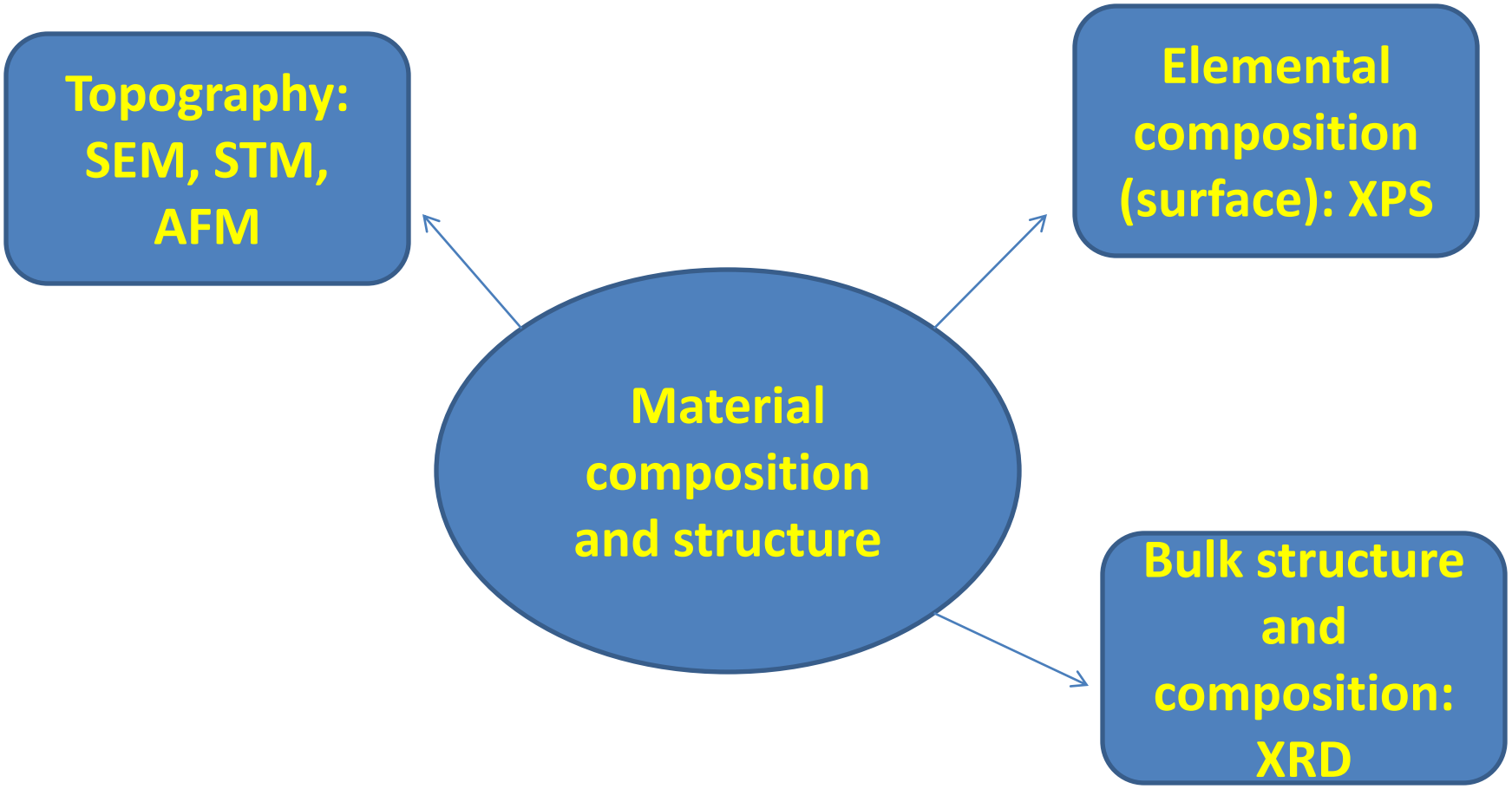
Material Characterization

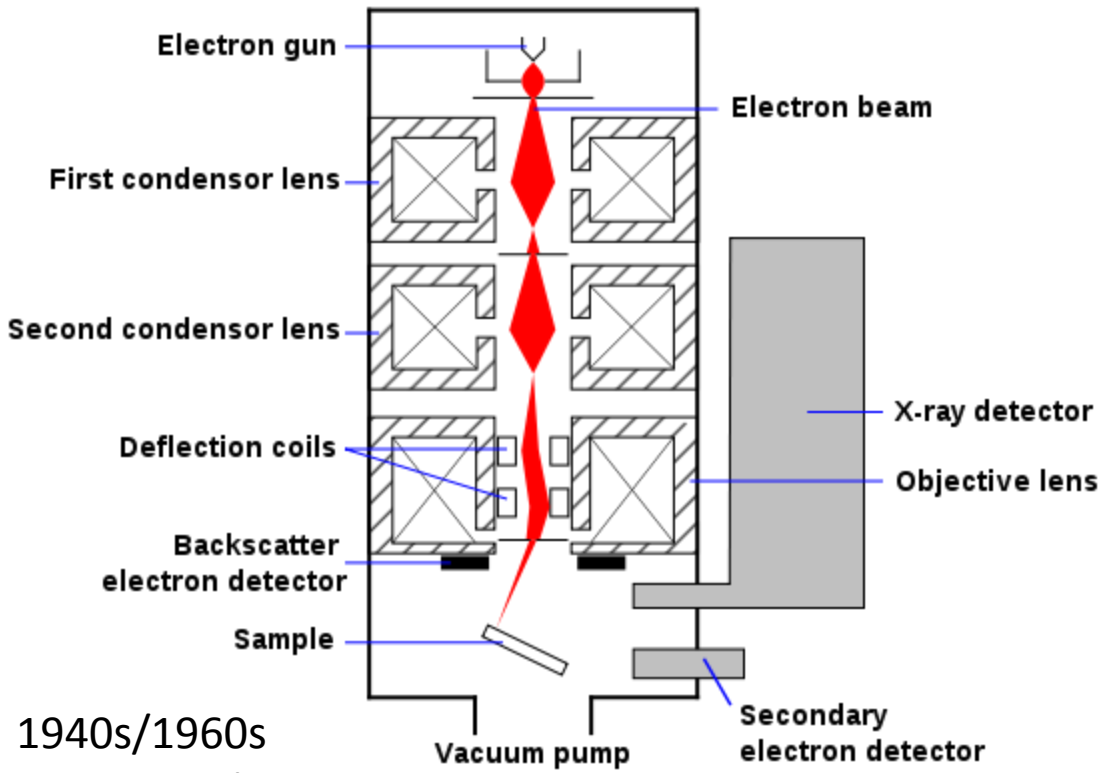
Chapter 21 pp. 589-602, 607-622

Information needed about the structure and composition (surface and bulk) of materials: *microscopic* and *nanoscopic* domains!

