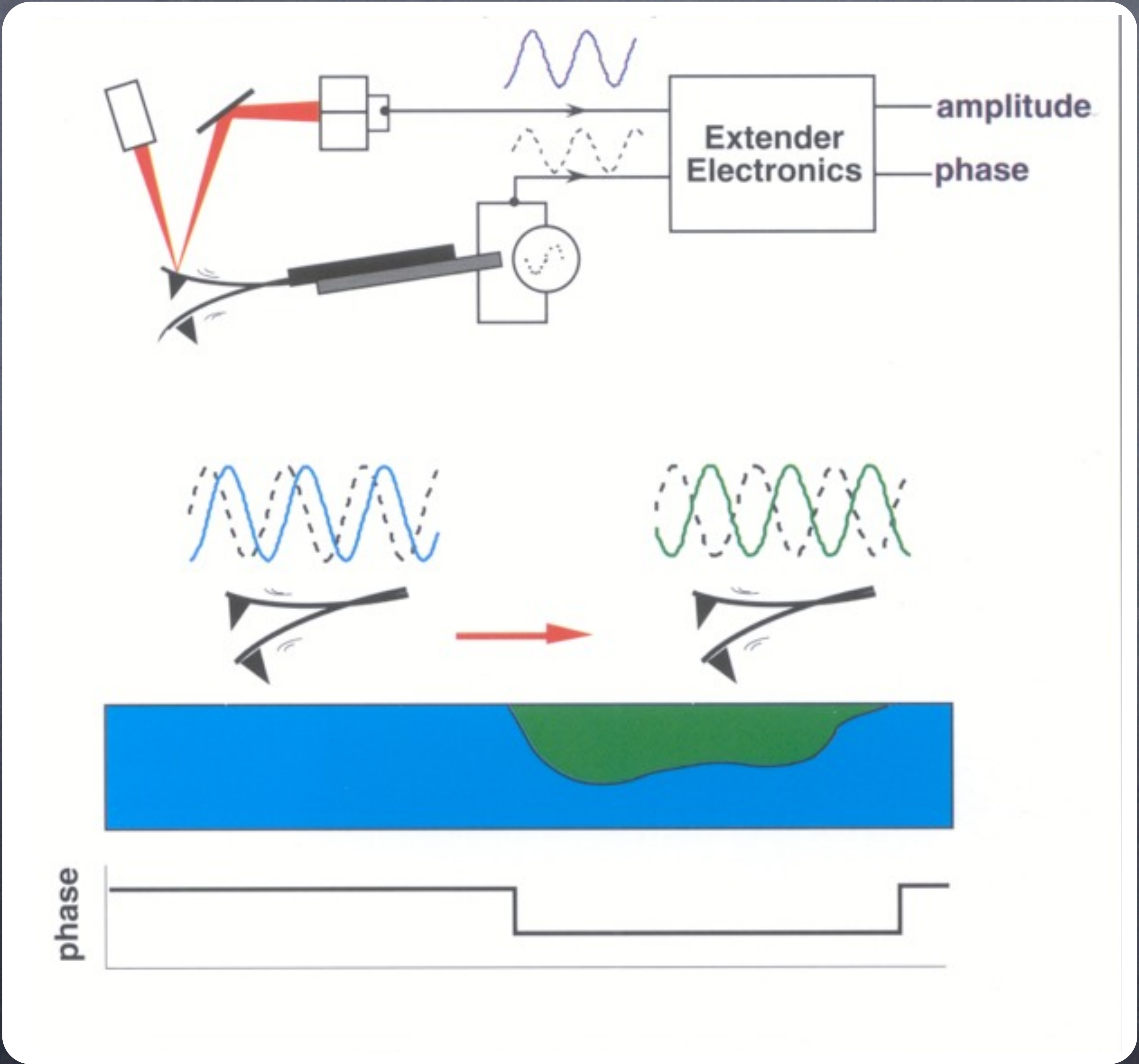
contact (repulsive) mode: tip makes soft "physical contact" with the sample, the tip is attached to the end of a cantilever with a low spring constant (lower than the effective spring constant holding the atoms of the sample together), the contact force causes the cantilever to bend to accommodate changes in topography

non–contact / intermittent contact: AFM cantilever is vibrated near the surface of a sample with spacing on the order of tens to hundreds of angstroms for non–contact or touching of the surface at lowest deflection for intermittent contact ("tapping mode")



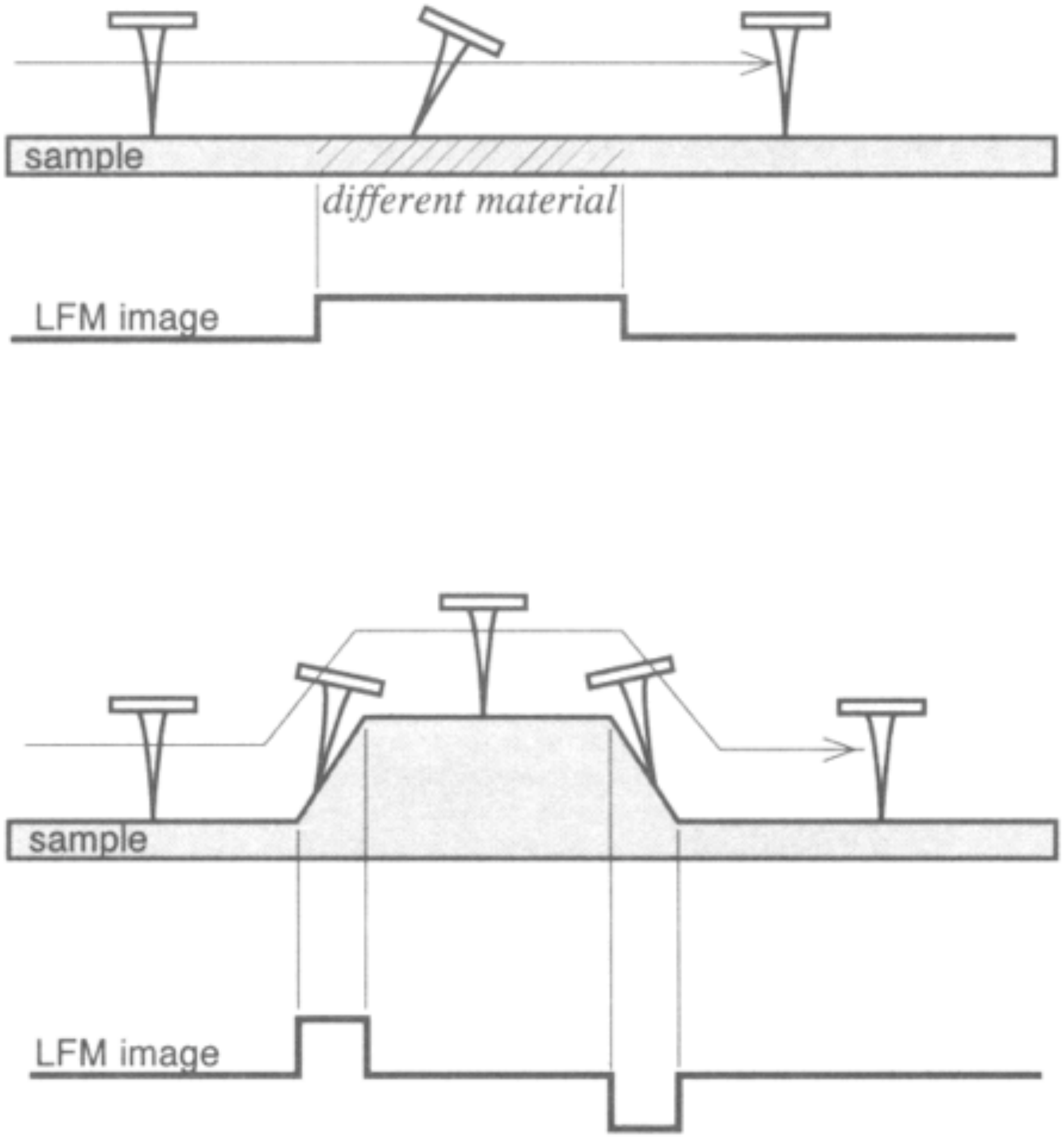
AFM: phase mode

phase mode: compare phase of driving signal and cantilever response (information on elastic modulus of surface material)

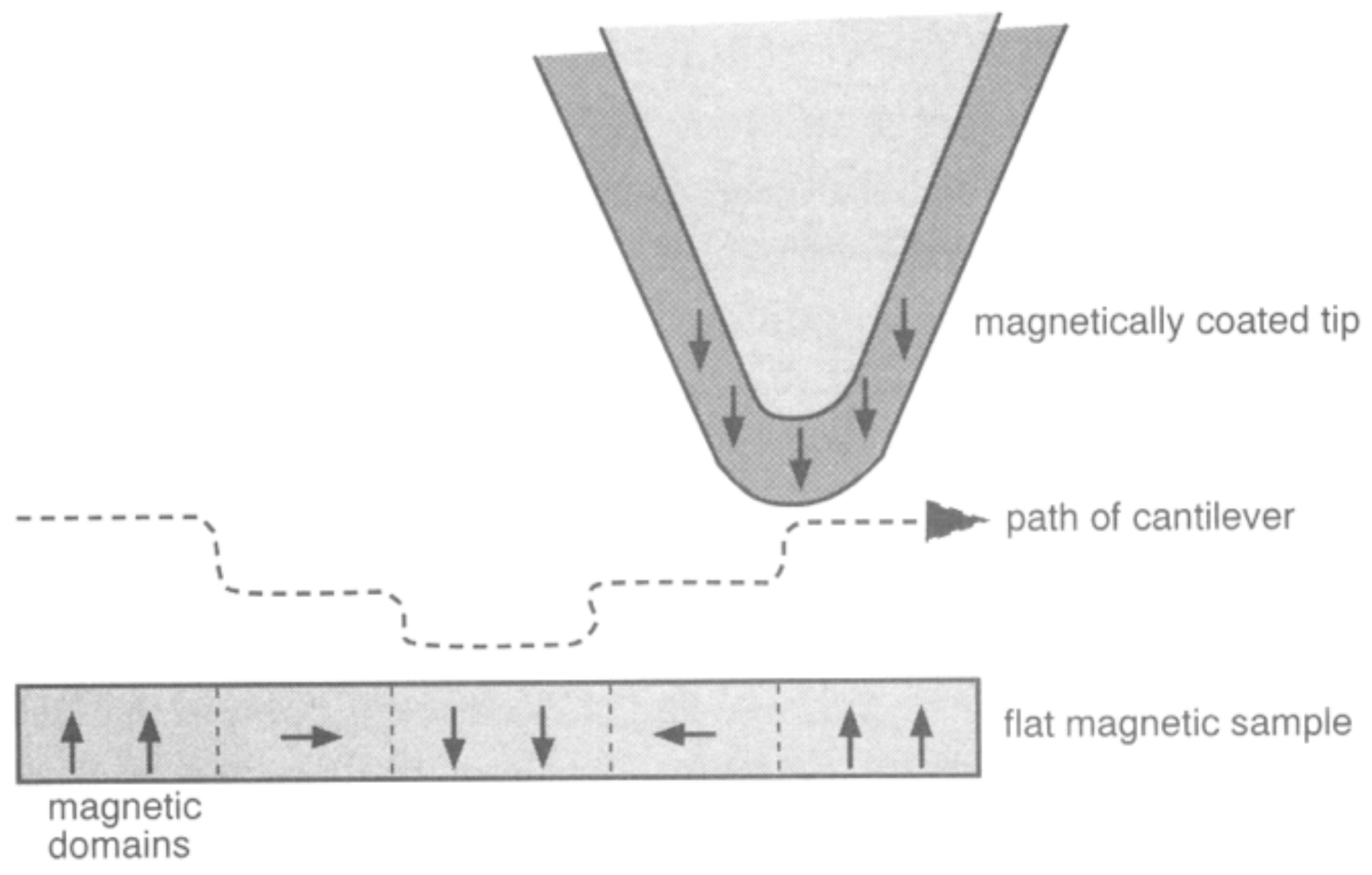


Lateral Force Microscopy (LFM)

