Surfaces and Interfaces:

Surfaces Characterization Techniques

Outline

Introduction
Wetting/Dewetting Contact Angle
Characterization of Surfaces

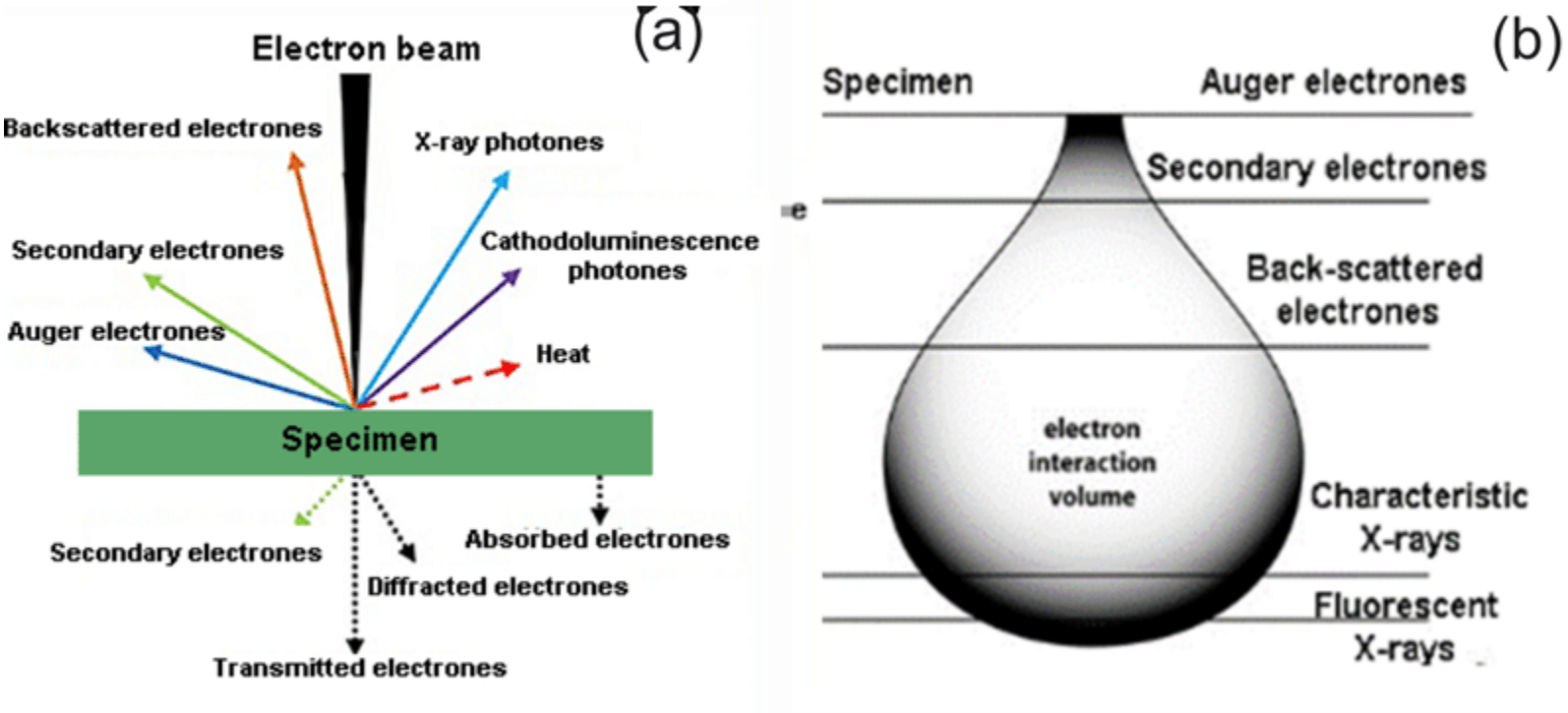
Spectroscopy: ESCA/XPS - Auger

Scanning Electron Microscopy

Microscopy on atomic scale: STM/AFM

Ellipsometry

Techniques with electron beam



ESCA / XPS - Auger Electron Spectroscopy

ESCA = electron spectroscopy for chemical analysis
XPS = x-ray photoelectron spectroscopy

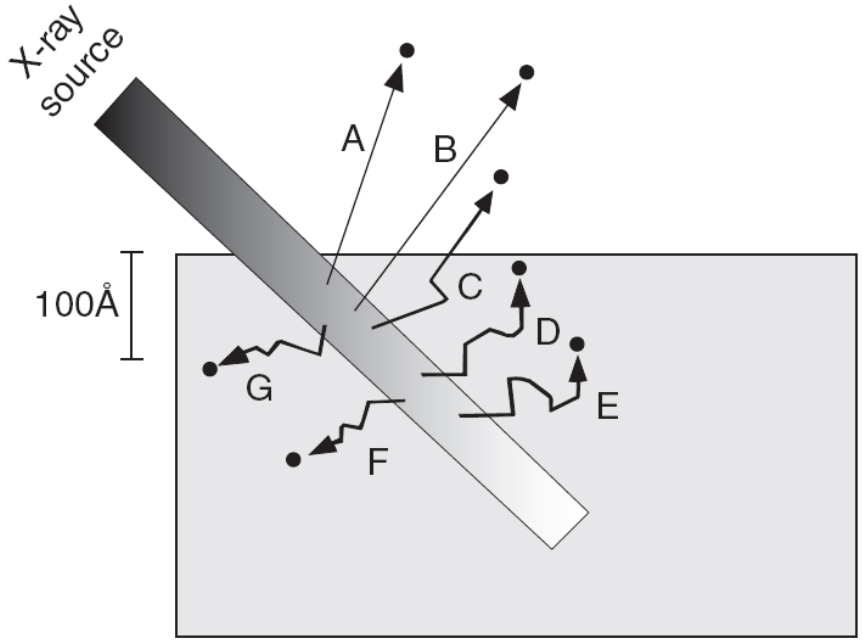
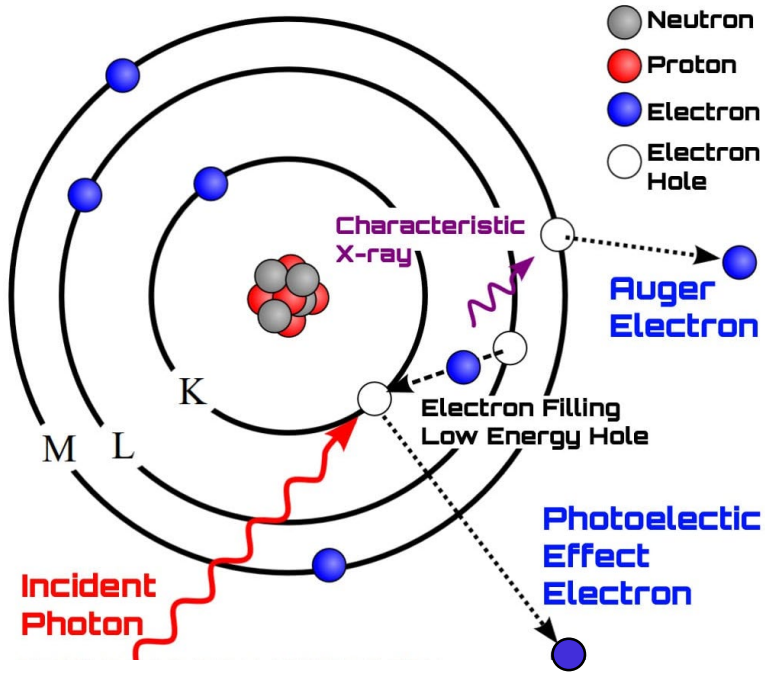
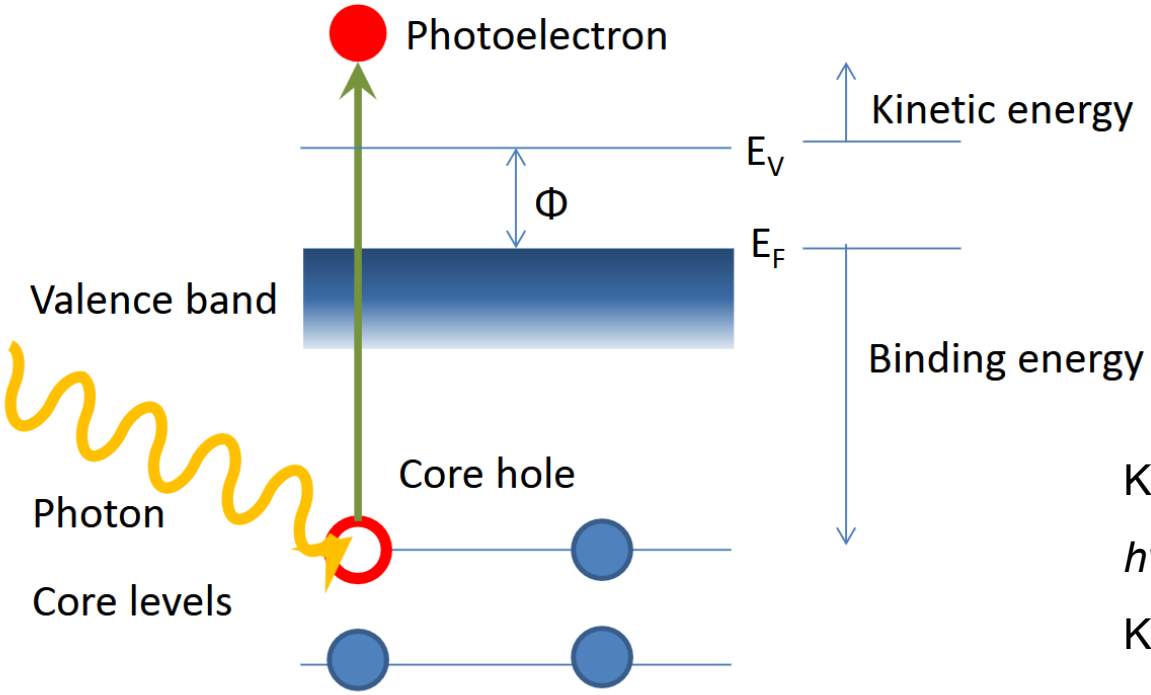


FIG. 7. ESCA is a surface-sensitive method. Although the X-ray beam can penetrate deeply into a specimen, electrons emitted deep in the specimen (D, E, F, G) will lose their energy in inelastic collisions and never emerge from the surface. Only those electrons emitted near the surface that lose no energy (A, B) will contribute to the ESCA signal used analytically. Electrons that lose some energy but still have sufficient energy to emerge from the surface (C) contribute to the background signal.