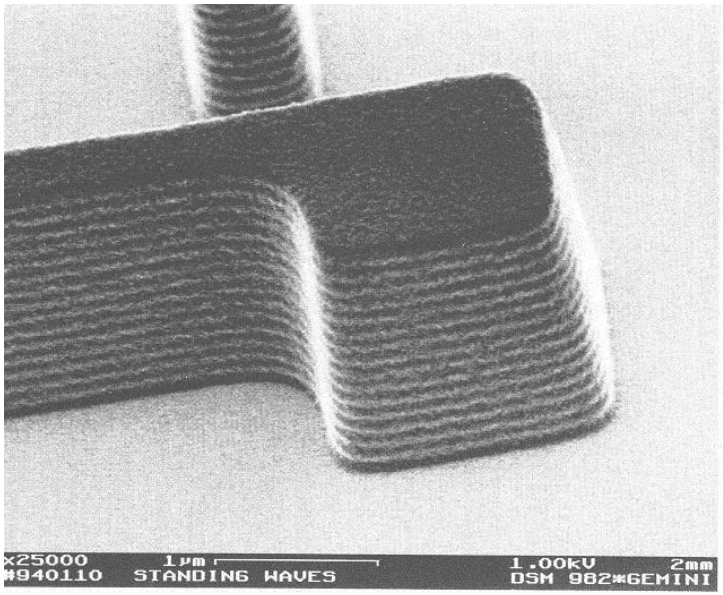


Scanning Electron Microscopy

The **scanning electron microscope** (**SEM**) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity.

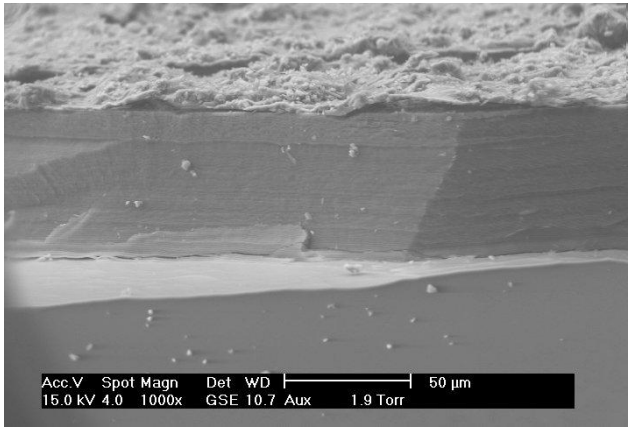


1940s/1960s commercial

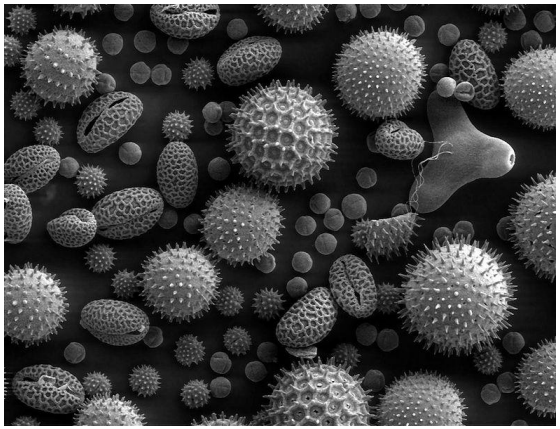


Photoresist layer on Si.

Scanning Electron Microscopy



Metal corrosion layer

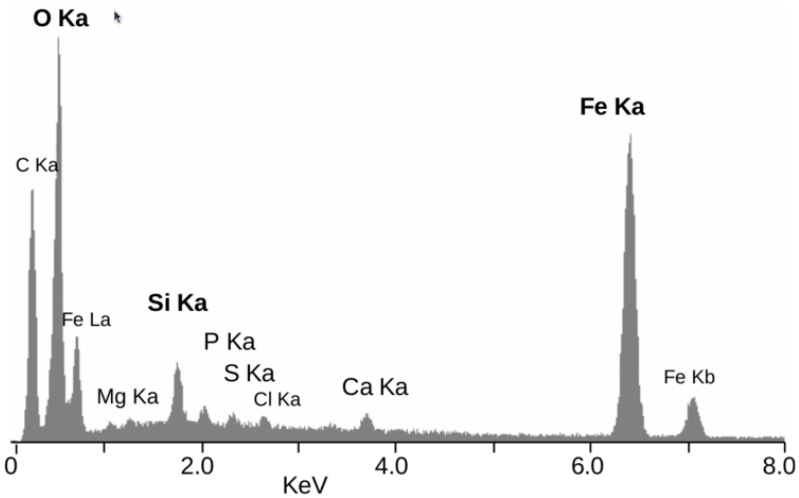


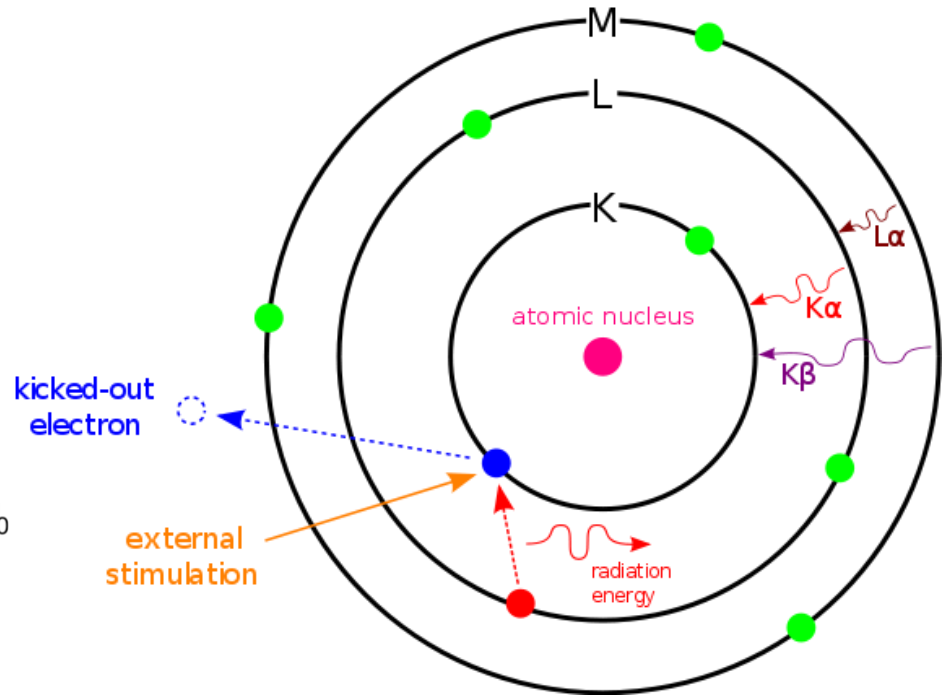
Pollen

Deer tick

Three different imaging modes: <u>secondary electrons</u> (low energy electrons from the surface of the material), <u>backscattered electrons</u> (more from bulk) and <u>x-rays</u> (from near-surface region).