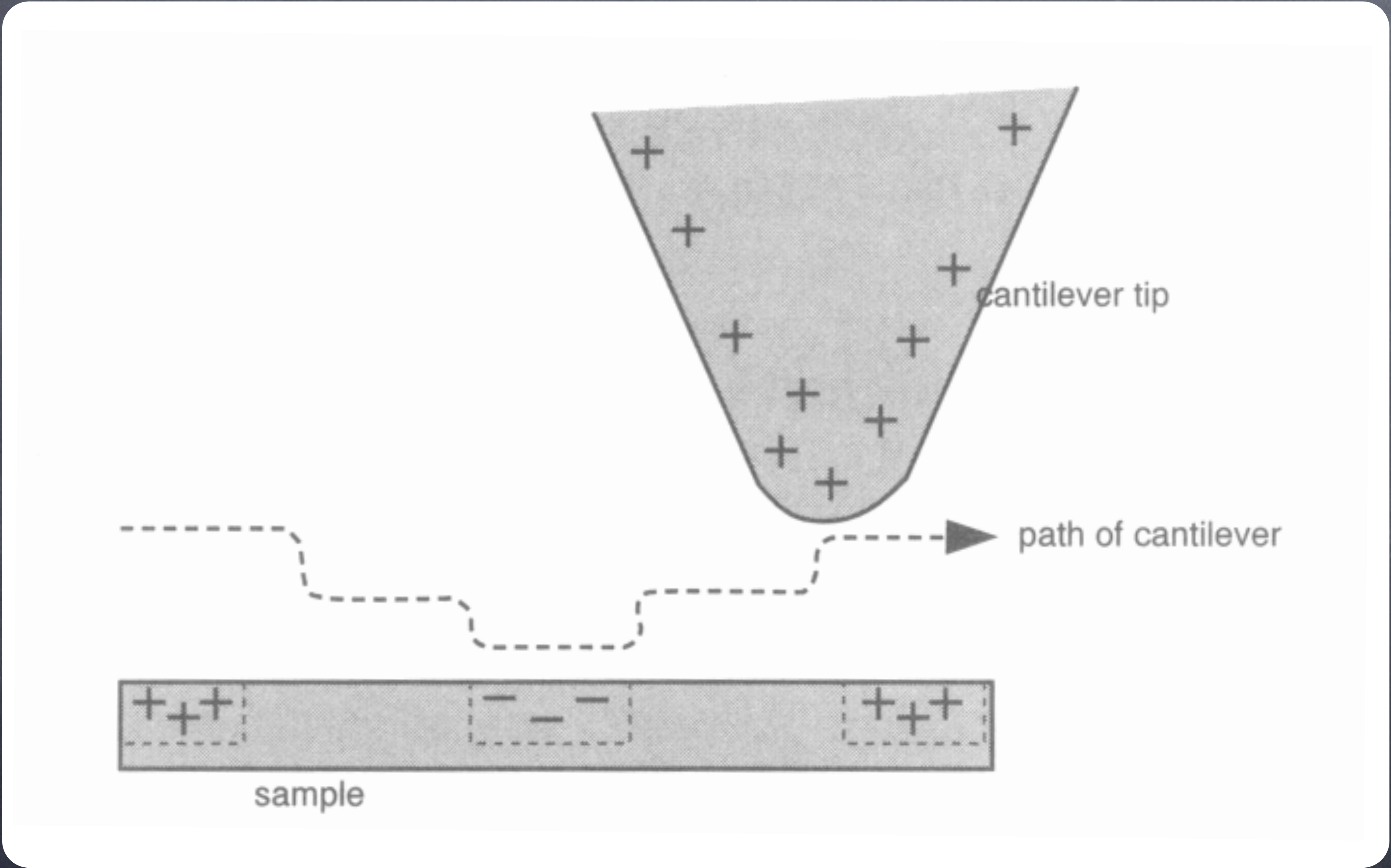
lateral force / friction mode: AFM cantilever in contact mode is laterally deflected in the sample plane due to scanning motion perpendicular to cantilever axes, lateral deflection is measured and gives information on surface material apart from topography



Magnetic Force Microscopy (MFM)

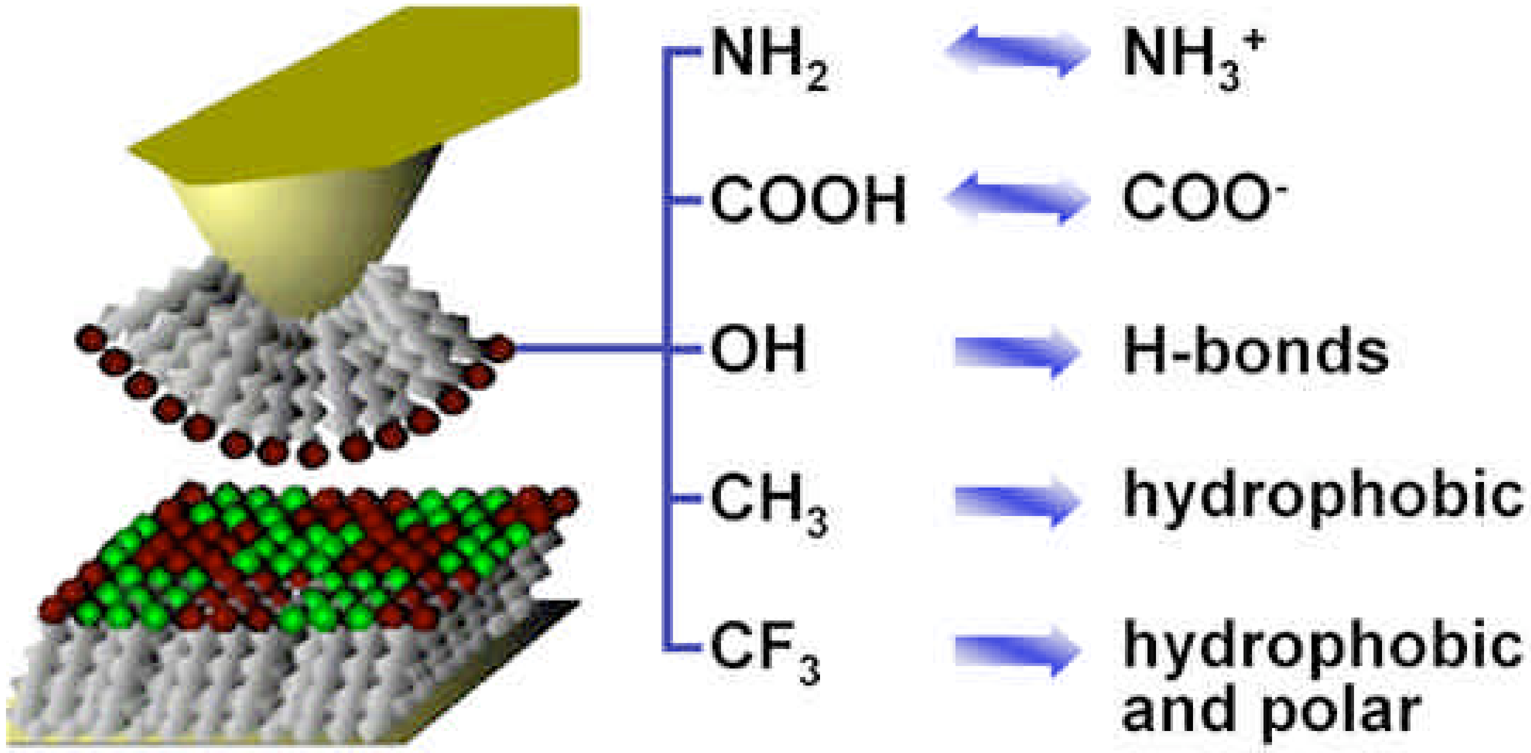


Electrostatic Force Microscopy (EFM)



Chemical Force Microscopy (CFM)