The Photoelectric Effect



KE=*hv*-BE-φ

hv: Incident light energy (known)

KE: Kinetic energy (measured)

BE: Binding energy (calculated)

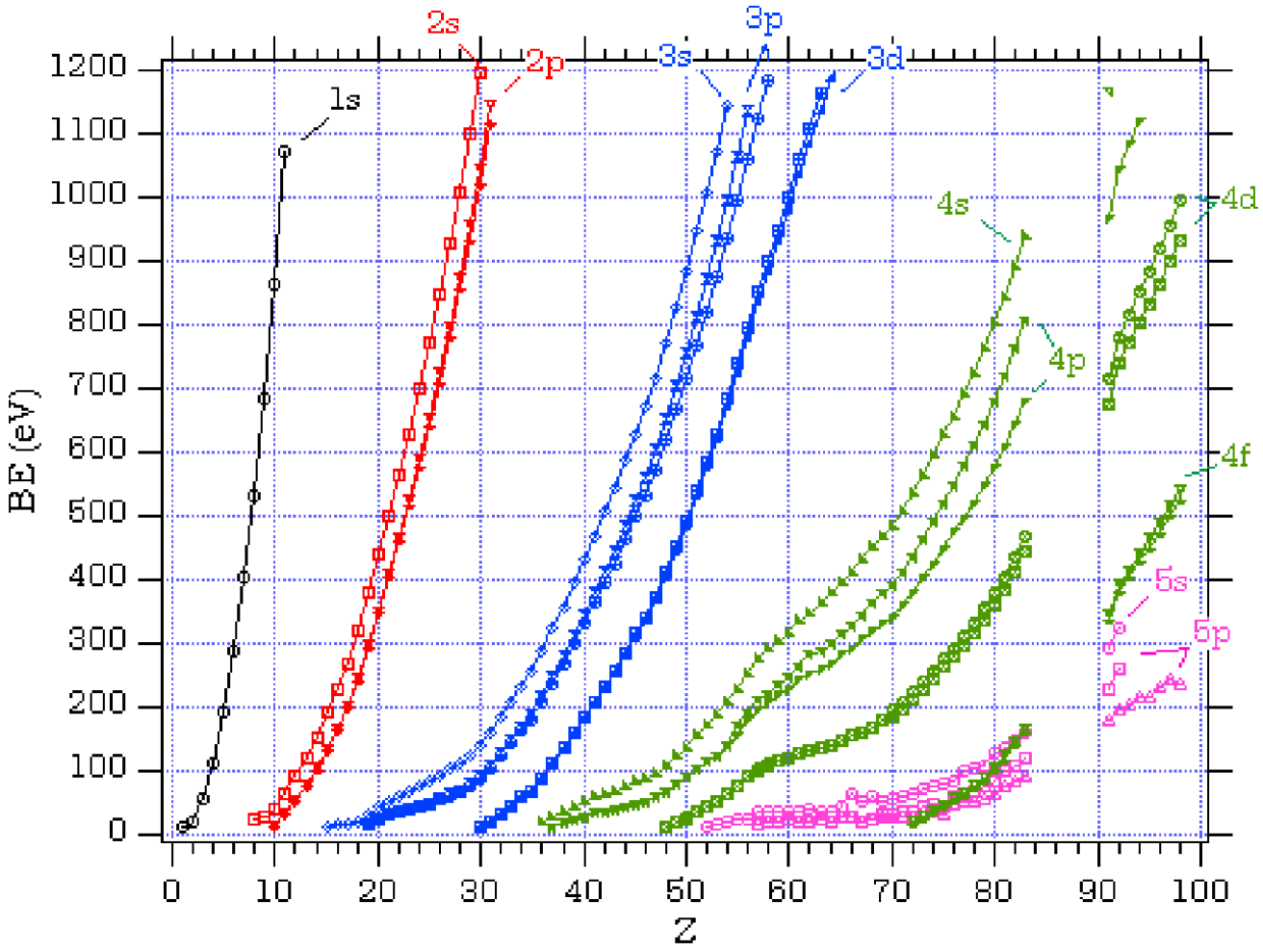
φ: Photoelectric workfunction (known)

KE = hν – BE – Φ for a solid

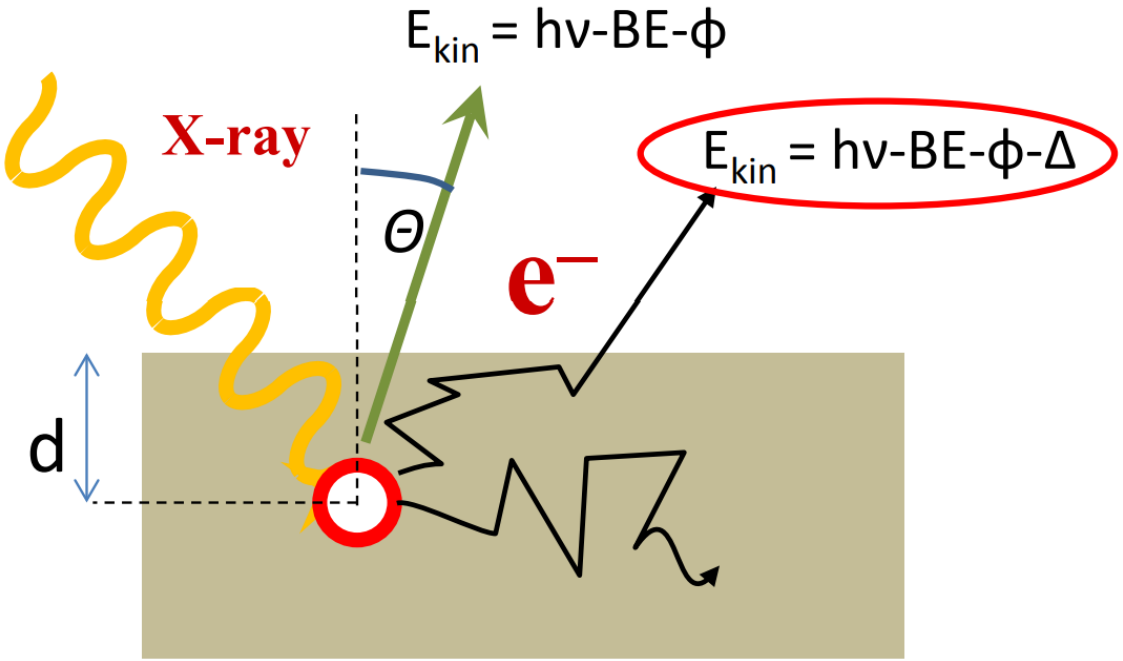
KE = hν – IP for a gas

Φ : photoelectric workfunction (4-6 eV)

The Binding Energy



XPS Probe Depth



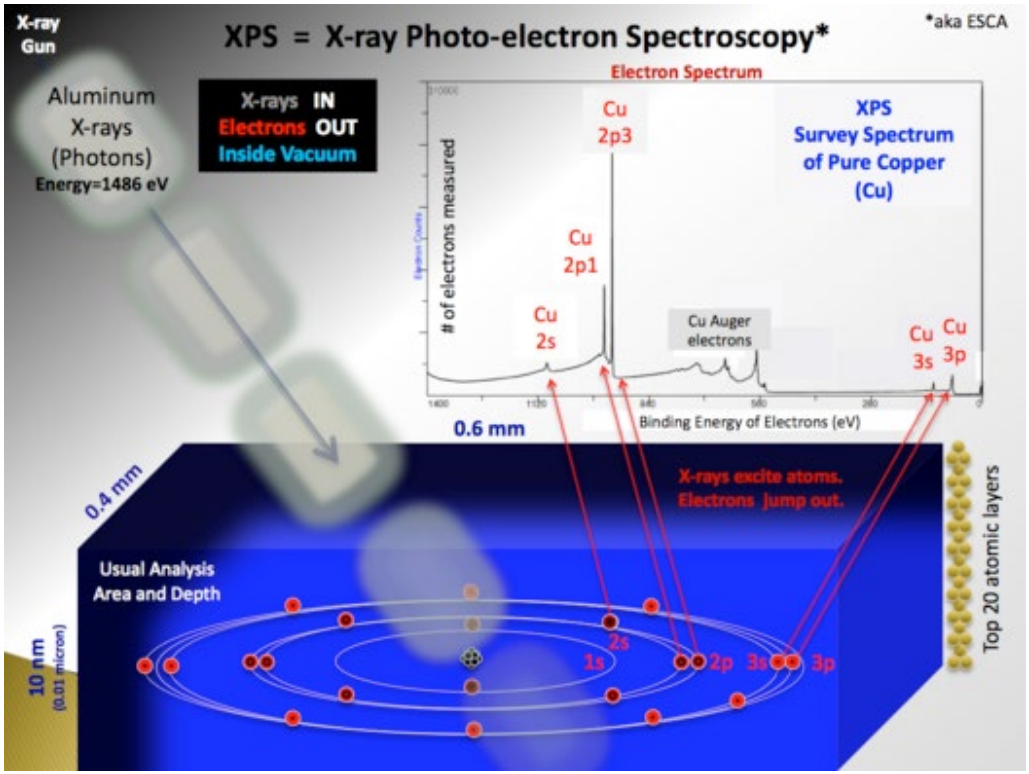
For an electron of intensity I_0 emitted at a depth d below the surface, the intensity I of the same electron as it reaches the surface is