SEM – X-ray Analysis

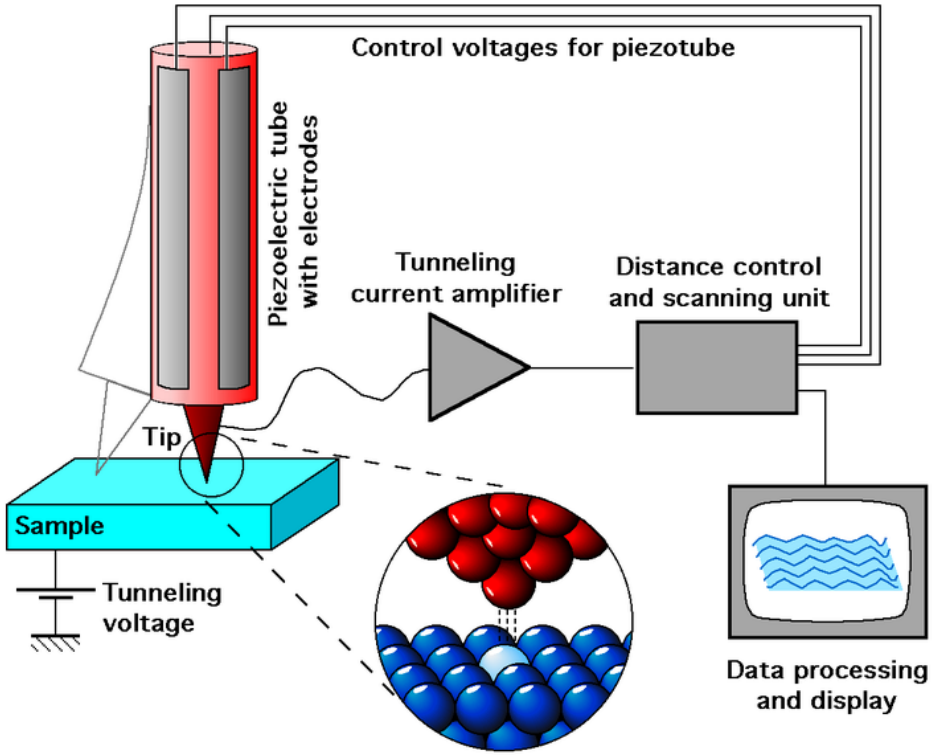


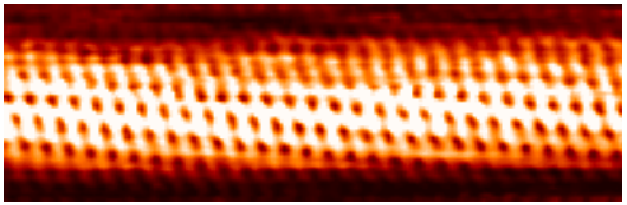


X-ray analysis provides both qualitative (elemental analysis) and quantitative (atomic percent) information about a solid sample. The information content relates to the surface and near-surface region.

Scanning Tunneling Microscopy

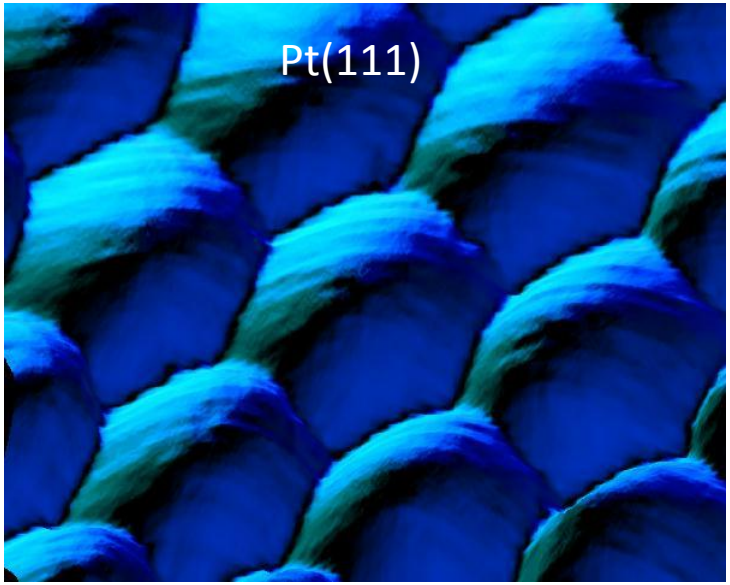
A **scanning tunneling microscope** (STM) is a powerful instrument for imaging surfaces at the atomic level. Its development in 1981 earned its inventors, Gerd Binnig and Heinrich Rohrer (at IBM Zürich), the Nobel Prize in Physics in 1986. For an STM, good resolution is considered to be 0.1 nm lateral resolution and 0.01 nm depth resolution. With this resolution, individual atoms within materials are routinely imaged and manipulated. The STM can be used not only in ultra high vacuum but also in air, water, and various other liquid or gas ambients.

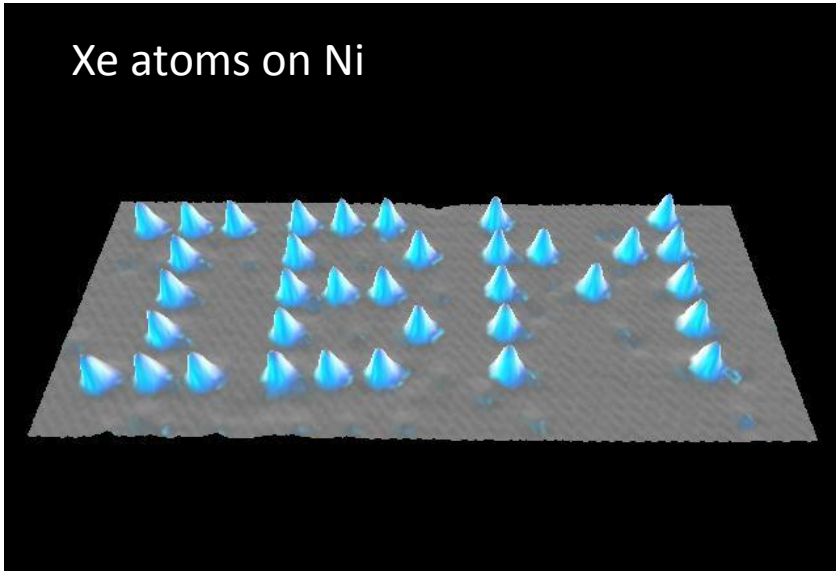




Scanning Tunneling Microscopy

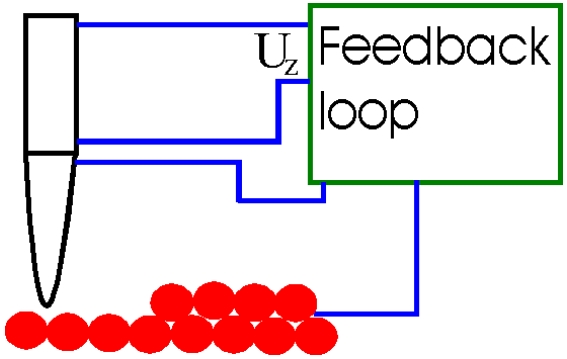
The STM is based on the concept of quantum tunneling. When a conducting tip is brought very near to the surface to be examined, a bias (voltage difference) applied between the two can allow electrons to tunnel through the vacuum between them. The resulting *tunneling current* is a function of tip position, applied voltage, and the local density of states (LDOS) of the sample.[4] Information is acquired by monitoring the current as the tip's position scans across the surface, and is usually displayed in image form. STM can be a challenging technique, as it requires extremely clean and stable surfaces, sharp tips, excellent vibration control, and sophisticated electronics.