Defined possibilities for chemical head groups



NH_2 ↔ NH_3^+

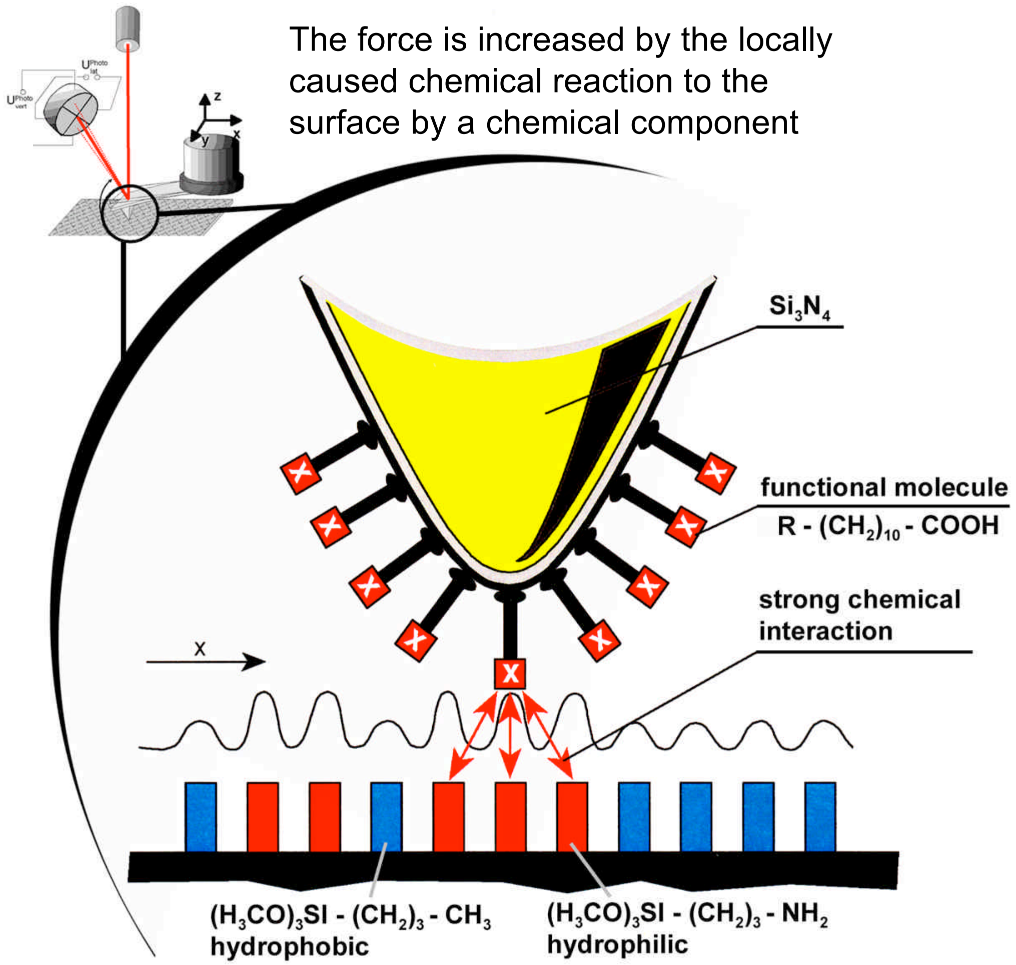
$COOH$ ↔ COO^-

OH → H-bonds

CH_3 → hydrophobic

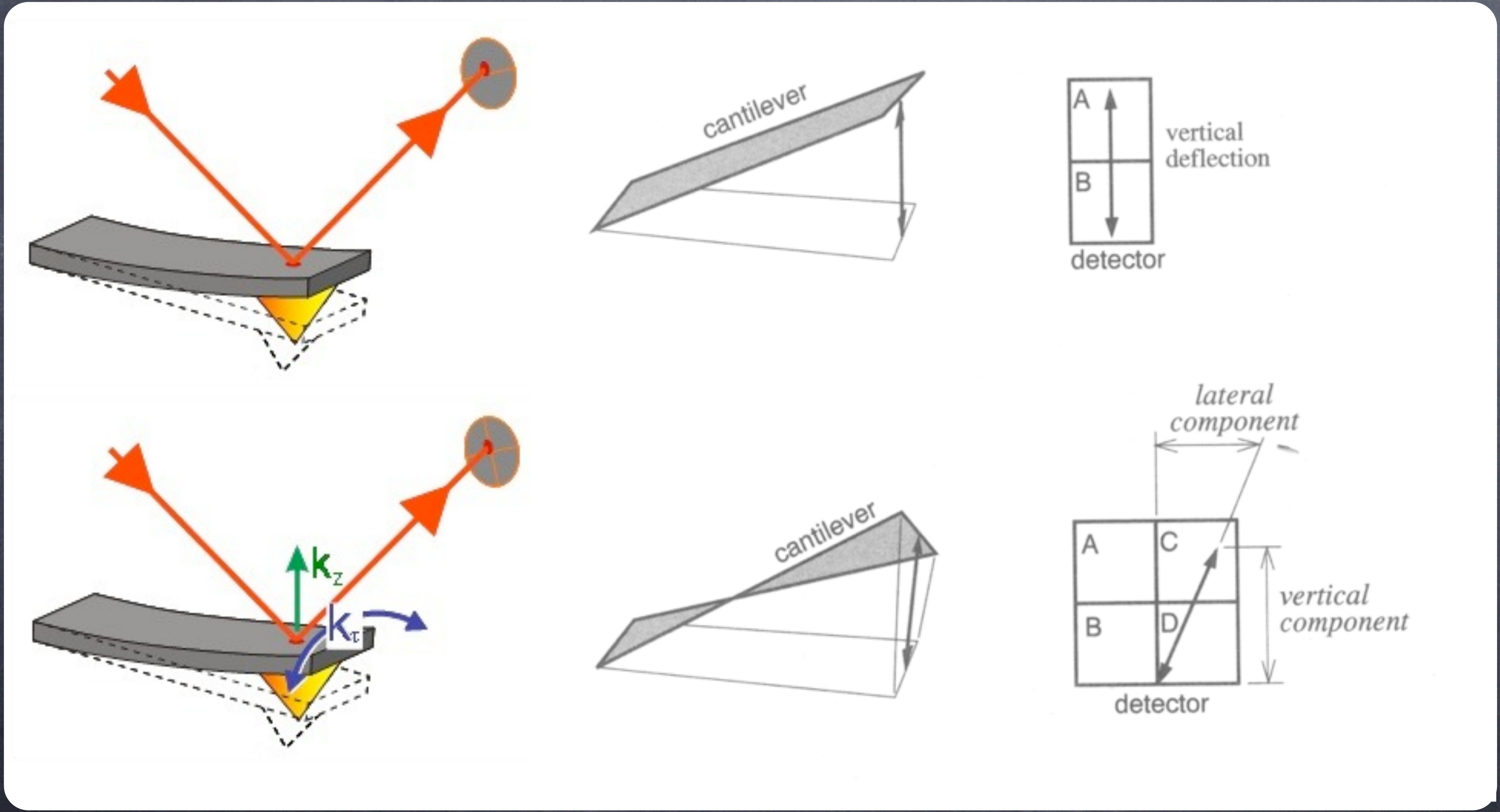
CF_3 → hydrophobic and polar

* further modifications can be discussed ** you can order chemical tips

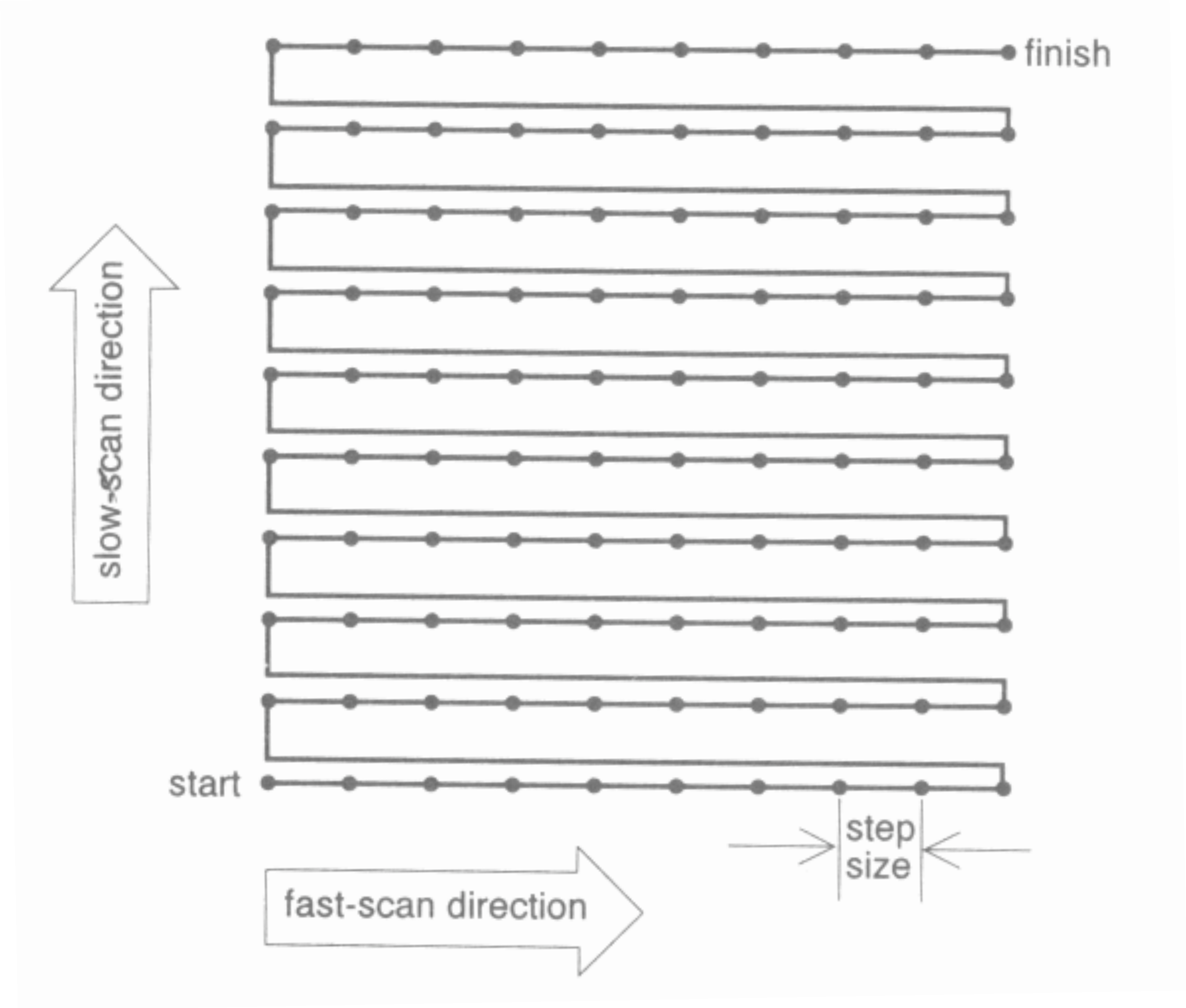


The force is increased by the locally caused chemical reaction to the surface by a chemical component