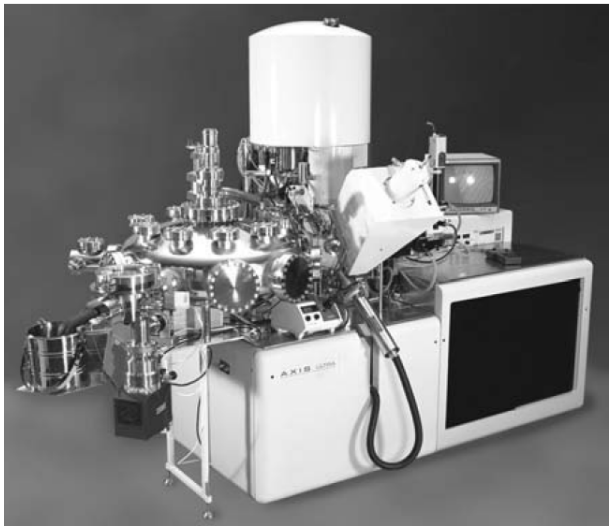
$$I = I_0 \exp\left(\frac{-d}{\lambda \cos\theta}\right)$$

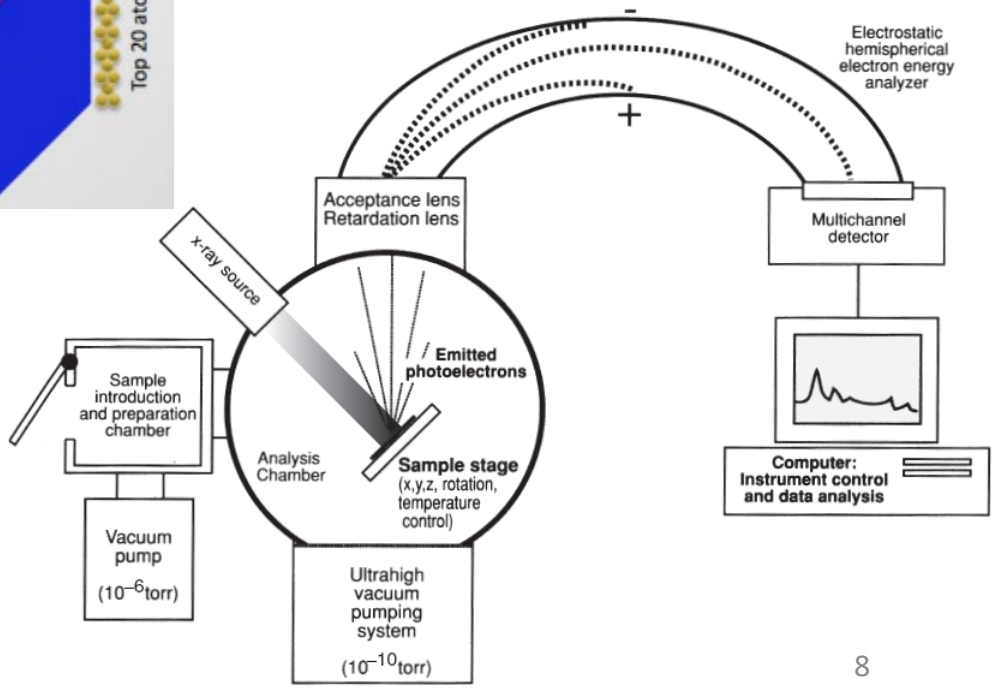
1: Sampling depth is defined as the depth from which 95% of all photoelectrons are scattered by the time they reach the surface (3λ).
2: Most λ's are in the range of 1 – 3.5 nm for Al K_α radiation.
3: The sampling depth (3λ) for XPS under these conditions is 3-10 nm.
4: Depth profiles can be obtained by varying the detection angle.

D. Son et al, *Polymers* **2020**, 12, 1053

ESCA / XPS


X-ray Gun
XPS = X-ray Photo-electron Spectroscopy*
*aka ESCA
Aluminum X-rays (Photons)
Energy=1486 eV
X-rays IN
Electrons OUT
Inside Vacuum
Electron Spectrum
# of electrons measured
Cu 2p3
Cu 2p1
Cu 2s
Cu Auger electrons
Cu 3s
Cu 3p
XPS Survey Spectrum of Pure Copper (Cu)
Binding Energy of Electrons (eV)
0.6 mm
0.4 mm
X-rays excite atoms. Electrons jump out.
Usual Analysis Area and Depth
10 nm (0.01 micron)
Top 20 atomic layers
2s
1s
2p
3s
3p




Electrostatic hemispherical electron energy analyzer
Acceptance lens Retardation lens
Multichannel detector
X-ray source
Emitted photoelectrons
Sample introduction and preparation chamber
Analysis Chamber
Sample stage (x,y,z, rotation, temperature control)
Computer: Instrument control and data analysis
Vacuum pump (10^{-6}torr)
Ultrahigh vacuum pumping system (10^{-10}torr)

Information derived from ESCA/XPS Experiment

In the outermost 100 Å of a surface, ESCA/XPS can provide:

- Identification of all elements (except H and He) present at concentrations >0.1 at %
- Semiquantitative determination of the approximate elemental surface composition (±10%)
- Information about the molecular environment (oxidation state, bonding atoms, etc.)
- Information about aromatic or unsaturated structures from shake-up $\pi^* \leftarrow \pi$ transitions
- Identification of organic groups using derivatization reactions
- Nondestructive elemental depth profiles 100 Å into the sample and surface heterogeneity assessment using angular-dependent ESCA studies and photoelectrons with differing escape depths
- Destructive elemental depth profiles several thousand angstroms into the sample using argon etching (for inorganics)
- Lateral variations in surface composition (spatial resolution 8–150 μm, depending upon the instrument)
- "Fingerprinting" of materials using valence band spectra and identification of bonding orbitals
- Studies on hydrated (frozen) surfaces

Example of ESCA Scan

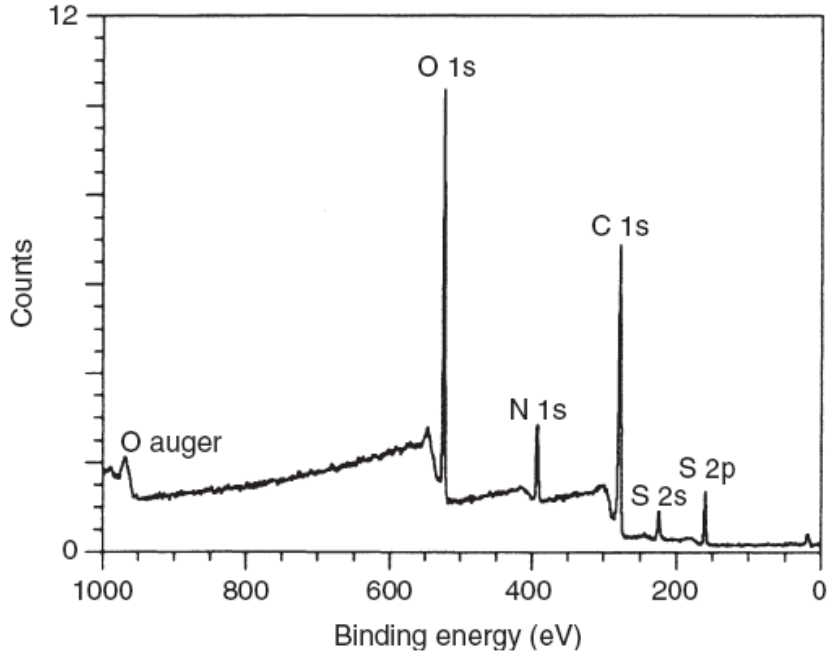


FIG. 8. ESCA wide scan of a surface-modified poly(methyl methacrylate) ophthalmologic device.

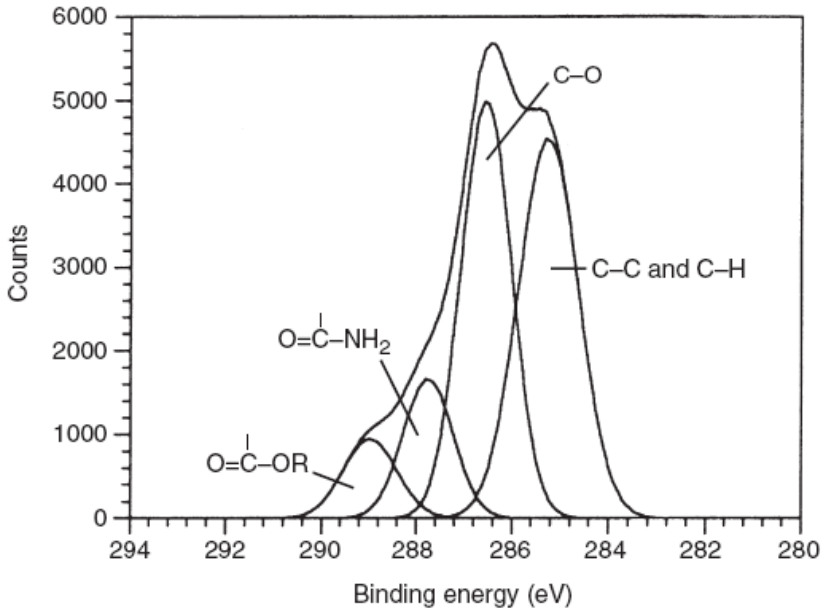
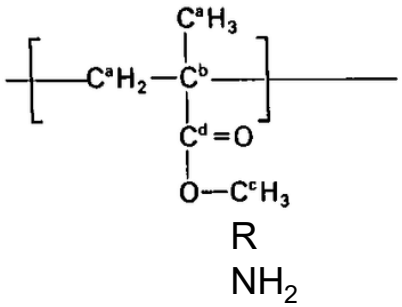


FIG. 9. The carbon 1s narrow scan ESCA spectrum of a surface-modified poly(methyl methacrylate) ophthalmologic device. Narrow scan spectra can be generated for each element seen in low-energy resolution mode in Fig. 8.