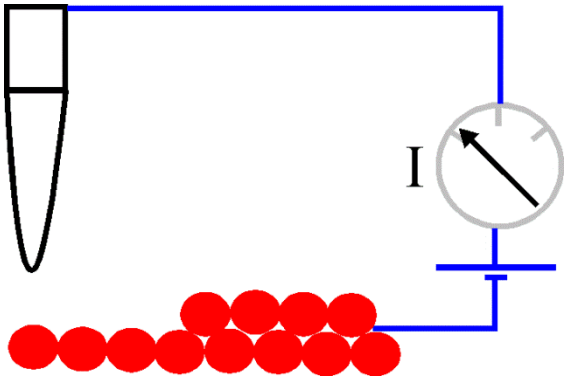


STM – Modes of Operation

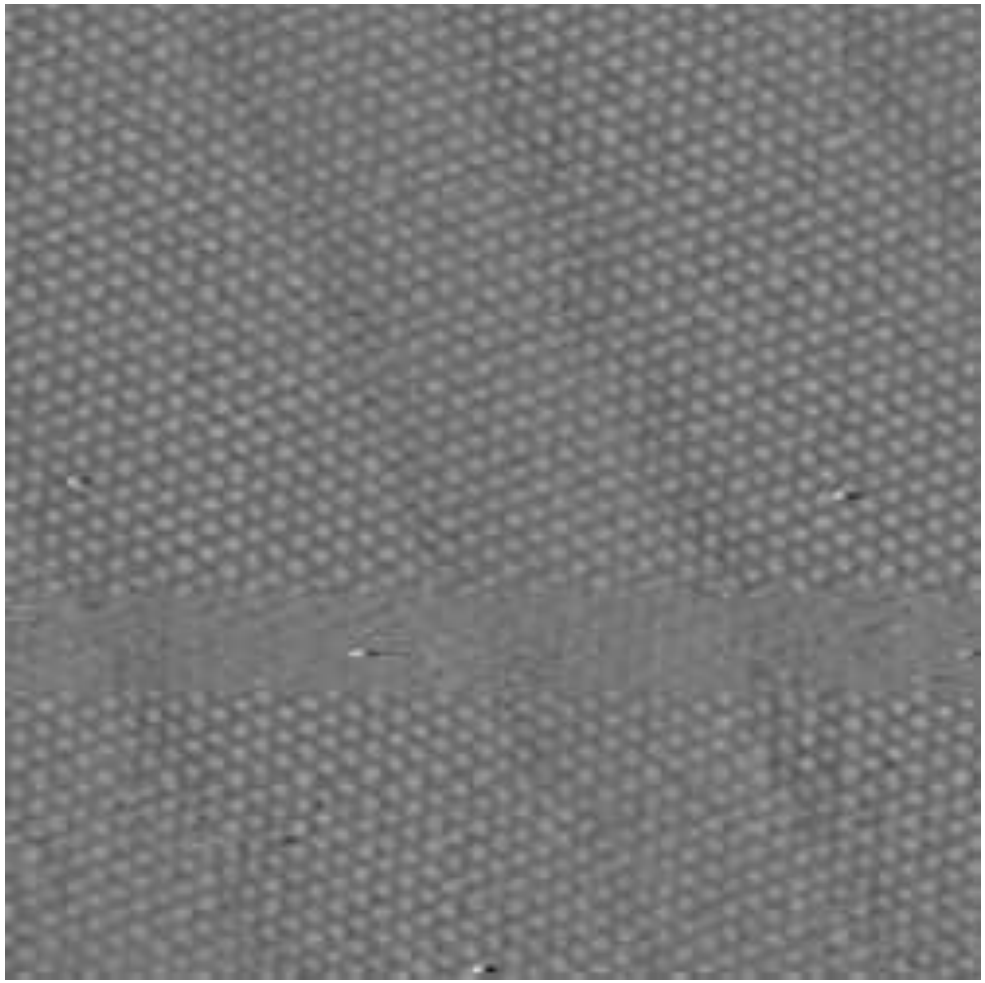
Constant Height Mode = By using a feedback loop the tip is vertically adjusted in such a way that the current always stays constant. As the current is proportional to the local density of states, the tip follows a contour of a constant density of states during scanning. A kind of a topographic image of the surface is generated by recording the vertical position of the tip.



Constant Current Mode = In this mode the vertical position of the tip is not changed, equivalent to a slow or disabled feedback. The current as a function of lateral position represents the surface image. This mode is only appropriate for atomically flat surfaces as otherwise a tip crash would be inevitable. One of its advantages is that it can be used at high scanning frequencies (up to 10 kHz).