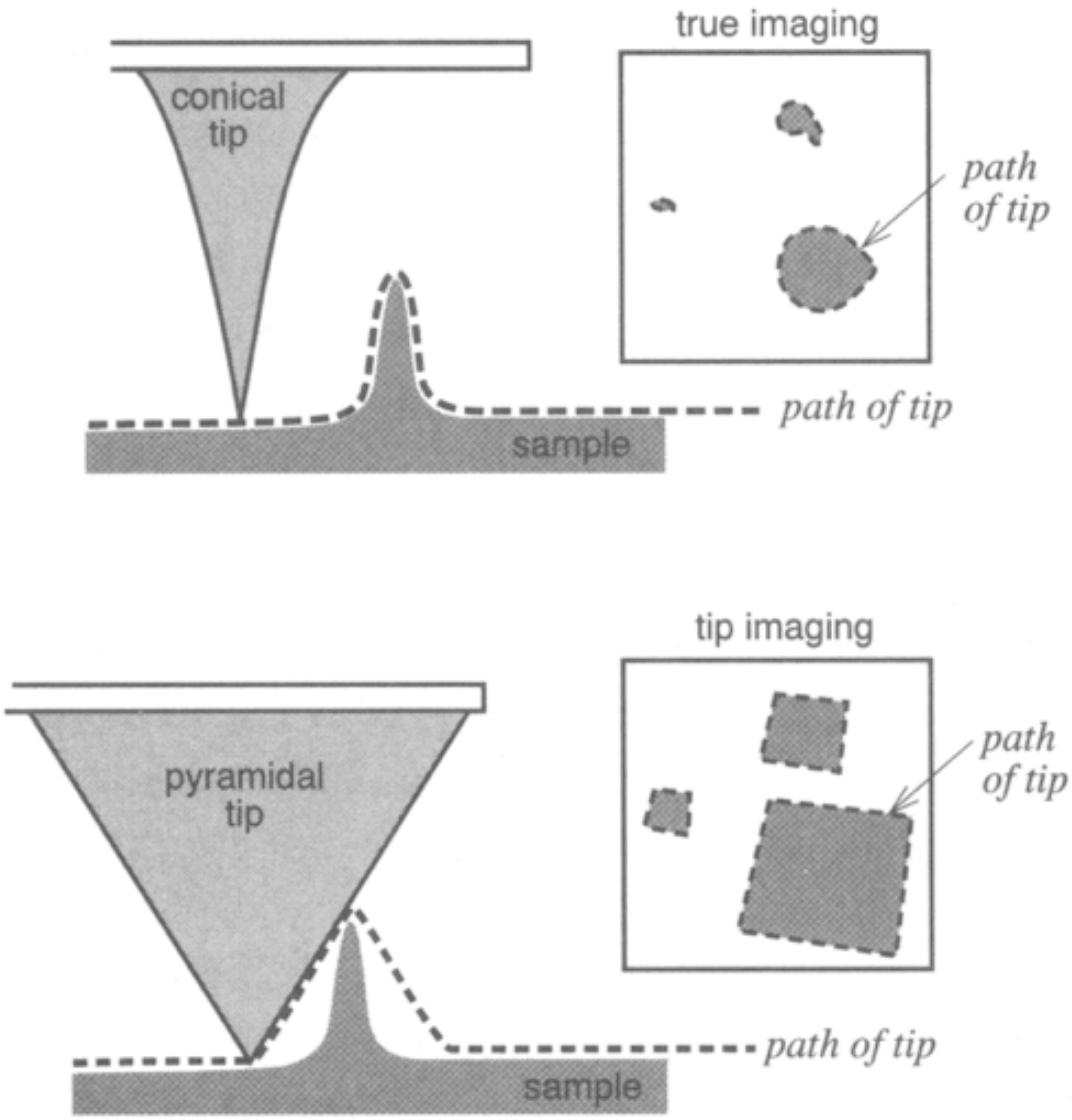
Cantilever deflection



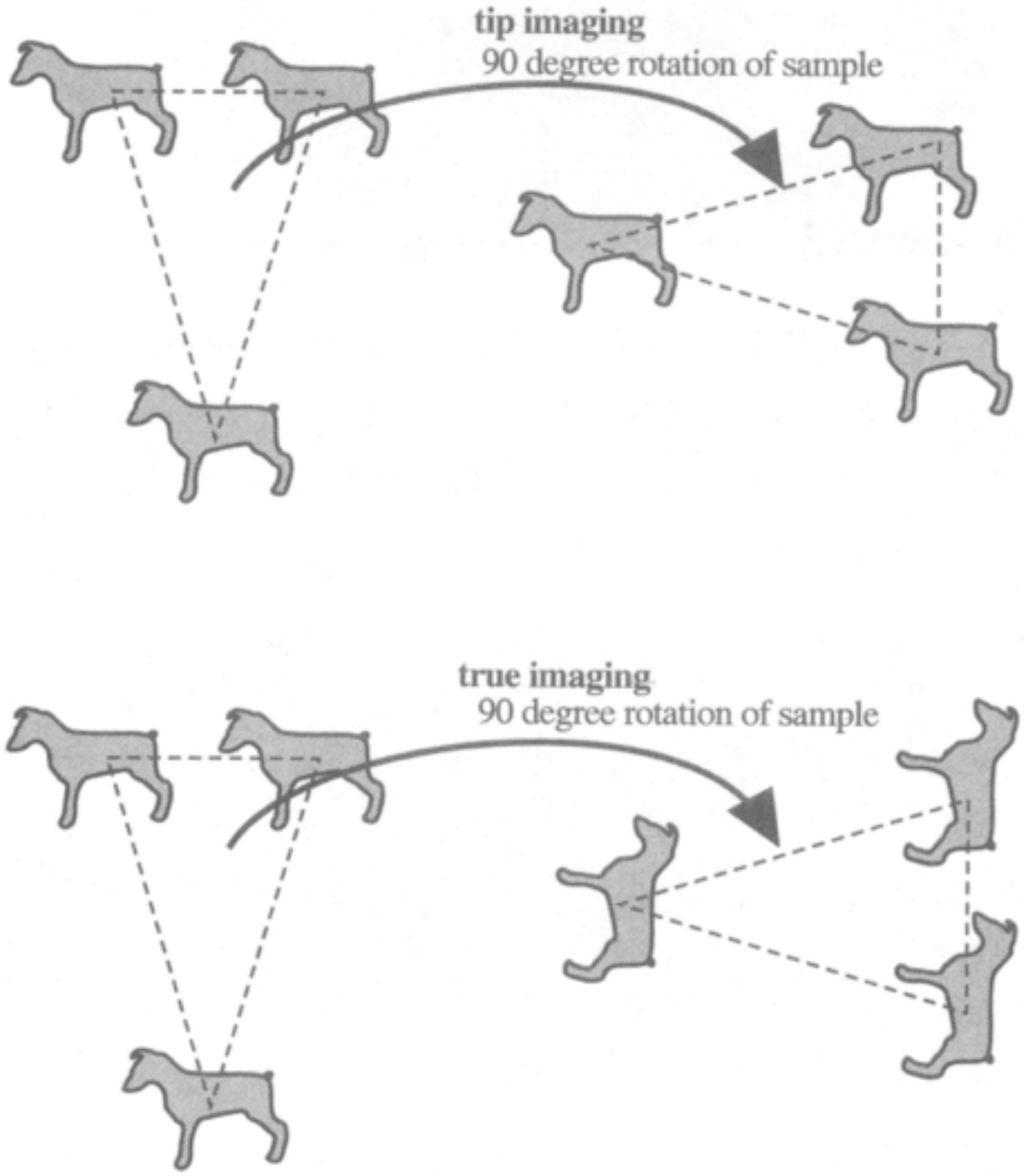
Scanner motion during acquisition



true imaging and tip imaging

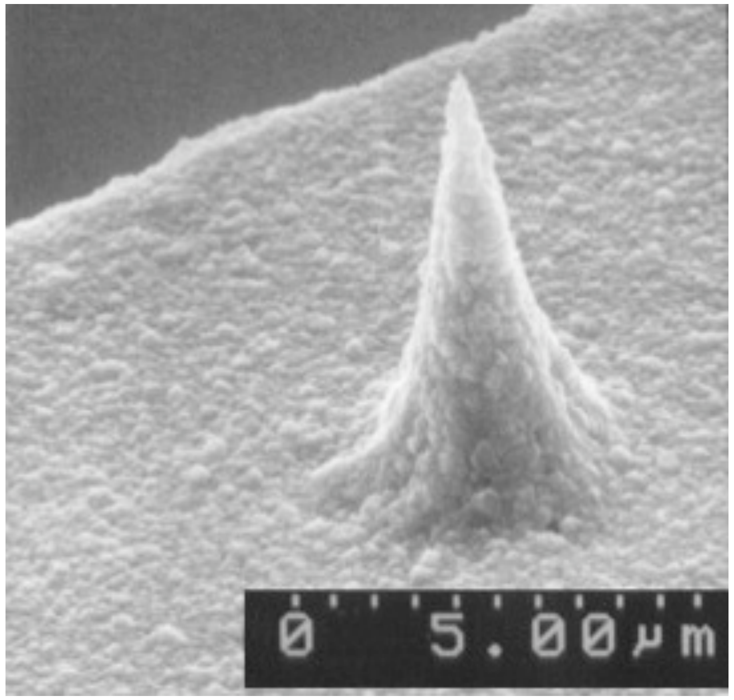


recognizing tip imaging

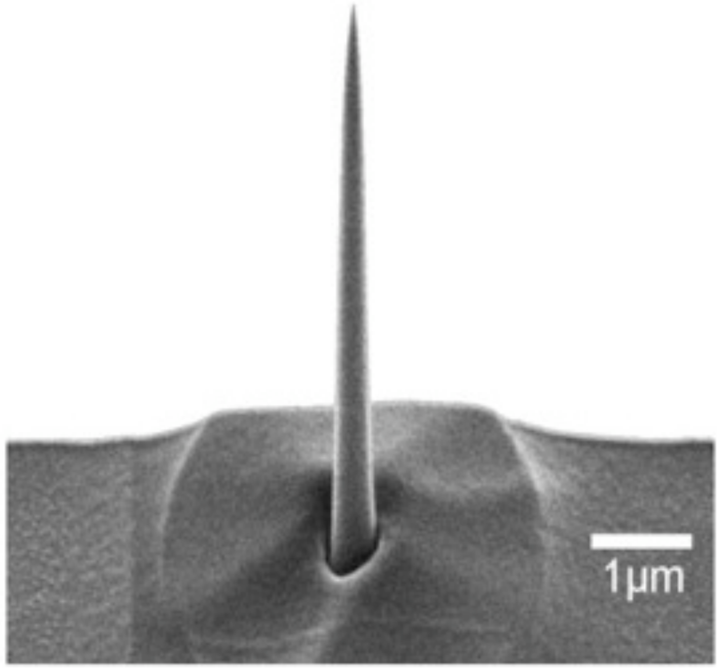


cantilever examples

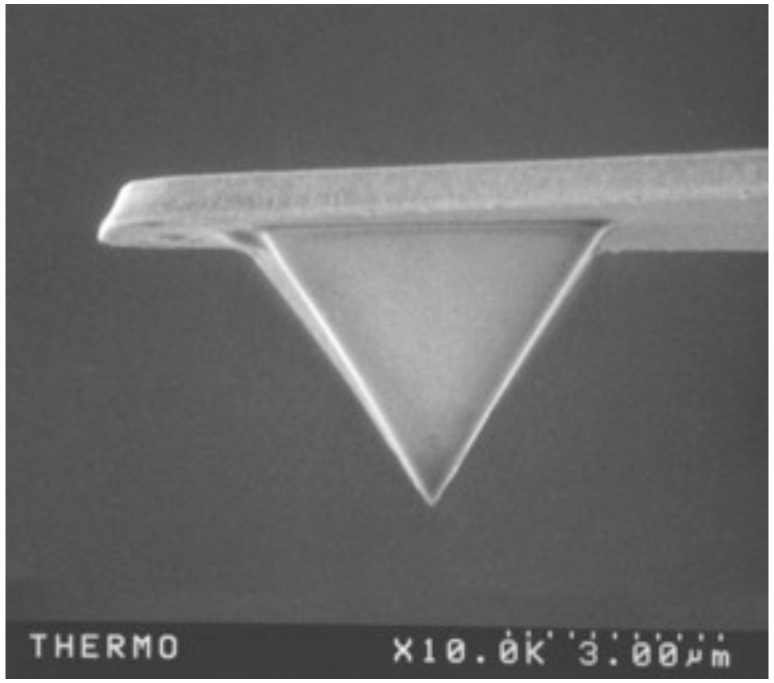
pyramidal, tetrahedral or conical tips are the most common tip shapes