Scanning Electron Microscopy

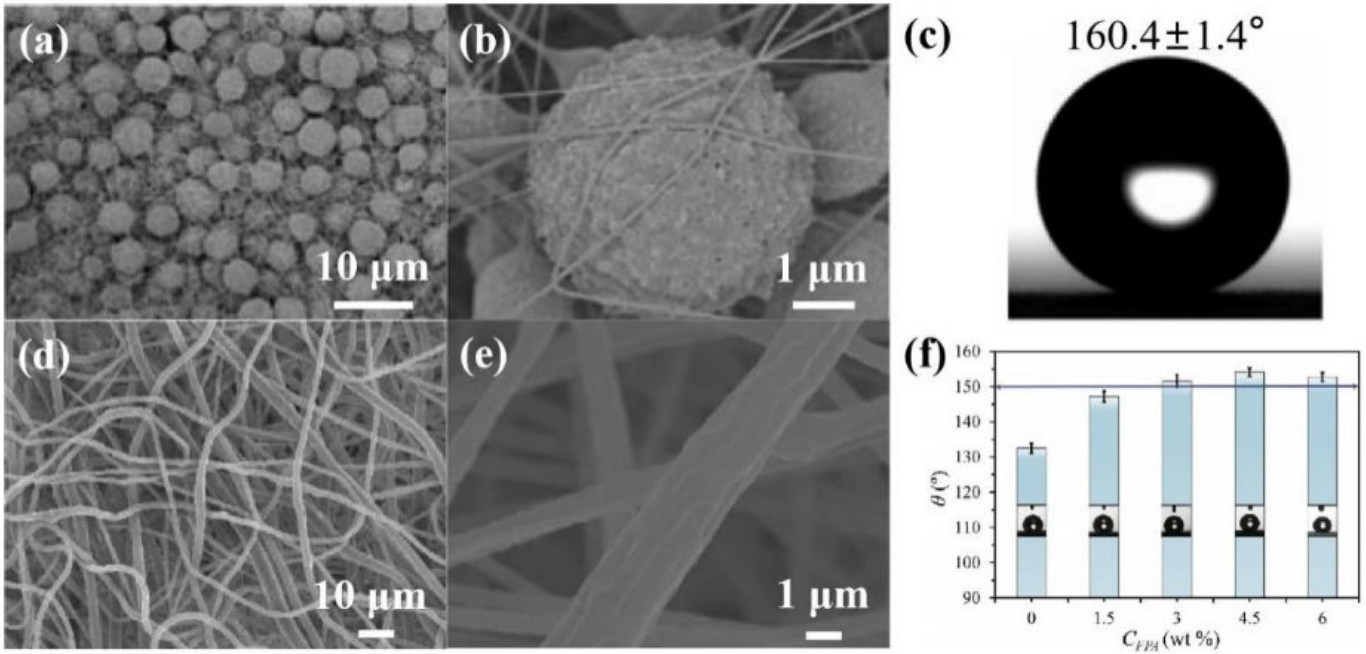


Figure 3. (**a**) and (**b**) are the SEM images of polystyrene (PS) fiber prepared from the 7 wt % PS/DMF. Solution with different magnifications, (**c**) water droplet on this surface; (**d**) and (**e**) are the SEM images of PSF-4.5 (weight concentration of fluorinated polyurethane additive (FPA)) and FPA-blended fibers (**f**) water contact angle (WCA) of droplets on different fibers. Adapted from

T. Xiang et al., Coatings 2019, 9, 753; doi:10.3390/coatings9110753

Scanning Tunneling Microscopy STM

Requires conductive or semi-conductive substrates

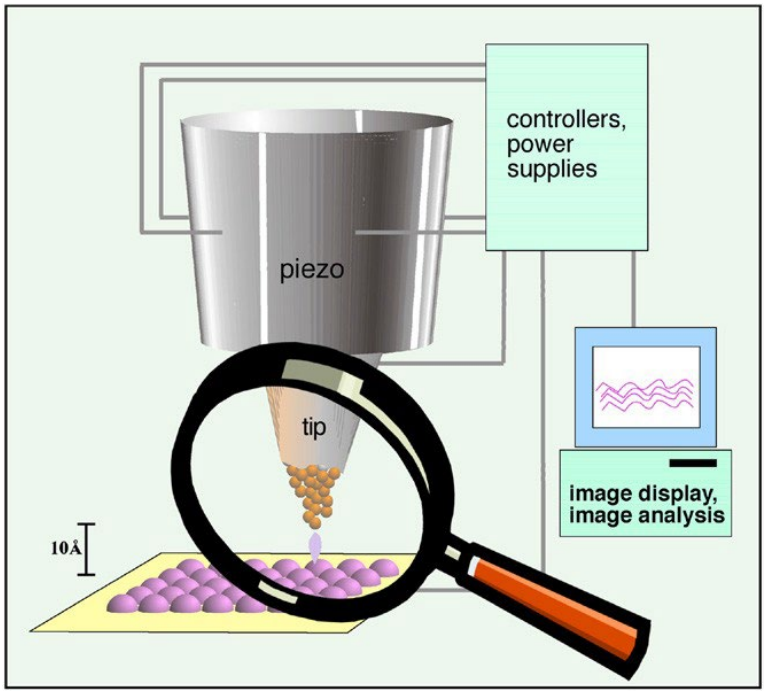


FIGURE I.1.5.13 Schematic diagram illustrating the principle of the scanning tunneling microscope – a tip terminating in a single atom permits localized quantum tunneling current from surface features (or atoms) to tip. This tunneling current can be spatially reconstructed to form an image.

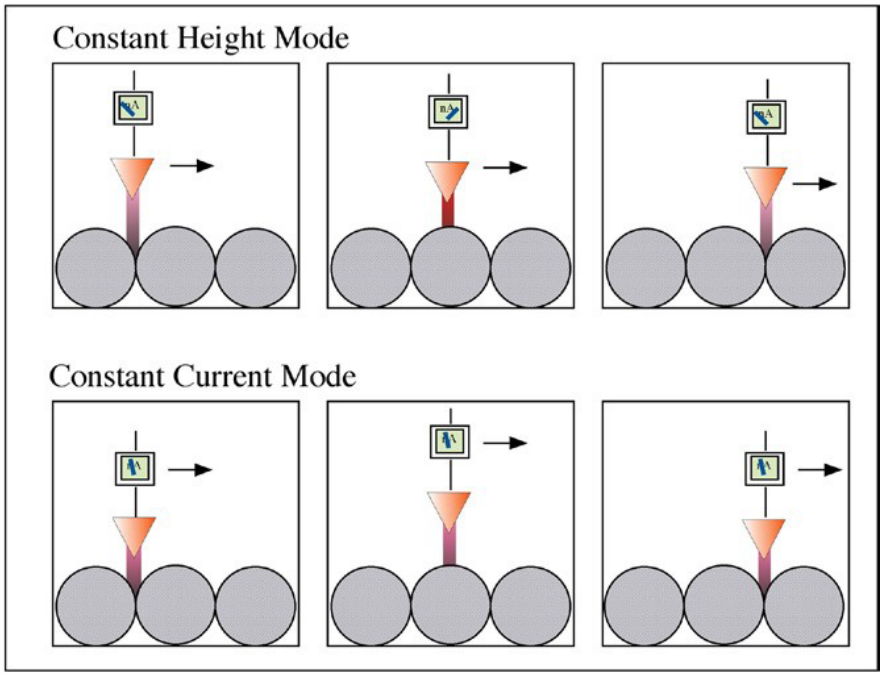


FIGURE I.1.5.14 Scanning tunneling microscopy can be performed in two modes. In constant height mode, the tip is scanned a constant distance from the surface (typically 5–10 Å) and the change in tunneling current is recorded. In constant current mode, the tip height is adjusted so that the tunneling current is always constant, and the tip distance from the surface is recorded as a function of distance traveled in the plane of the surface.

Ch. 1, Buddy D. Ratner, A. S. Hoffman, Frederick J. Schoen, J. E. Lemons, Biomaterials Science, 2nd edition (Wiley)

Example of STM Image

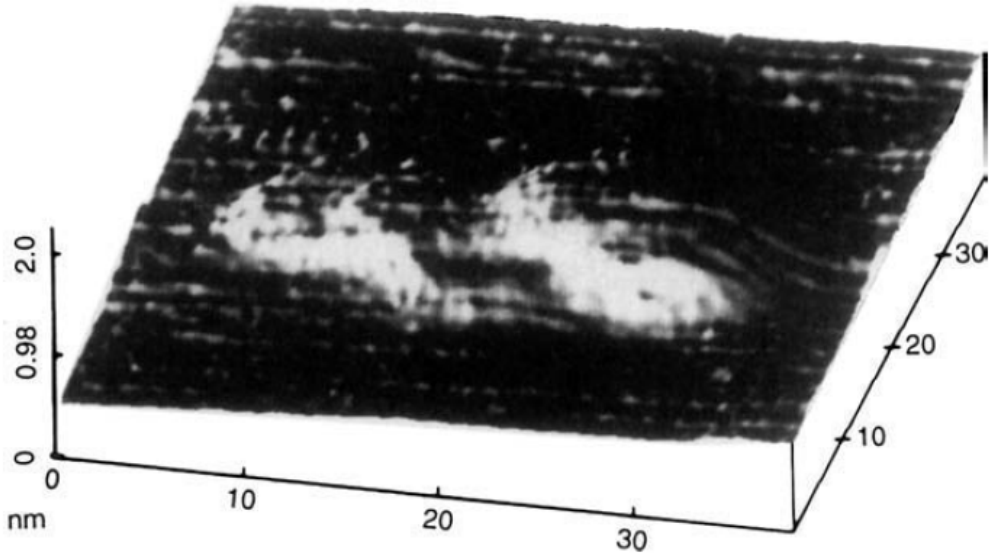
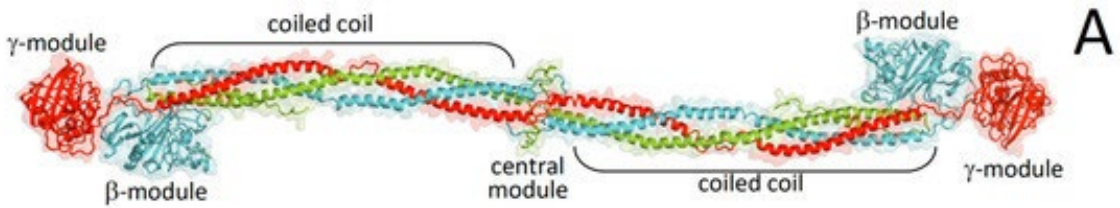