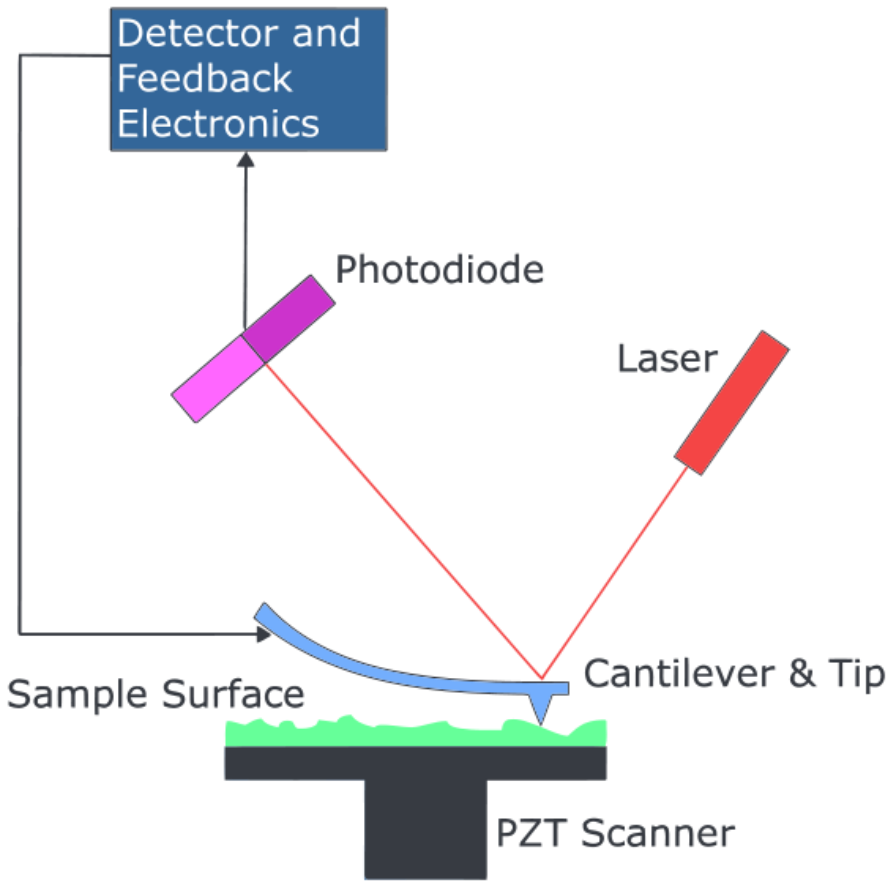


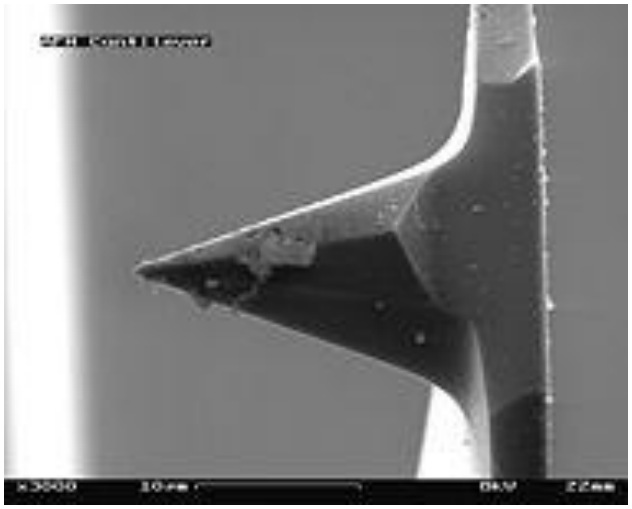
Atomic Image of Au(111)



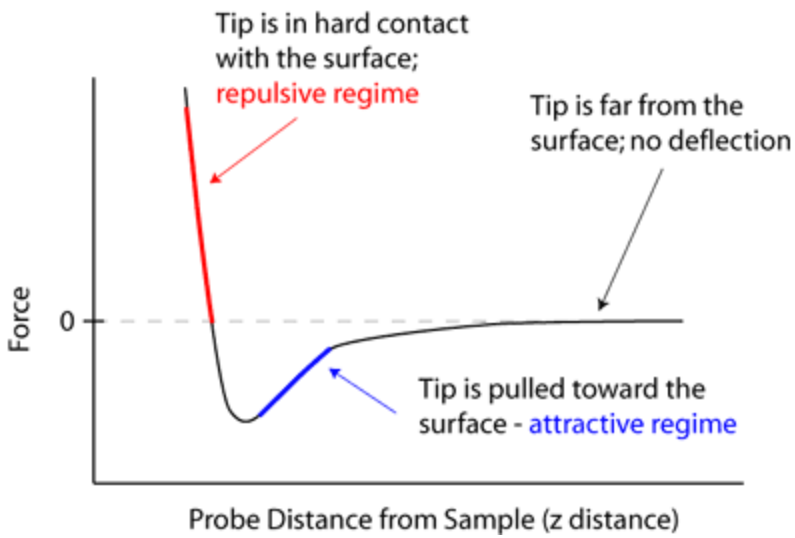
Atomic Force Microscopy (AFM)

Atomic or near-atomic resolution images of topography of conductors, semiconductors and insulators.

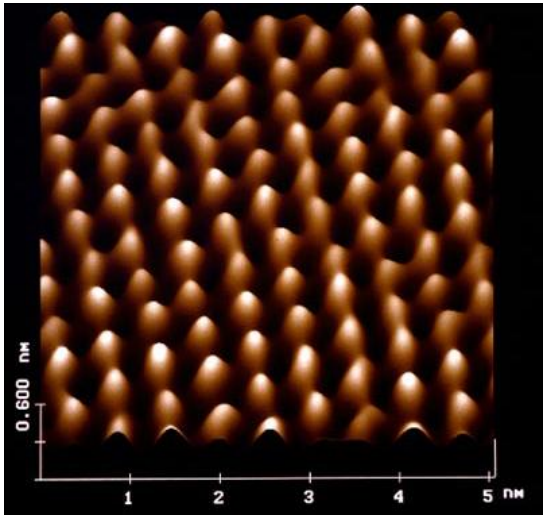




Atomic Force Microscopy



A.



B.