Diamond-coated AFM tip



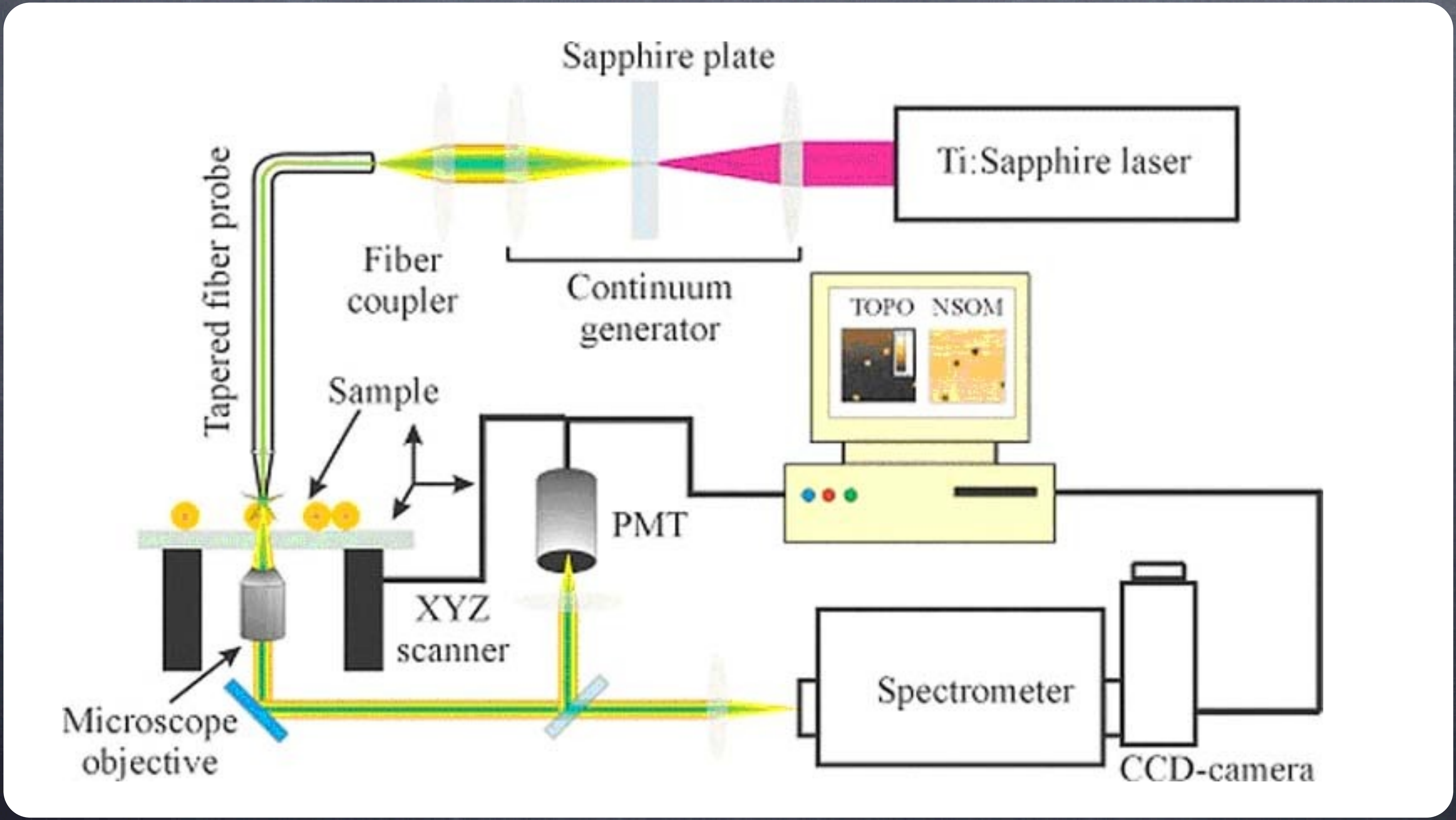
FIB sharp tip



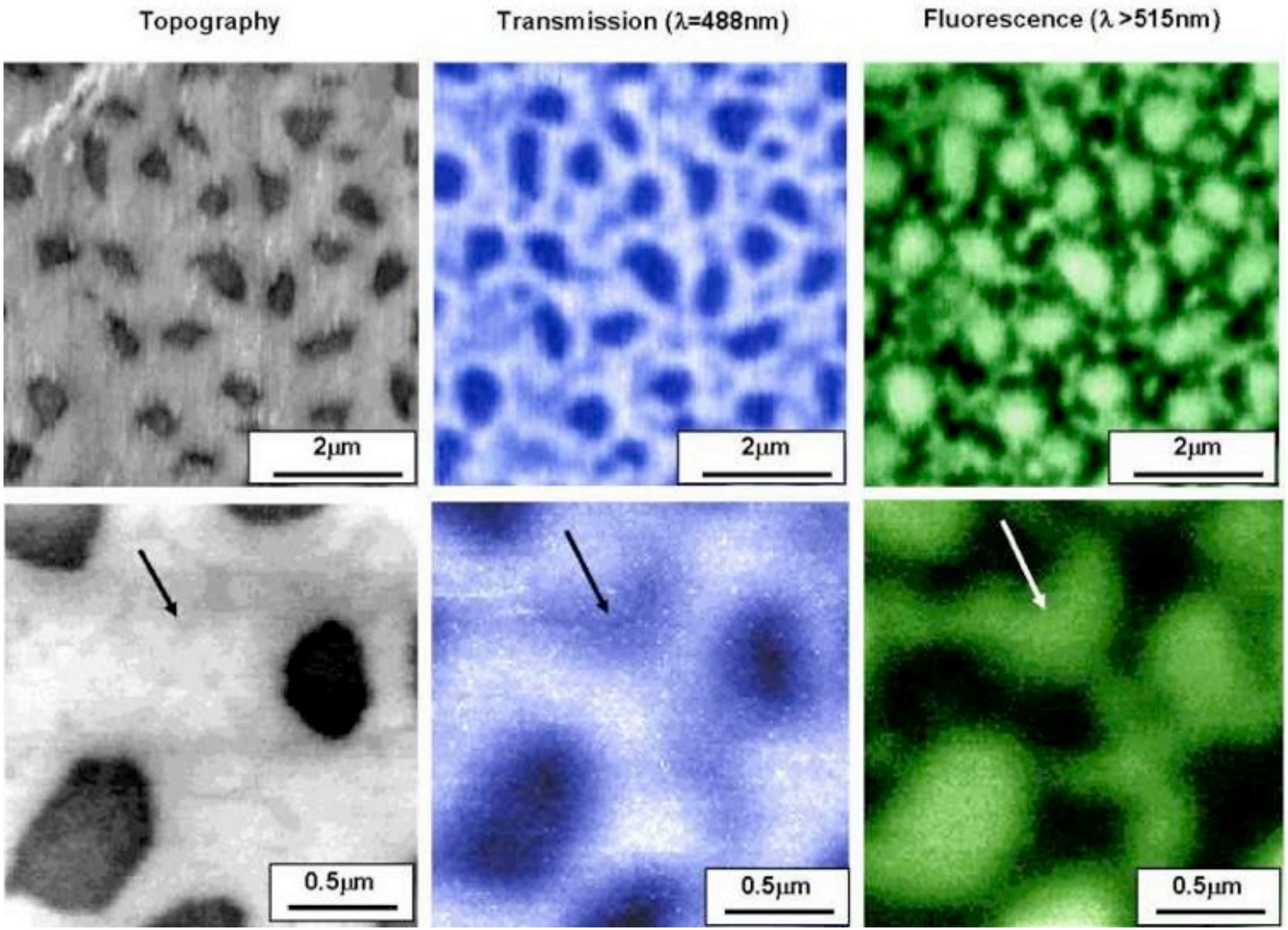
Gold-coated Si_3N_4 tip

Nearfield Scanning Optical Microscopy

integration of optical microscopy tools with scanning probe techniques allows resolution far beyond optical diffraction limit, sample is excited by light coming from a wave guide tip with sub-micron aperture which is scanned over the surface, light coming from the probe is collected in an optical microscope objective, light intensity is recorded with respect to tip y-x-position



NSOM: examples



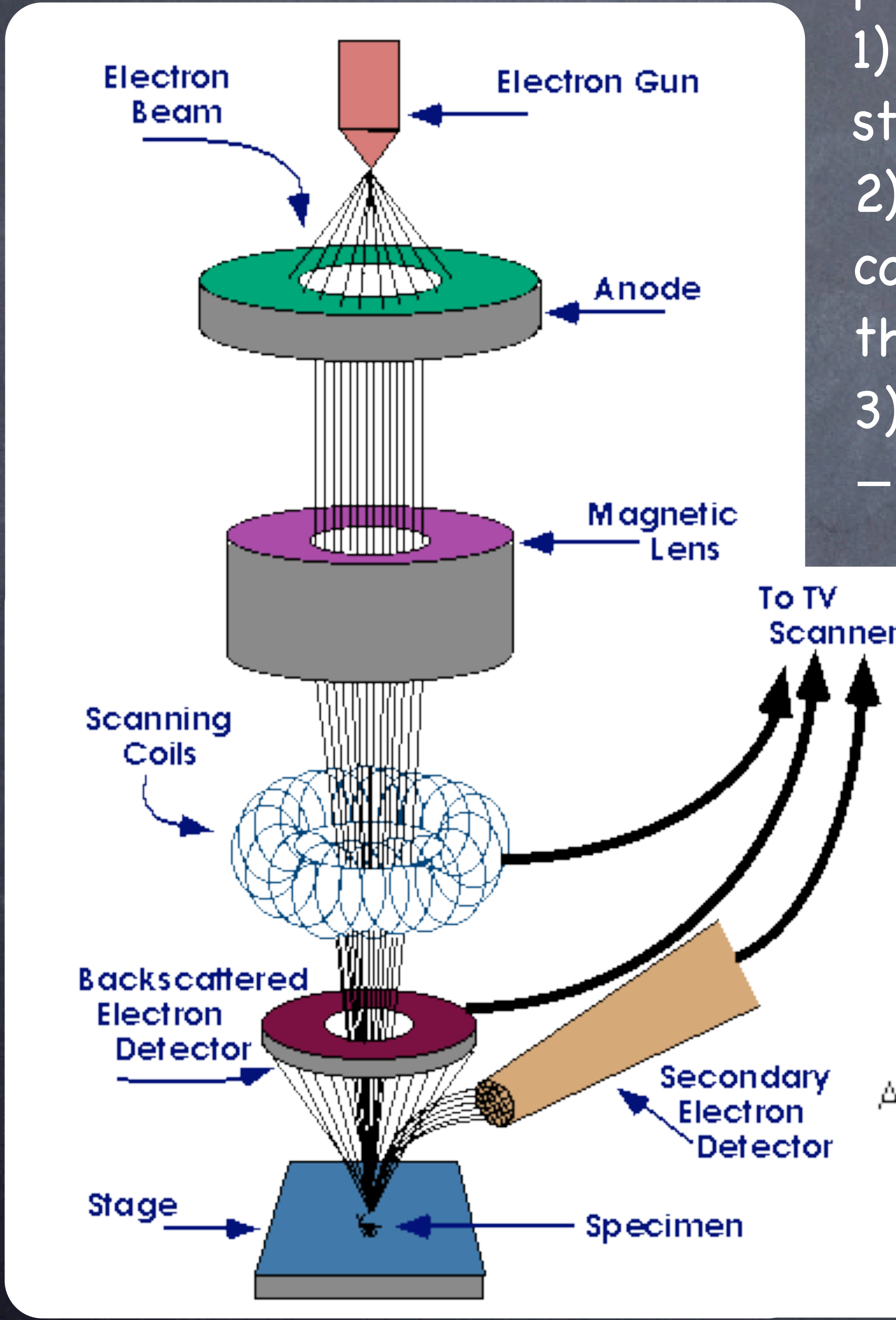
Shear force (topography), transmission NSOM, and fluorescence NSOM images of a phase separated polymer blend sample

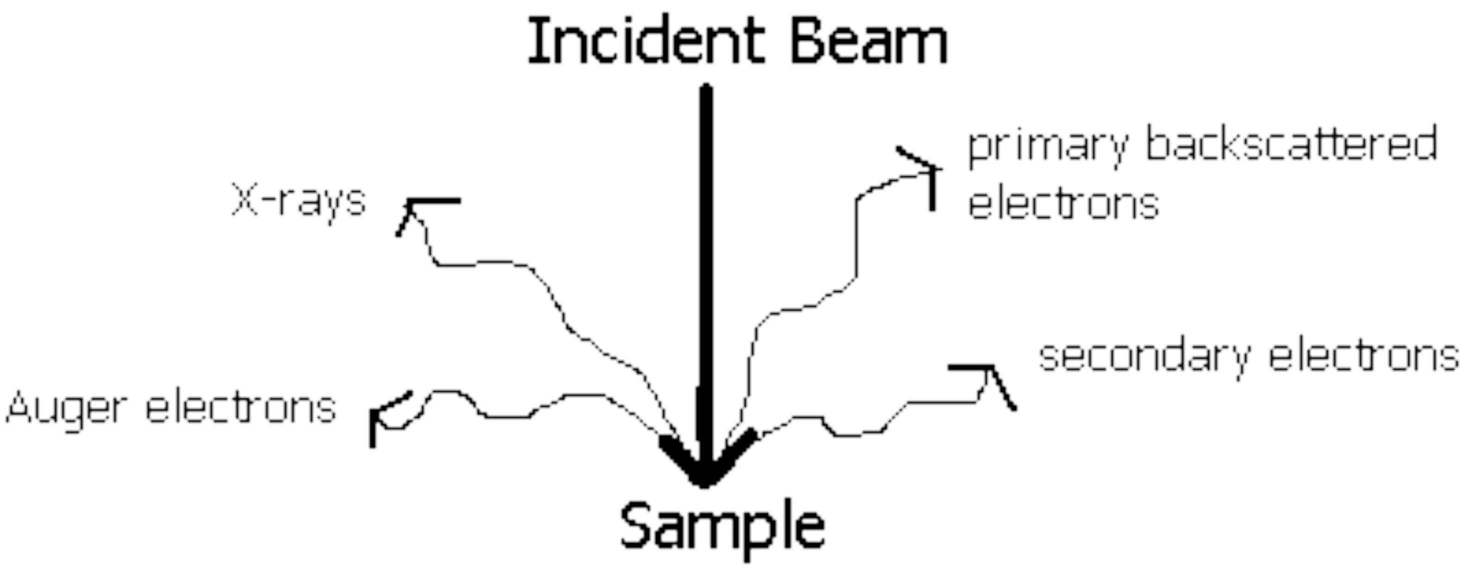
Scanning Electron Microscopy (SEM)

scanning of electron beam (0.2 – 30 keV) over a (usually conducting) specimen and detection of secondary low energy or backscattered electrons, resolution from mm down to about 5 nm