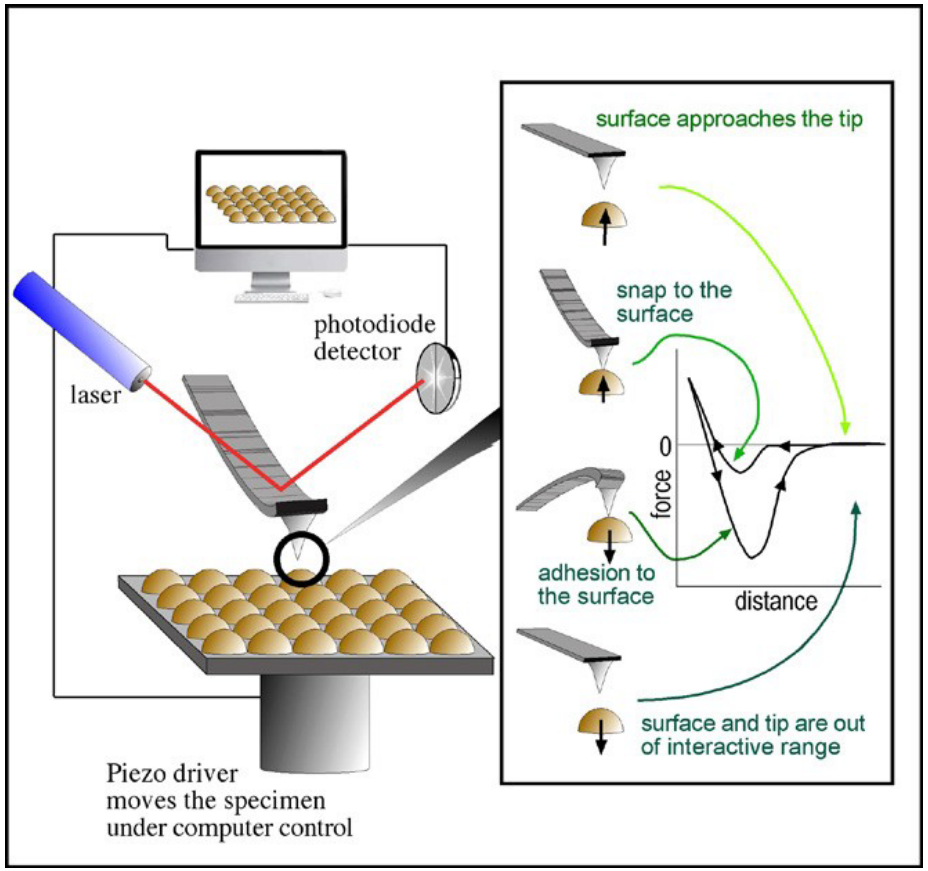
FIG. 15. Scanning tunneling micrograph image of a fibrinogen molecule on a gold surface, under buffer solution (image by Dr. K. Lewis).



K.B. Lewis, B.D. Ratner, Colloids and Surfaces B: Biointerfaces 7 11996) 259 269
E. Bellacchio Int. J. Mol. Sci. 2020, 21(23), 9016

Atomic Force Microscopy AFM

AFM allows imaging of surfaces at sub-nanometer resolution, and also provides detail on surface mechanics and molecular interactions.



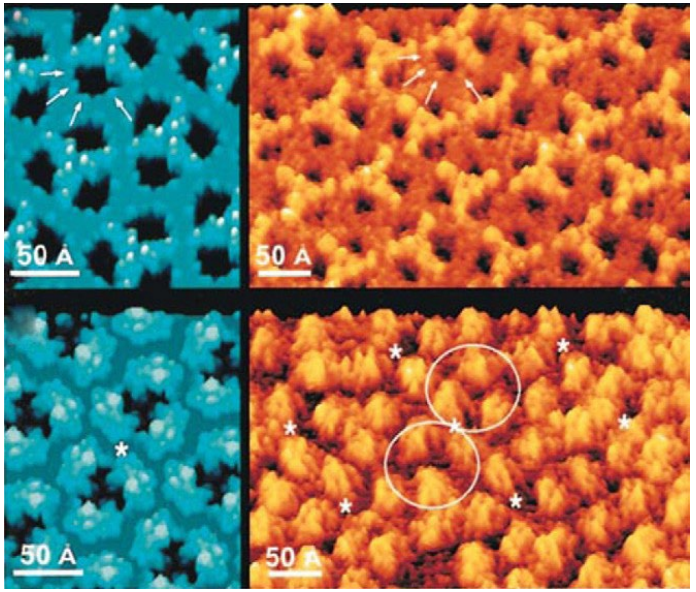


FIGURE I.1.5.16 An AFM image of porin proteins from the outer membrane of *E. coli* imaged with nanoscale resolution. Comparison of high-resolution AFM images of OmpF crystals (in brown-yellow) and the atomic model rendered at 3 Å (in blue).

1) **Contact mode**: repulsive force; high resolution but may damage the sample and the tip.

2) **Noncontact mode**: attractive force; hard material, relatively low sensitivity.

3) **Tapping mode**: external oscillating signal; high resolution, suitable for high roughness surface and soft and sticky materials.

Scanning Probe Microscopy Modes

Name	acronym	Use
Contact mode	CM-AFM	Topographic imaging of harder specimens
Tapping (intermittent force) mode	IF-AFM	Imaging softer specimens
Non-contact mode	NCM-AFM	Imaging soft structures
Force modulation (allows slope of force-distance curve to be measured	FM-AFM	Enhances image contrast based on surface mechanics
Scanning surface potential microscopy (Kelvin probe microscopy)	SSPM, KPM	Measures the spatial distribution of surface potential
Magnetic force microscopy	MFM	Maps the surface magnetic forces
Scanning thermal microcopy	SThM	Maps the thermal conductivity characteristics of a surface
Recognition force microscopy	RFM	Uses a biomolecule on a tip to probe for regions of specific biorecognition on a surface
Chemical force microscopy	CFM	A tip derivatized with a given chemistry is scanned on a surface to spatially measure differences of interaction strength
Lateral force microscopy	LFM	Maps frictional force on a surface
Electrochemical force microscopy	EFM	The tip is scanned under water and the electrochemical potential between tip and surface is spatially measured
Nearfield scanning optical microscopy	NSOM	A sharp optical fiber is scanned over a surface allowing optical microscopy or spectroscopy at 100 nm resolution
Electrostatic force microscopy	EFM	Surface electrostatic potential are mapped
Scanning capacitance microscopy	SCM	Surface capacitance is mapped
Conductive atomic force microscopy	CAFM	Surface conductivity is mapped with an AFM instrument
Nanolithographic AFM	NAFM	An AFM tip etches, oxidizes or reacts a space permitting pattern fabrication at 10 nm or better resolution
Dip-pen nanolithography	DPN	An AFM tip, inked with a thiol or other molecule, writes on a surface at the nanometer scale

Ch. 1, Buddy D. Ratner, A. S. Hoffman, Frederick J. Schoen, J. E. Lemonds, Biomaterials Science, 2nd edition (Wiley)

Topography, Friction & Elasticity of Polymers

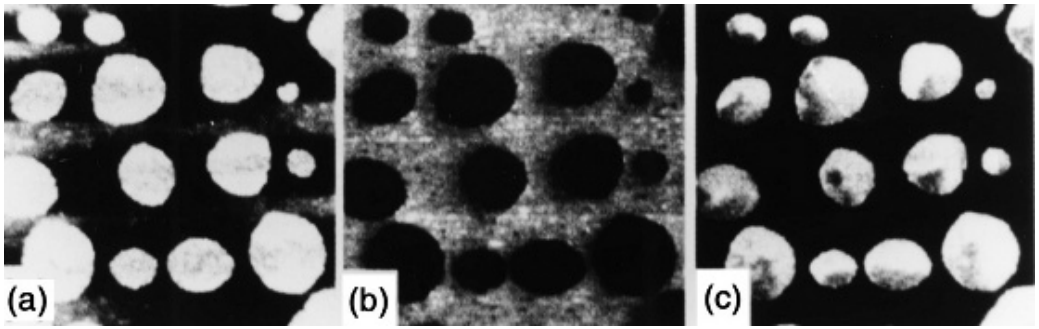


Figure 12.9 SFM studies of topography, friction, and elasticity on the same area, 3 X 3 μm^2.
(*a*) Topography with islandlike hydrocarbon domains (bright) of 300 to 1000 nm diameter on top of a fluorocarbon film (dark). The height of the islands is 2.5 ± 0.5 nm. (*b*) Friction force map shows lower friction (dark) on hydrocarbon islands. (*c*) Elastic compliance (elasticity) map indicates higher Young's modulus (bright) for the hydrocarbon domains.

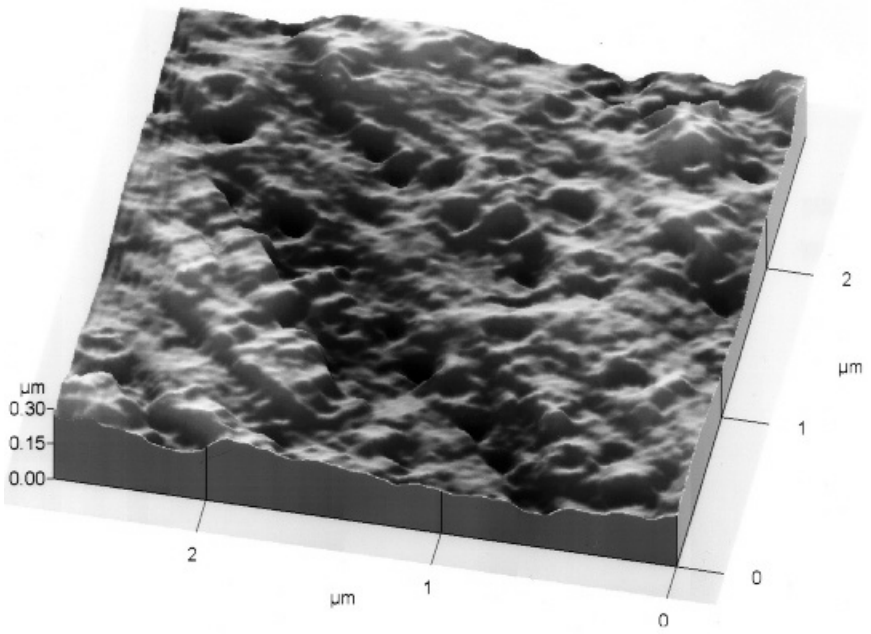
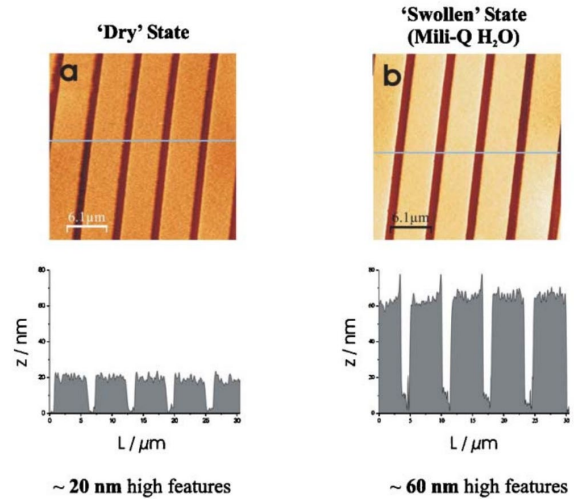