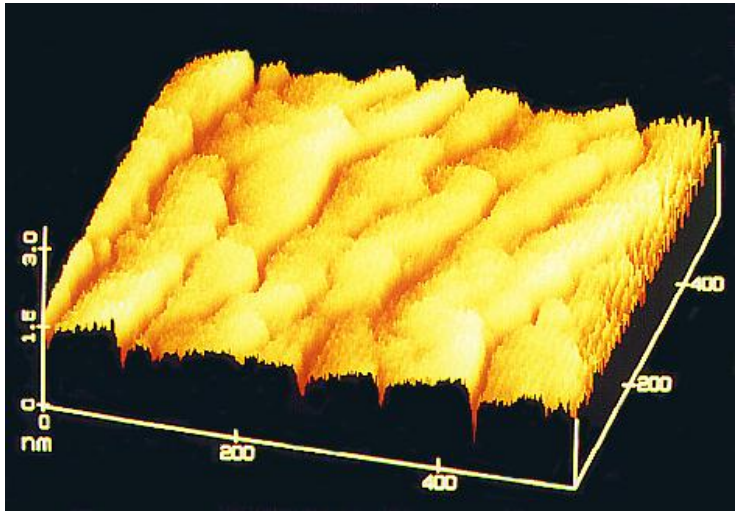
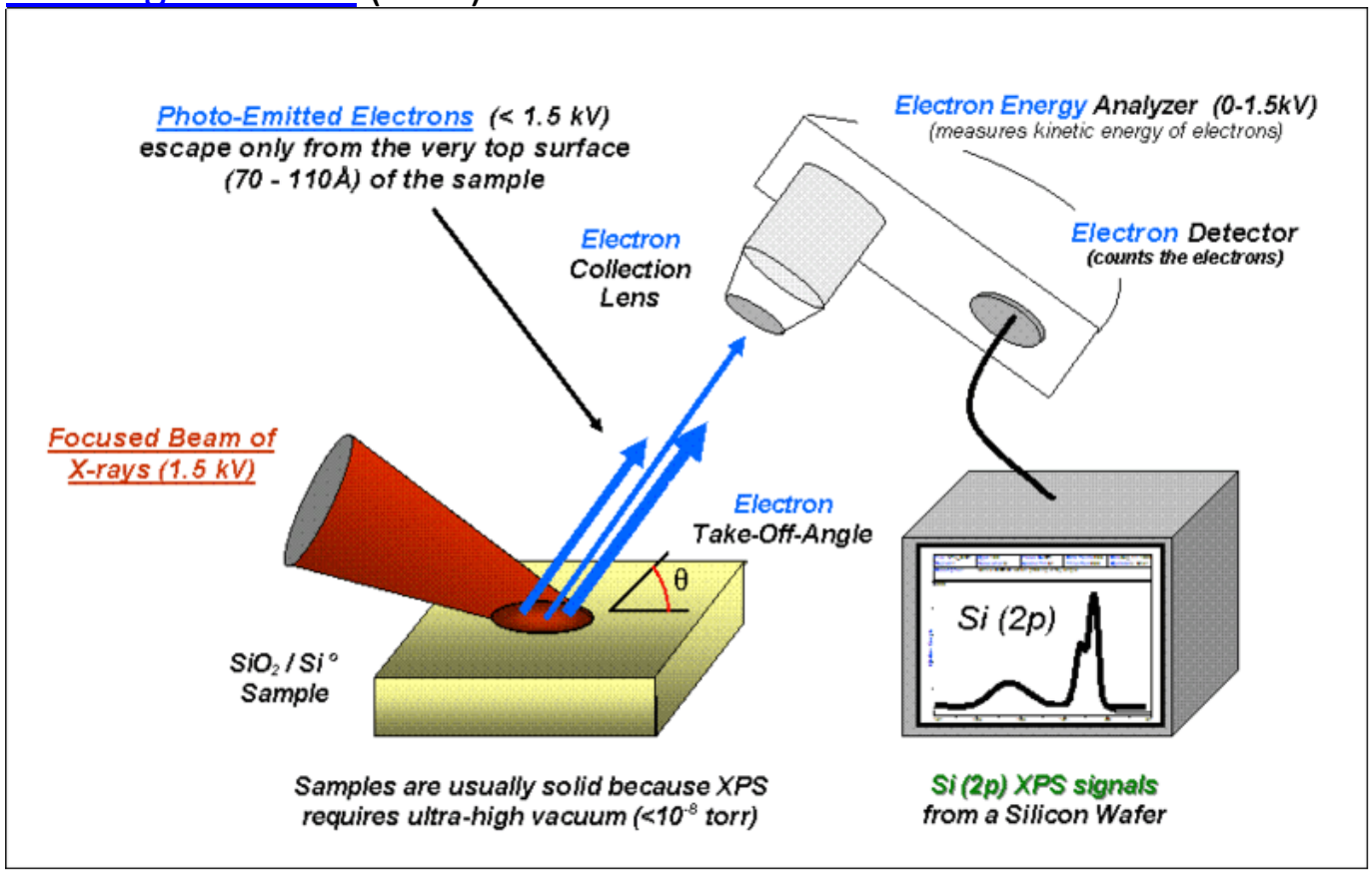


FIGURE 3. IMAGES GENERATED USING CONTACT MODE AFM. (A) A 5nm SCAN ATOMIC SCALE IMAGE SHOWING SURFACE ATOMS ON FRESHLY CLEAVED MICA. IMAGE (A) WAS TAKEN WITH A NANOSCOPE SPM (COURTESY DIGITAL INSTRUMENTS, SANTA BARBARA, CA), AND (B) AN IMAGE OF BOVINE BONE OBTAINED IN THE WET CELL.

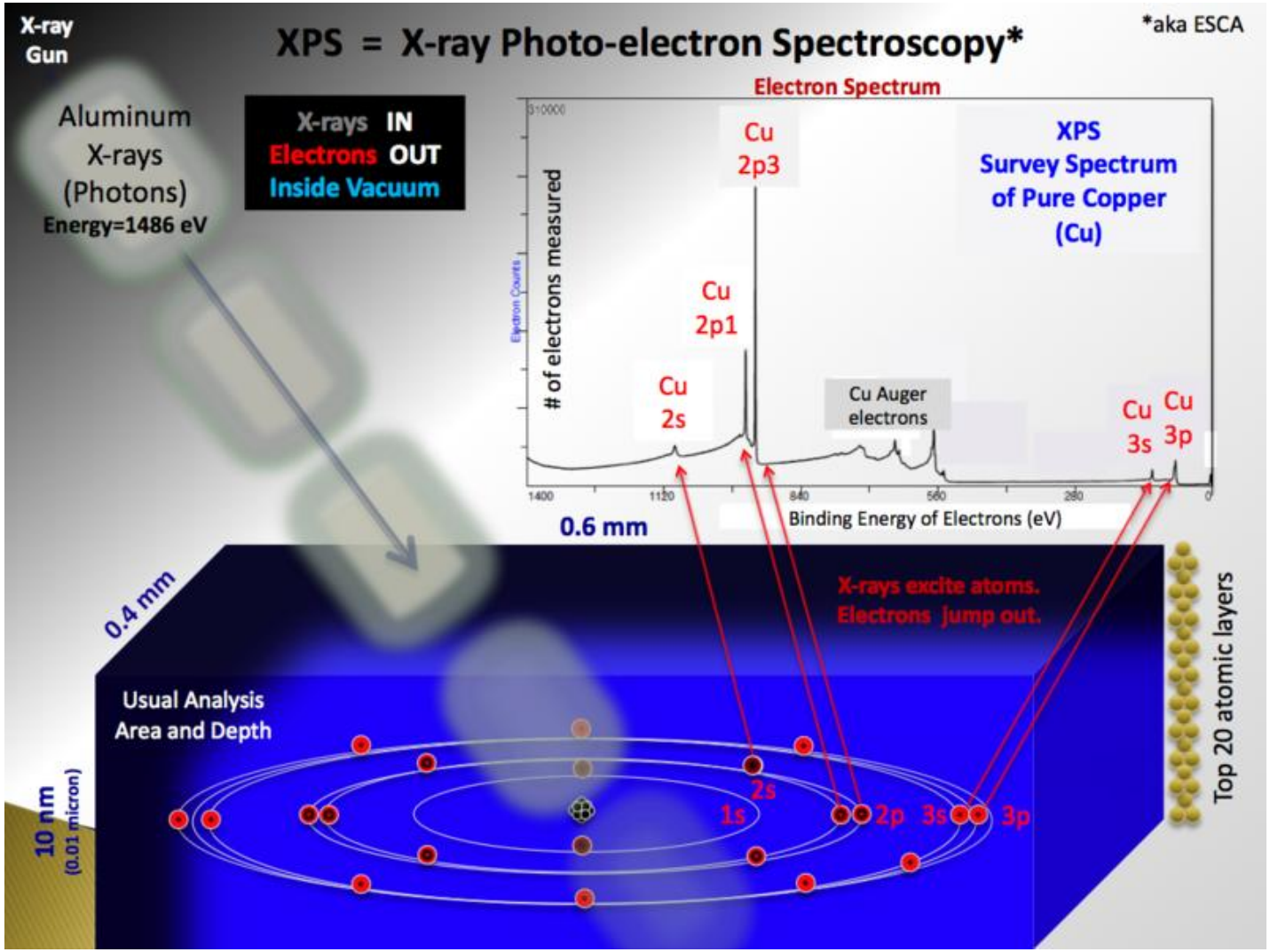
http://chemeducator.org/sbibs/s0001005/spapers/15bla897.pdf

X-ray Photoelectron Spectroscopy (XPS)

X-ray **photoelectron** **spectroscopy** (XPS) is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. XPS requires ultra high vacuum (UHV) conditions.