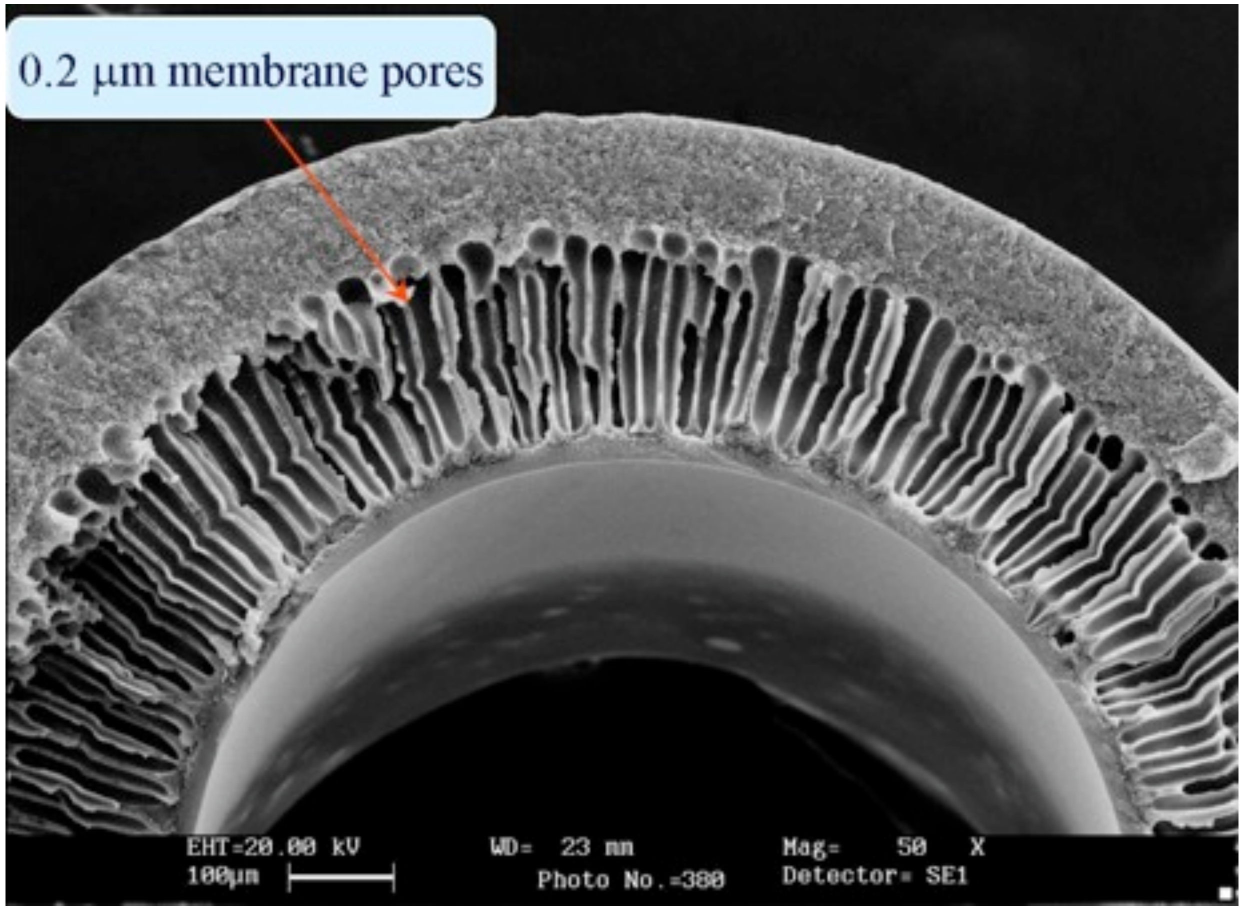
provides information on:

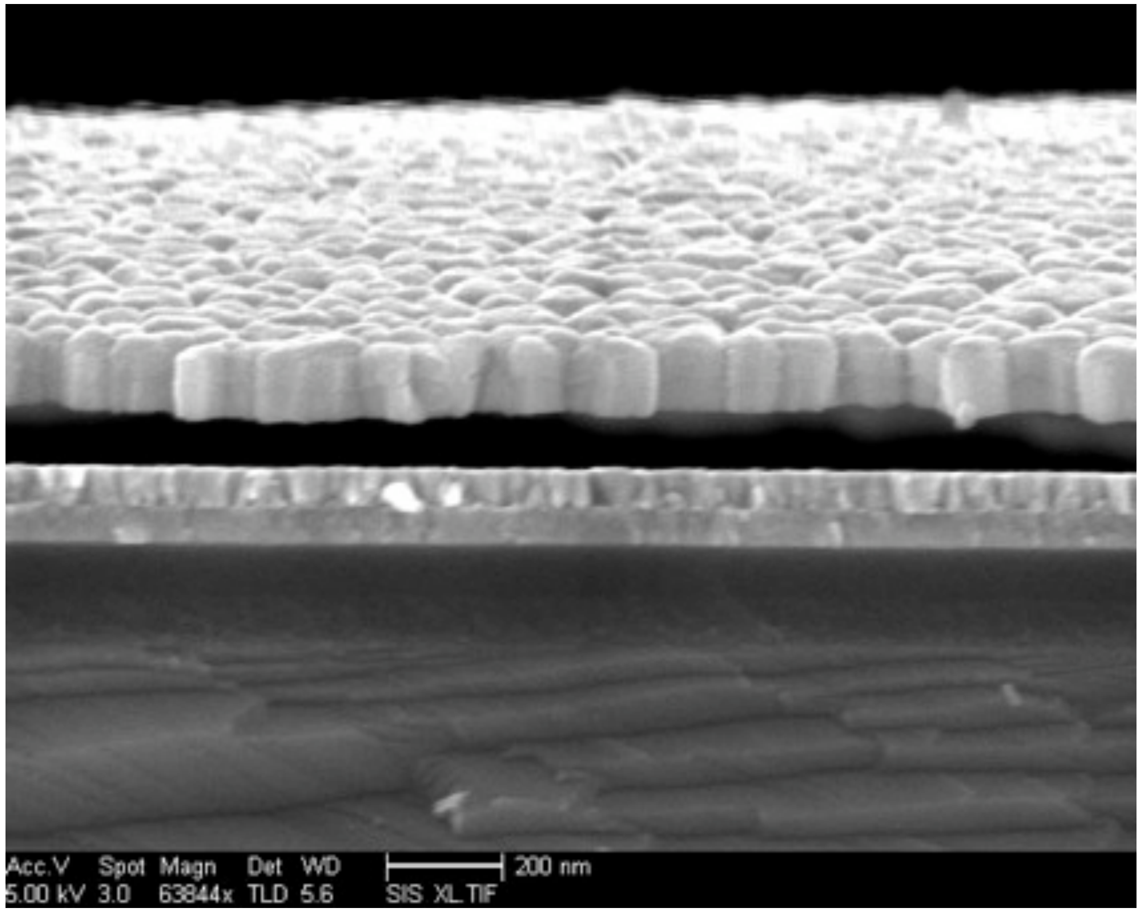
1) topography / morphology (surface profile, structural features)
2) composition (intensity of backscattered electrons correlates to the atomic number of elements within the sampling volume)
3) sometimes crystallographic information (single –crystal particles > 20 µm)