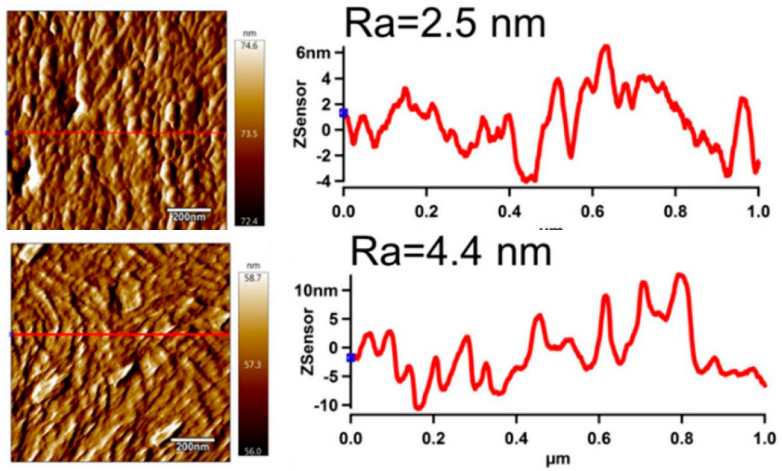
Figure 12.10 An AFM scan of the stress-whitened zone on an epoxy toughened with core-shell SBR/P(MMA–*stat*–AN) latexes. Note the evidence for a dilational band.

AFM Applications



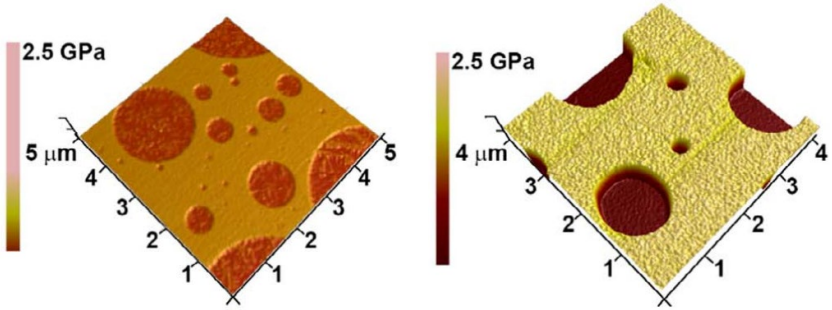
dry and swollen brushes thicknesses

T. Farhan et al, *Soft Matter*, **2005**, 1, 66



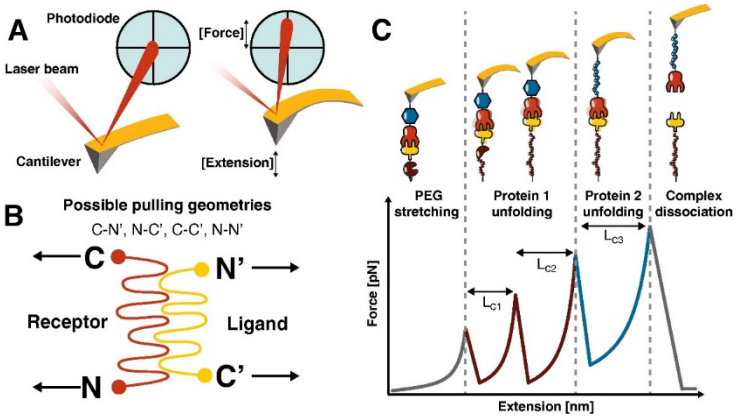
polymer surface roughness

S. Habib et al, *Polymers* **2019**, 11, 1704



polymer mechanical properties

A. Buonerba et al, *European Polymer Journal,* **2018**, 99, 368

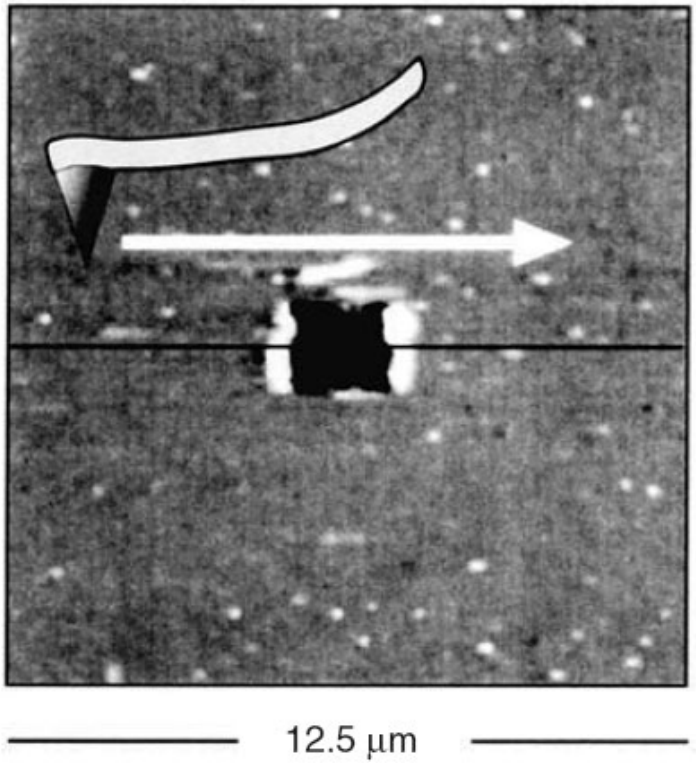


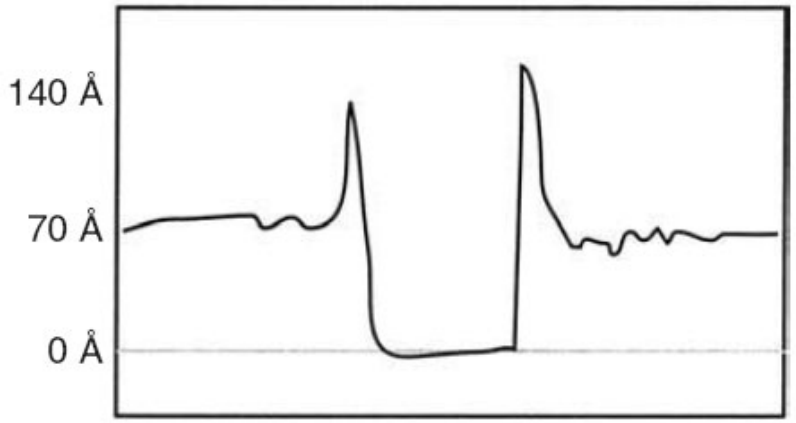
single molecule force microscopy

W. Ott et al, *Journal of Structural Biology* **2017**, 197, 3.

Film Thickness by AFM

An AFM tip, using relatively high force, was used to scratch a rectangular feature into a thin (70 Å) plasma-deposited film. The AFM also characterized the feature created.