X-ray Photoelectron Spectroscopy (XPS)



X-ray Photoelectron Spectroscopy (XPS)

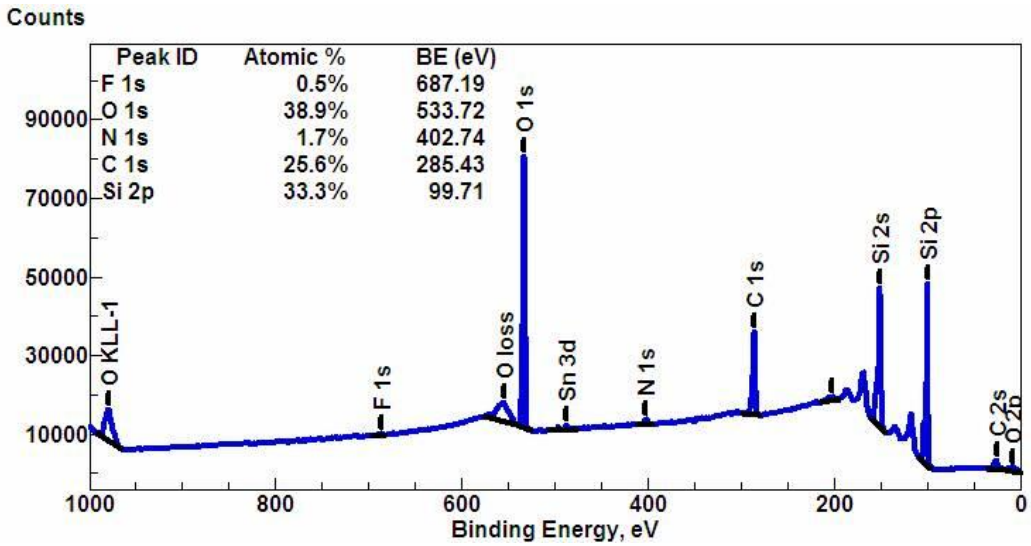
XPS is a surface chemical analysis technique that can be used to analyze the surface chemistry of a material in its "as received" state, or after some treatment

- XPS detects all elements with an atomic number (Z) of 3 (lithium) and above. It cannot detect hydrogen (Z = 1) or helium (Z = 2) because the diameter of these orbitals is so small, reducing the catch probability to almost zero.
- Detection limits for most of the elements are in the parts per thousand (ppt) (0.1%) range. Detections limits of parts per million (ppm) (0.0001%) are possible, but require special conditions: concentration at top surface or very long collection time (overnight).
- XPS is routinely used to analyze inorganic compounds, metal alloys, semiconductors, polymers, elements, catalysts, glasses, ceramics, paints, papers, inks, woods, plant parts, make-up, teeth, bones, medical implants, bio-materials, viscous oils, glues, ion modified materials and many others

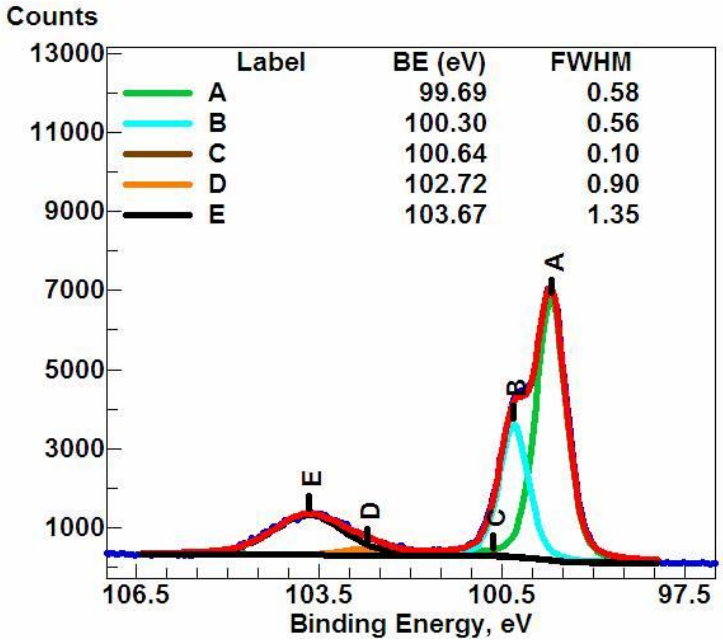
X-ray Photoelectron Spectroscopy (XPS)

$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi)$$

where E_{binding} is the binding energy (BE) of the electron, E_{photon} is the energy of the X-ray photons being used, E_{kinetic} is the kinetic energy of the electron as measured by the instrument and φ is the work function of the spectrometer (not the material).