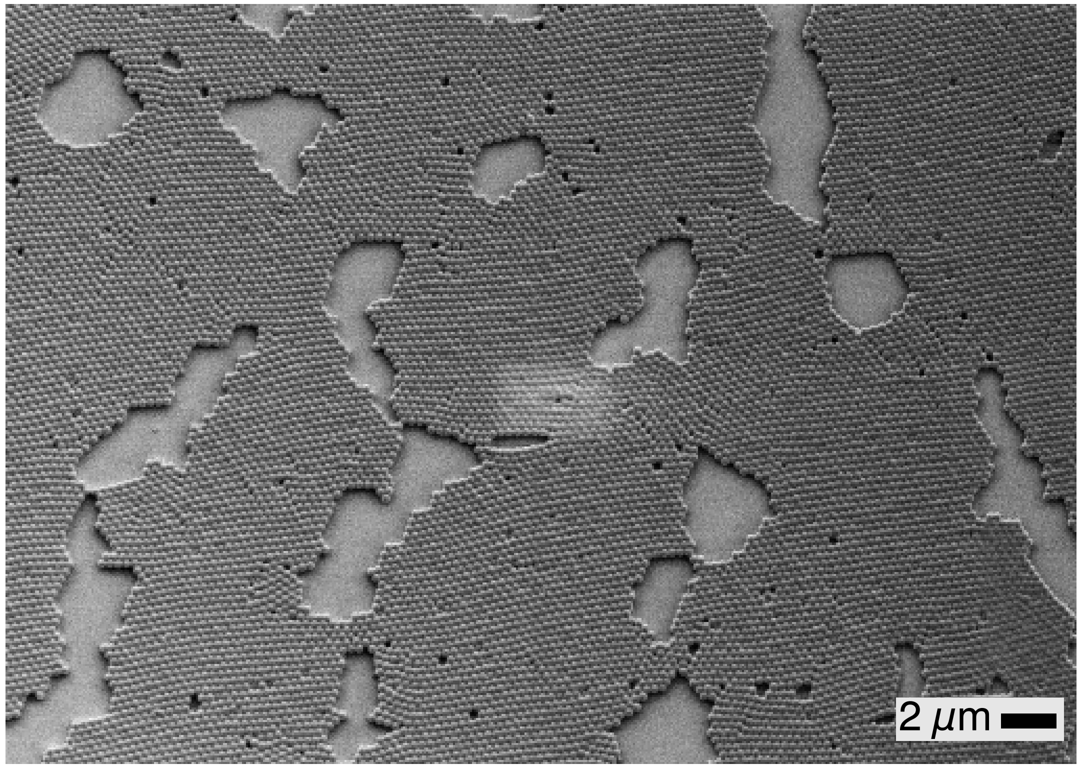


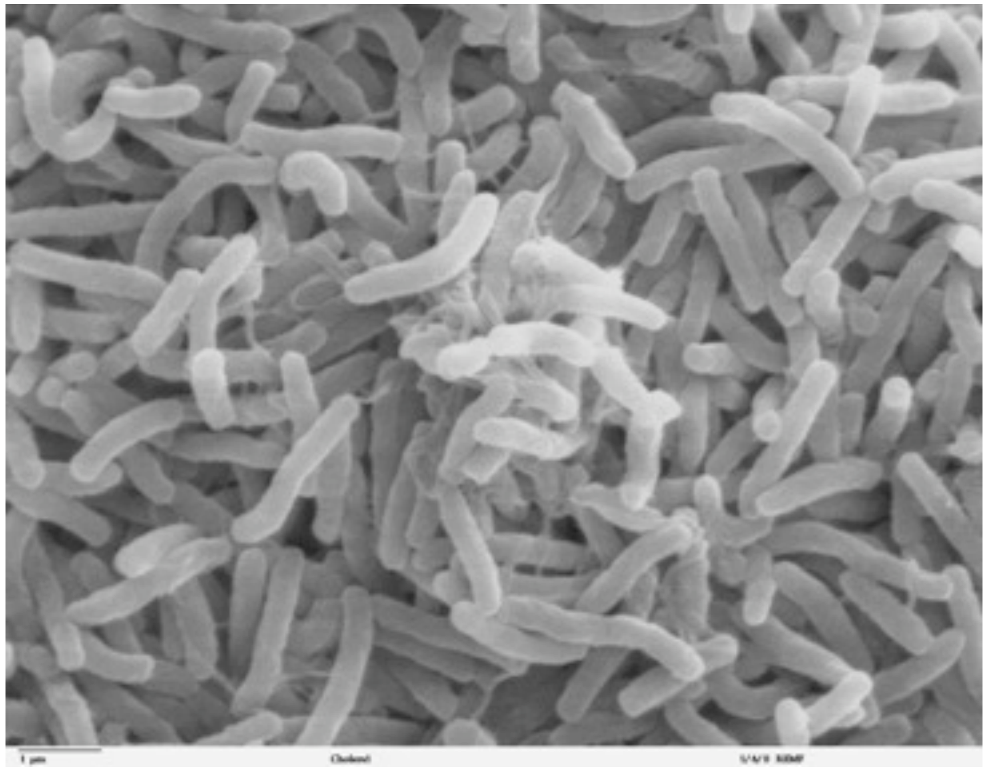


SEM: examples



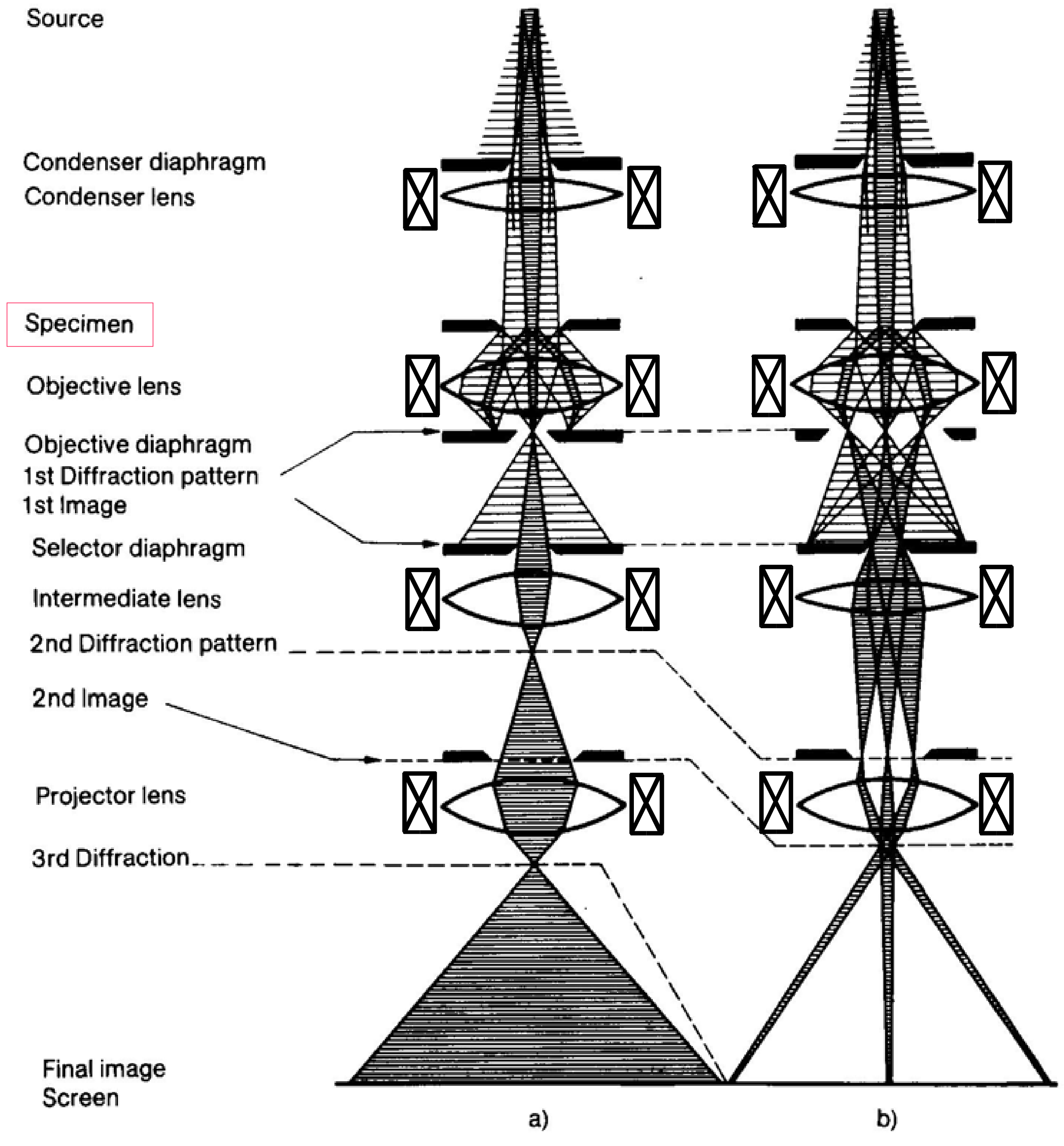






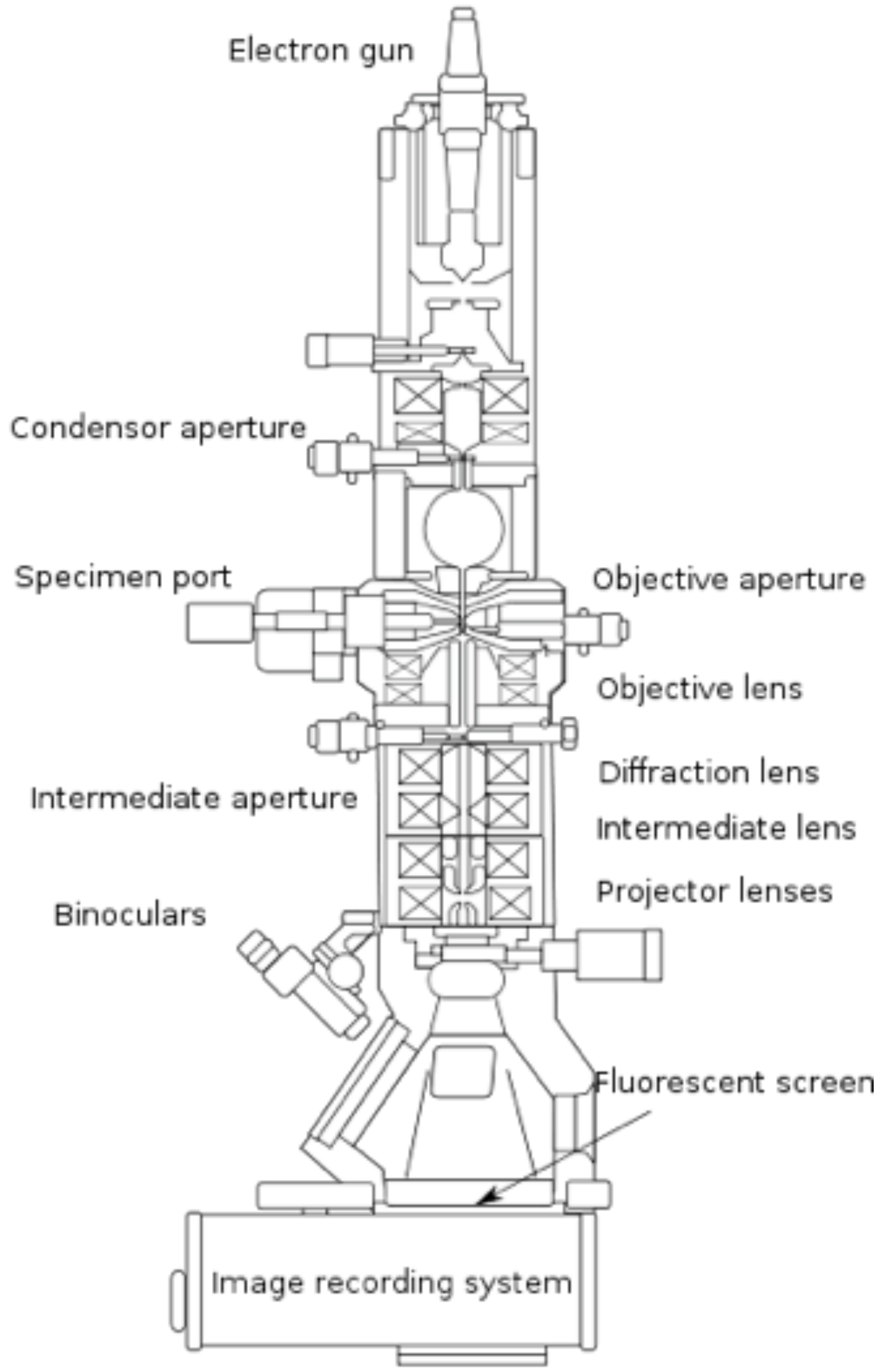
Transmission Electron Microscopy

transillumination of a thin specimen (~ 30–100 nm) with high energy electron beam allowing high resolution imaging or electron beam diffraction in crystalline samples:
acceleration voltage 100 keV → λ = 3.7 pm; 1 MeV → λ = 0.87 pm