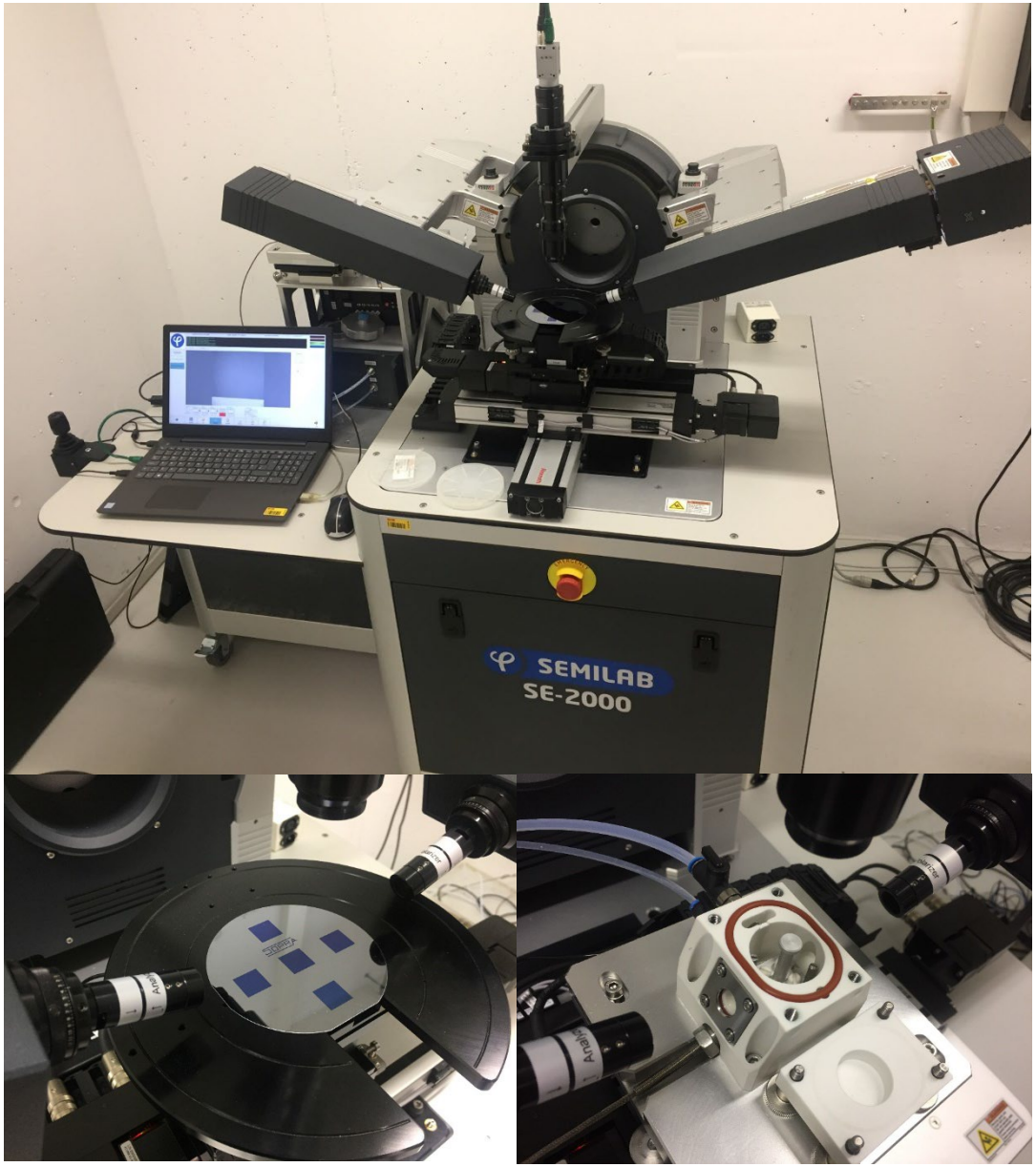




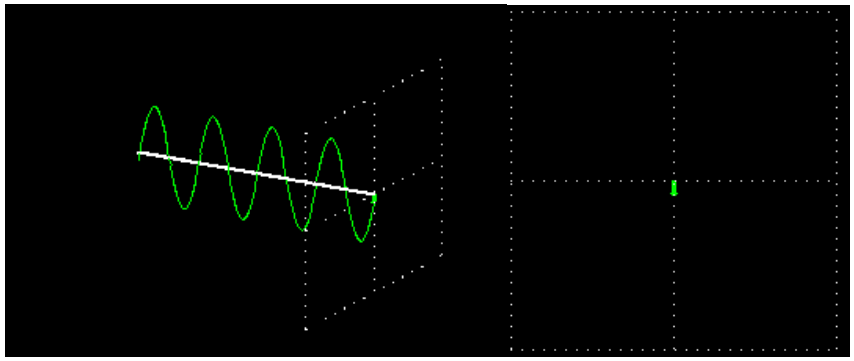
Ellipsometry

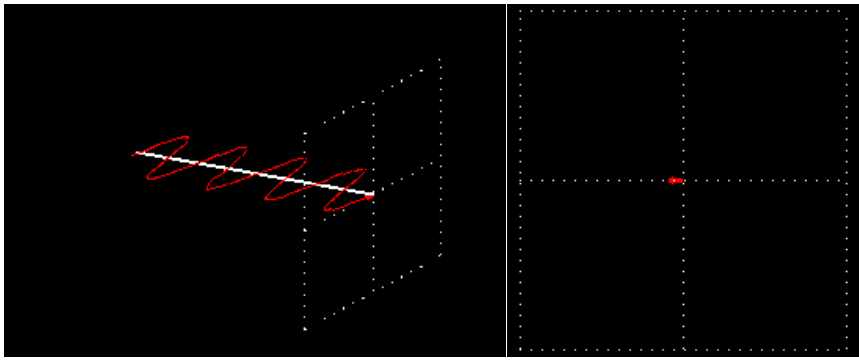
In thin film analysis:

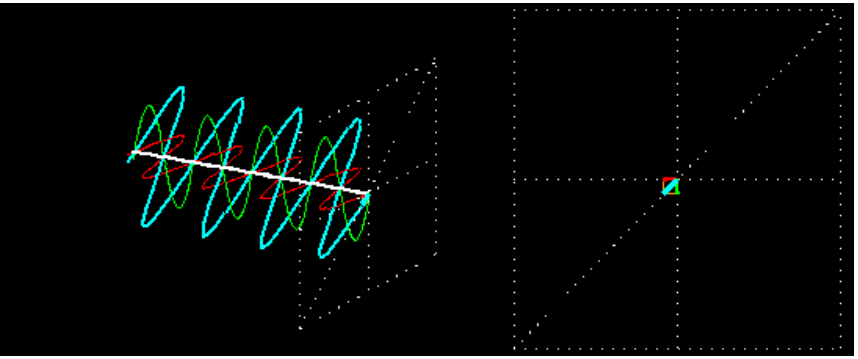
- film thickness
- Surface roughness
- optical properties (complex refractive index)
- material composition
- crystalline nature
- electrical conductivity

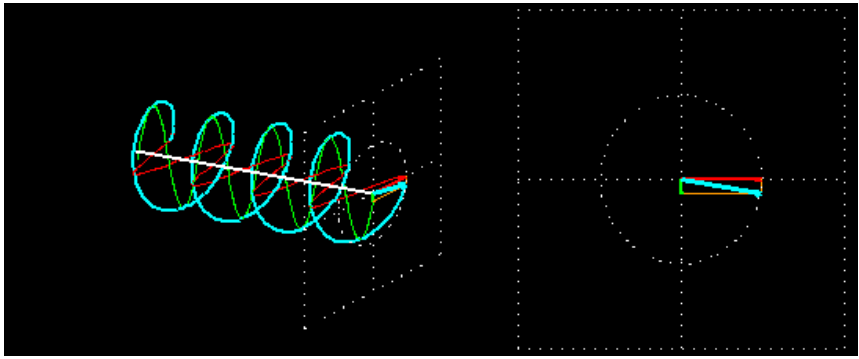


Ellipsometry – Polarization of Light







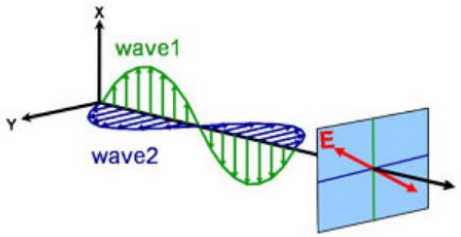


animations taken from http://cddemo.szialab.org/

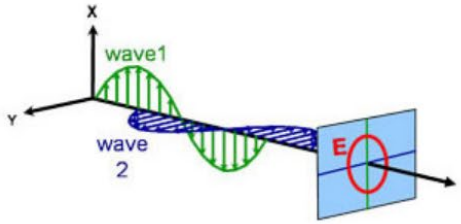
Ellipsometry – Polarization of Light

Orthogonal waves combined to demonstrate polarization:

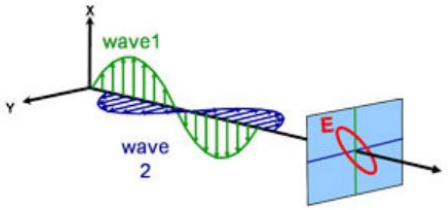
Linear

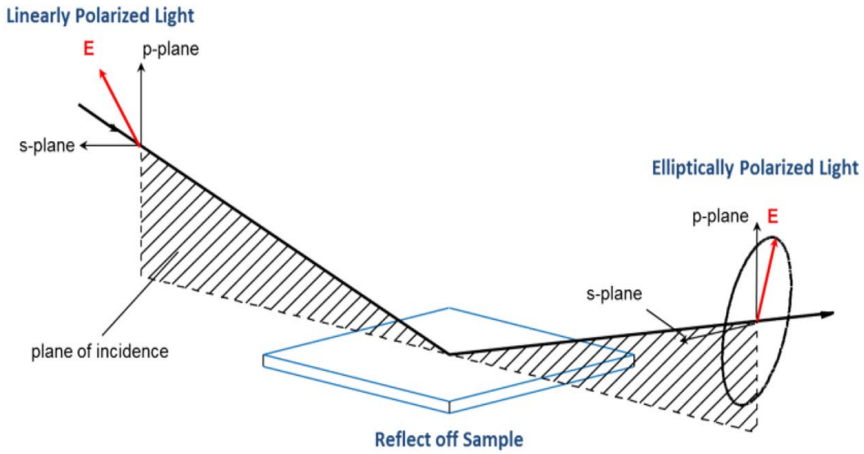


Circular



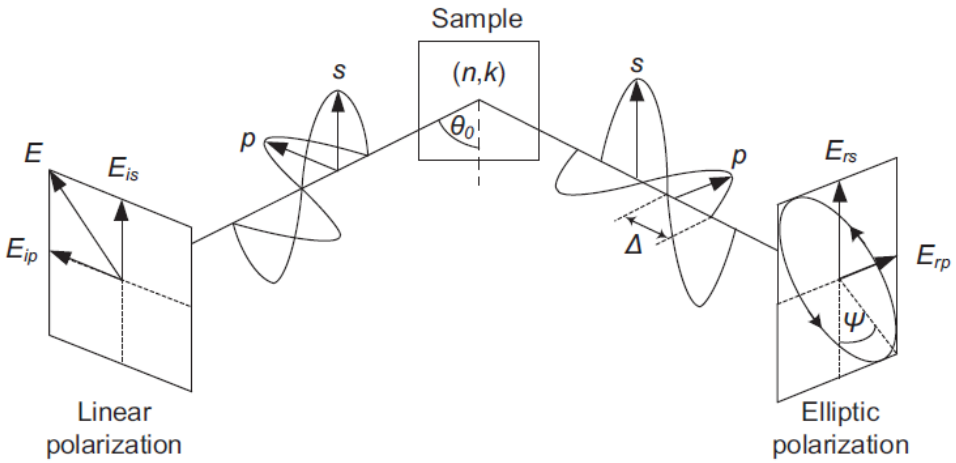
Elliptical





Interaction of Light and Matter

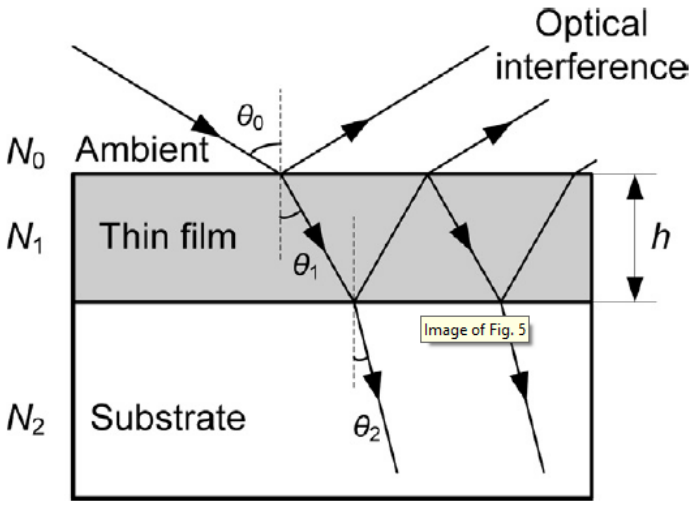
Polarized light interacts with sample upon reflection



The incident light is linear with both p- and s- components.
The reflected light has undergone amplitude and phase changes for both p- and s-polarized light and ellipsometry measures their changes

$$n_0 sin\theta_0 = n_1 sin\theta_1$$

n: refractive index



W. Ogieglo et al., *Progress in Polymer Science* **2015**, 42, 42
H. Fujiwara, I. Wiley, Spectroscopic ellipsometry principles and applications, John Wiley & Sons, **2007**
H. G. Tompkins and W. A. McGahan, Spectroscopic ellipsometry and reflectometry : a user's guide, **1999**

Interaction of Light and Matter

The change in polarization is the ellipsometry measurement,

commonly written as complex reflectance ratio

$$\rho = \frac{r_s}{r_p} = \tan\Psi * e^{i\Delta}$$

r_s *and* r_p: *amplitudes of s and p component, after reflection normalized to their initial value*

Ψ : *amplitude ratio upon reflection*

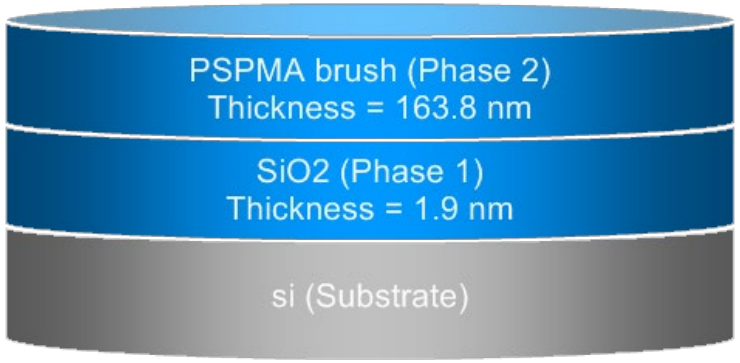
Δ : *phase shift*

The change of polarization upon reflection on the surface can be expressed in terms of the two angles Ψ and Δ, which is the typical outcome of an ellipsometric measurement, usually measured as a function of wavelength, angle of incidence or both.

Data Fitting

Structure of sample has to be known or needs to be assumed

most models are based on the assumption that the sample is composed of a small number of discrete, well-defined layers that are optically homogeneous and isotropic



The **complex reflectance ratio ρ** can be expressed in terms of n_i, k_i (complex refractive index) and d_i (thickness)

-> n_i and k_i are functions of the wavelength

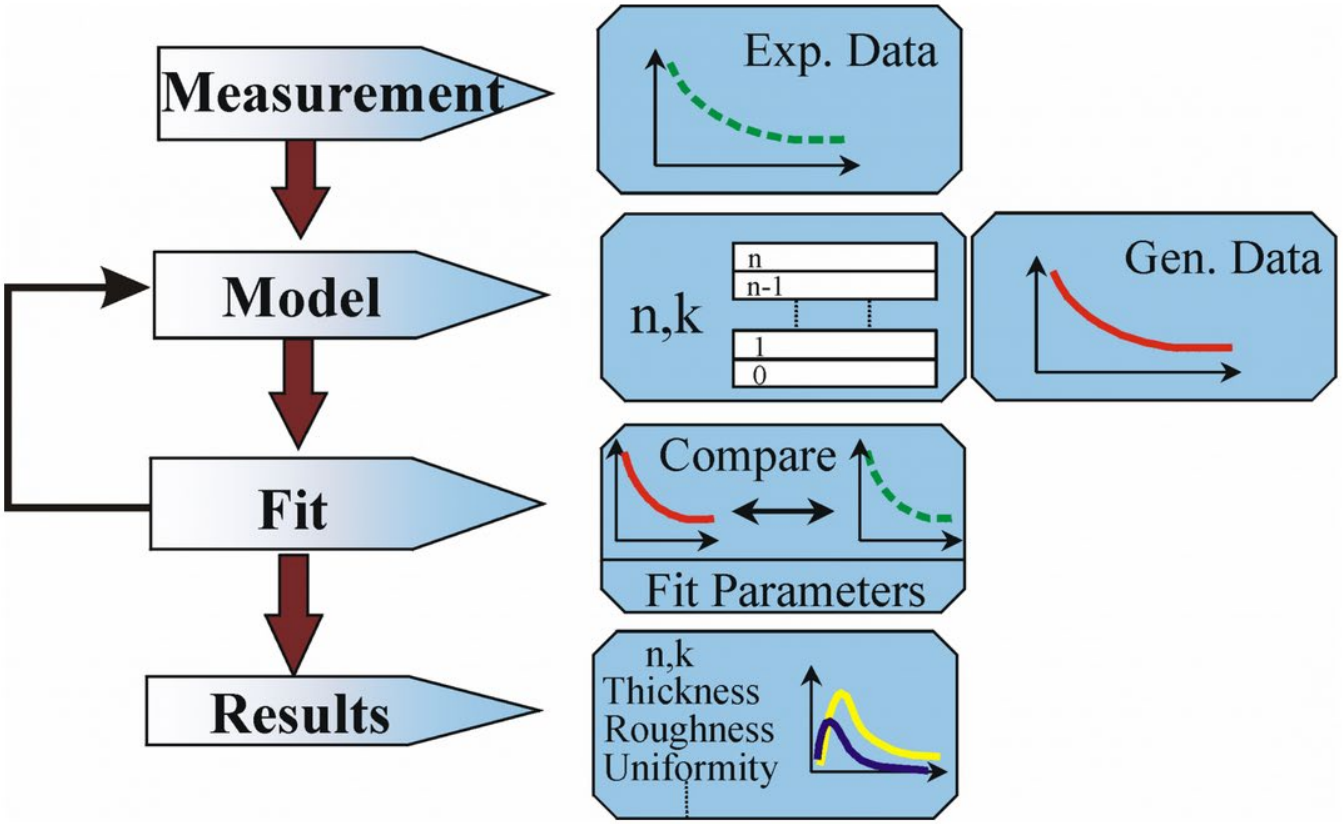
-> dispersion laws are mathematical functions modelling the optical properties of a material (e.g. *Cauchy's equation*)

-> ellipsometry software usually also provides a database with optical properties for a wide range of materials

Cauchy's equation

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \qquad k(\lambda) = D + \frac{E}{\lambda^2} + \frac{F}{\lambda^4}$$

Analysis Workflow

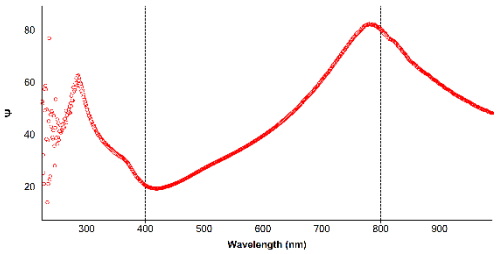


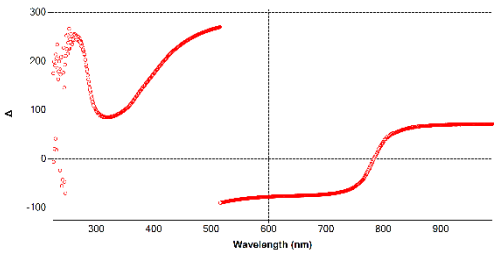
Flow chart for ellipsometry data analysis.

Analysis Workflow

Measurement

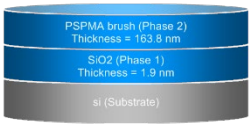
Poly(3-Sulfopropyl methacrylate) brush on silicon wafer

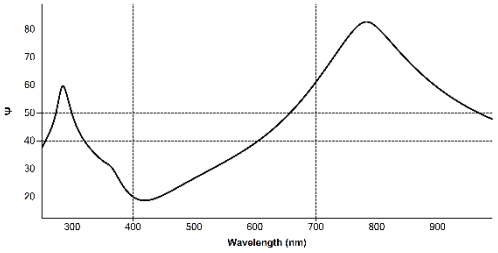


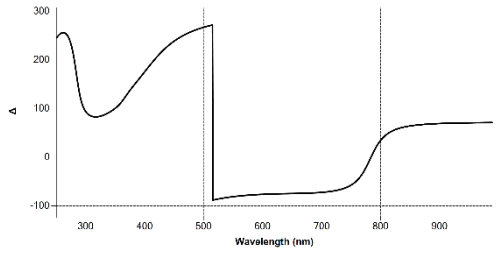


Simulation based on model

- structure
- thickness of layers *d*
- material's *n*, *k*
- composition



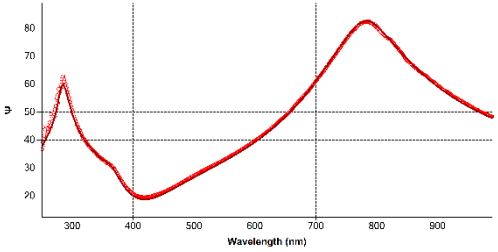


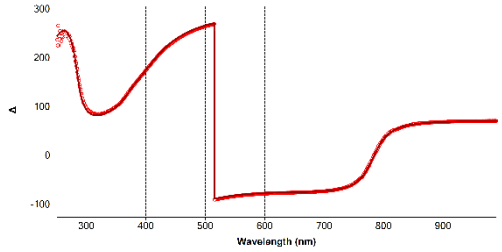


Experimental measurement

=

Simulation?





d_i, n_i, k_i