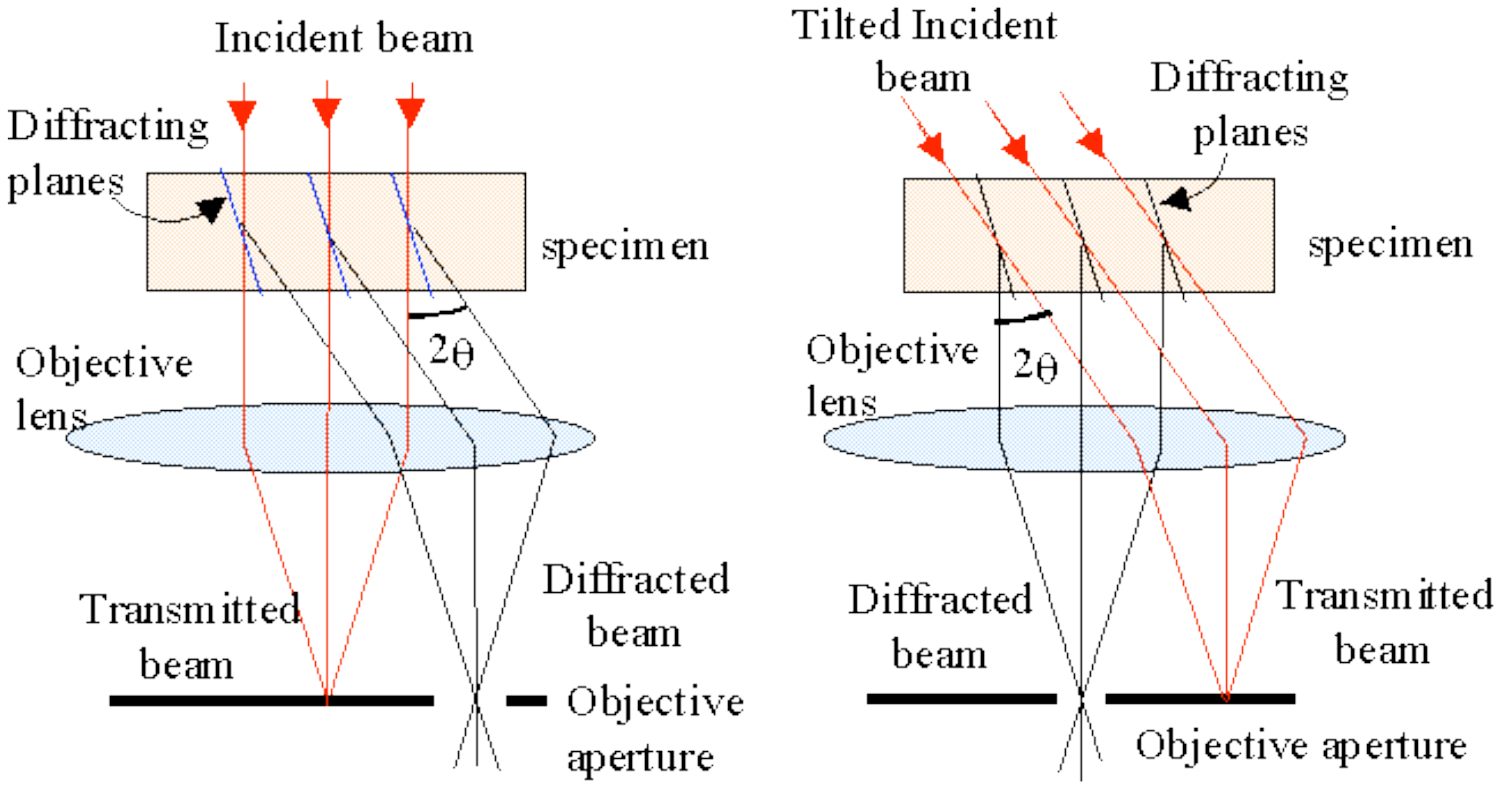


a) Bright field imaging

b) Selected area diffraction



TEM: dark field

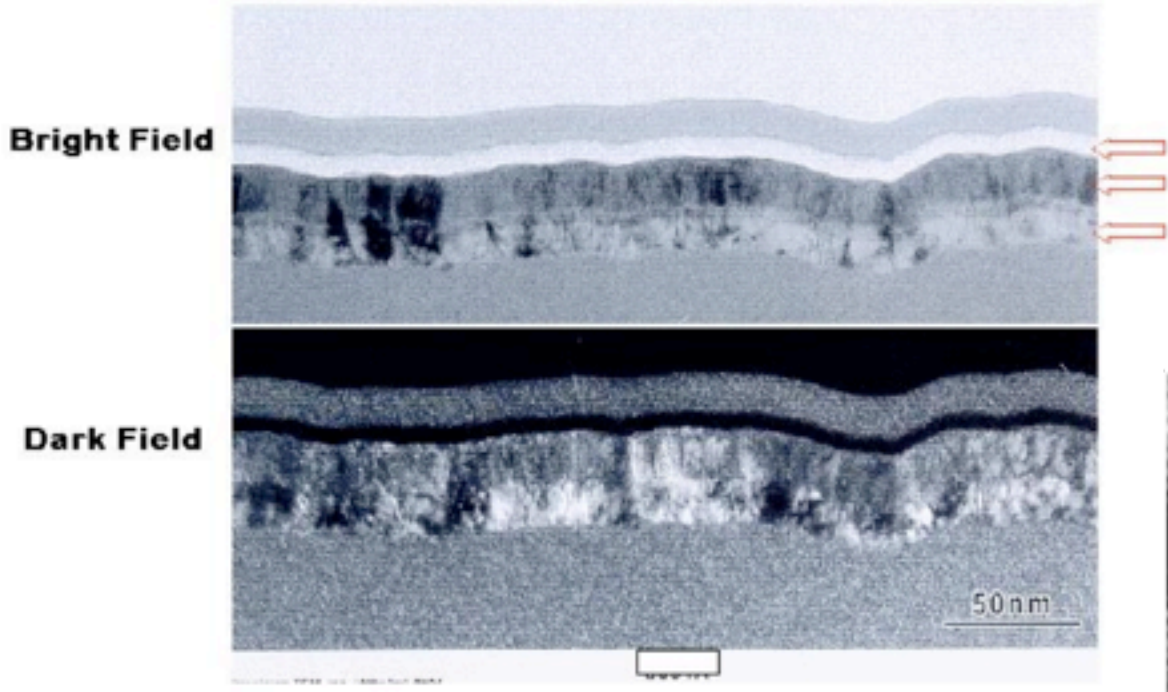


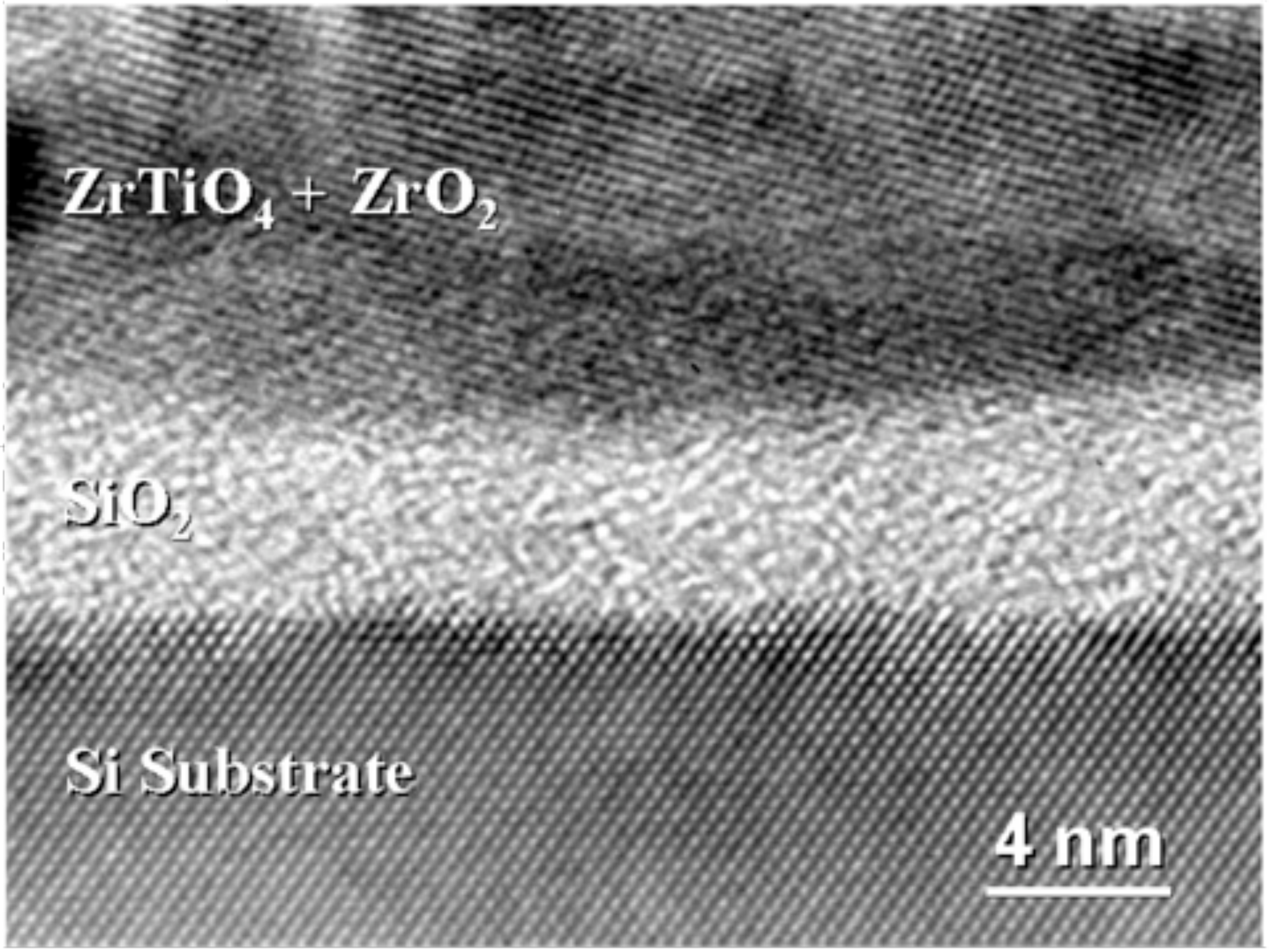
Off-axis Dark Field

On-axis Dark Field

TEM: examples

Cross Section TEM of a Hard Disk

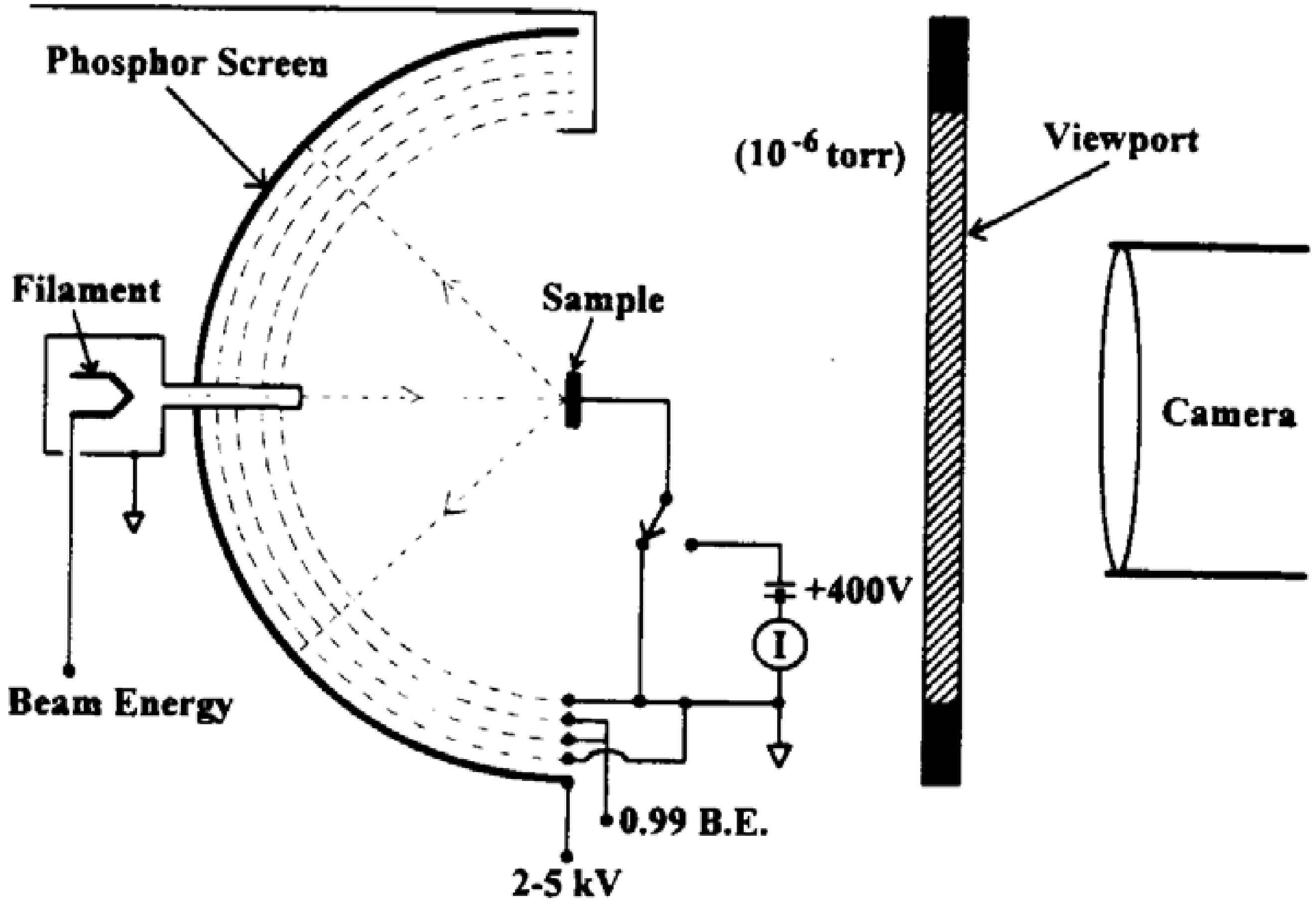


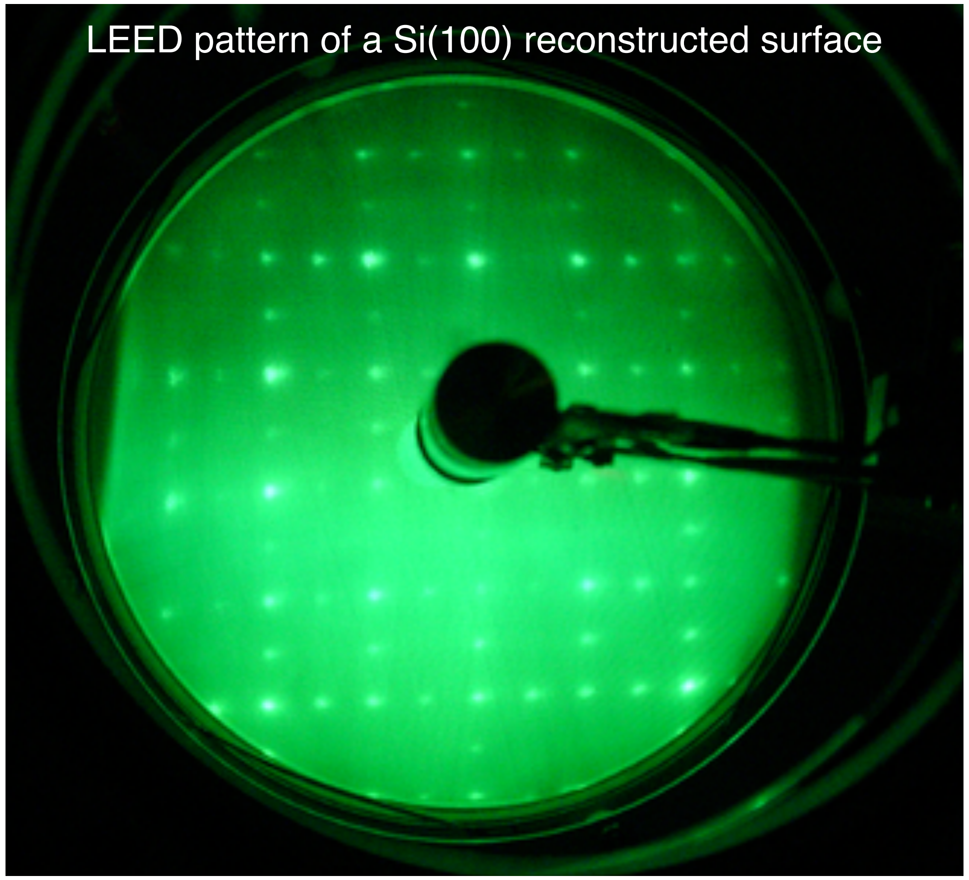


Low Energy Electron Diffraction

LEED is used to study the symmetry, periodicity and atomic arrangement of solid crystal surfaces and thin films. The LEED pattern symmetry, peak position and intensities give direct information on surface lattice parameters and the position of atoms in the surface unit cell.

LEED principle: low energy electrons (10–500 eV) are impinging onto a substrate surface and ~ 1 % (high interaction of electrons with matter) are elastically reflected to a phosphor screen, a diffraction pattern can be observed if lateral order at surface is beyond 20 nm




LEED pattern of a Si(100) reconstructed surface

other methods

Wikipedia lists a long list of analysis methods....

http://en.wikipedia.org/wiki/List_of_materials_analysis_methods