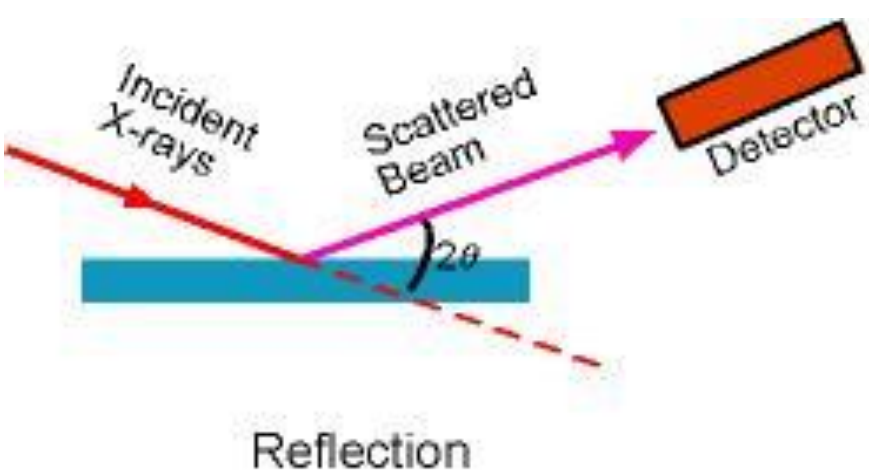
Survey Scan

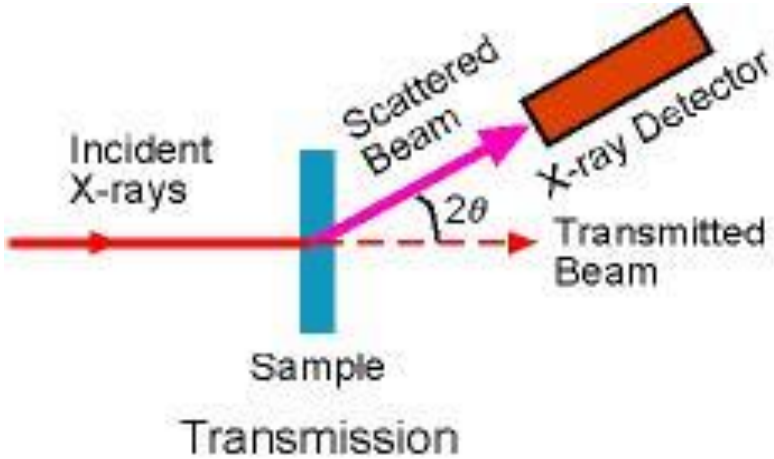


Si 2p region

X-ray Diffraction (XRD)

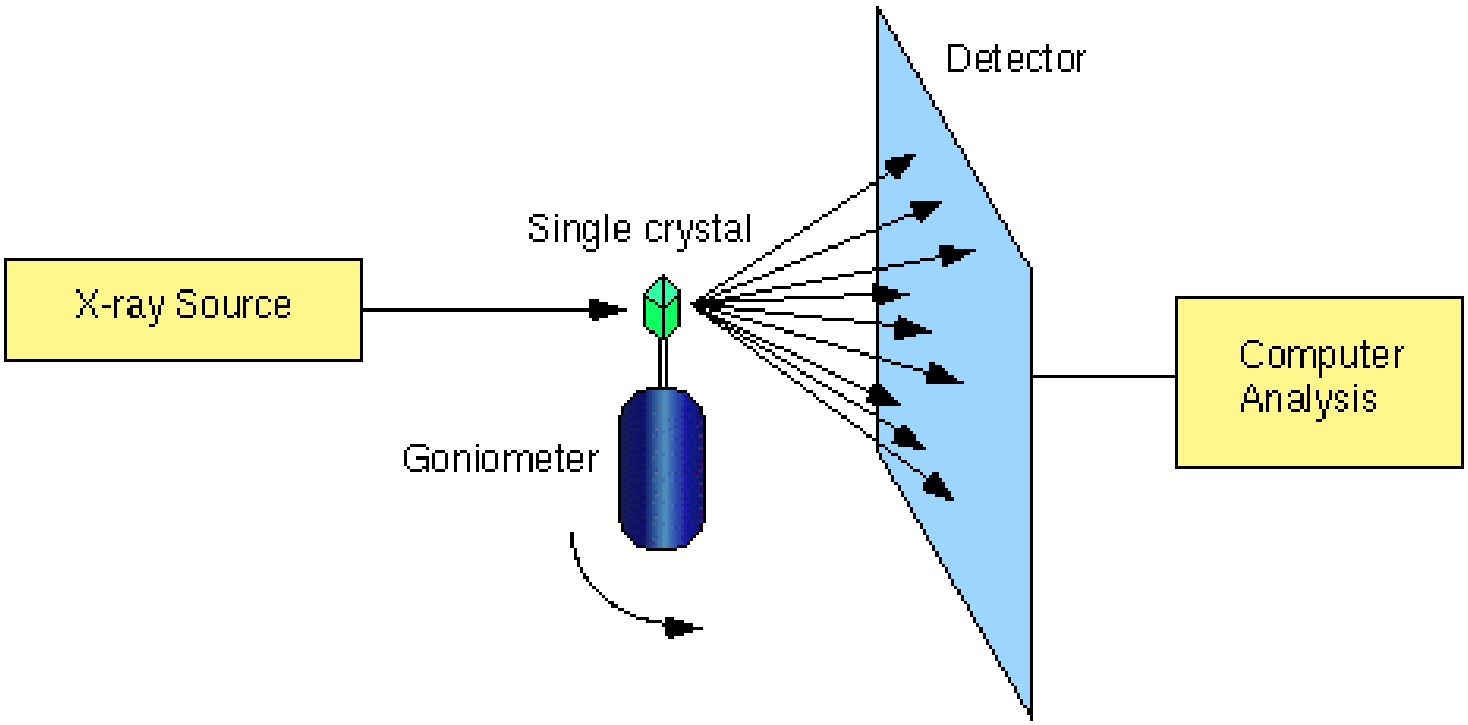
Powder XRD (X-ray Diffraction) is perhaps the most widely used x-ray diffraction technique for characterizing materials. As the name suggests, the sample is usually in a powdery form, consisting of fine grains of single crystalline material to be studied. The technique is used also widely for studying particles in liquid suspensions or polycrystalline solids (bulk or thin film materials).





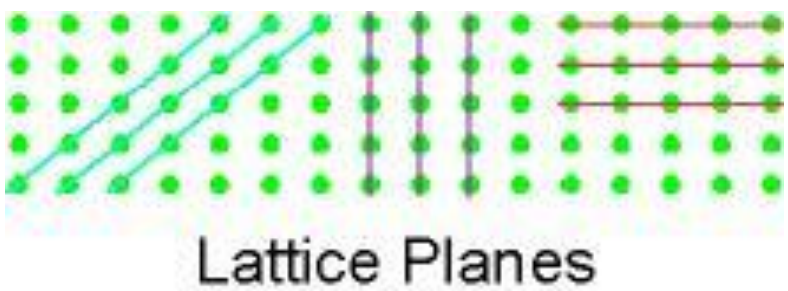
http://www.mrl.ucsb.edu/mrl/centralfacilities/xray/xray-basics/index.html#x2

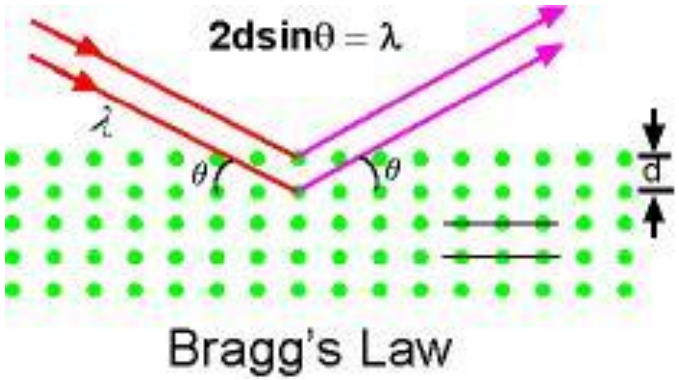
X-ray Diffraction (XRD)



X-ray Diffraction (XRD)

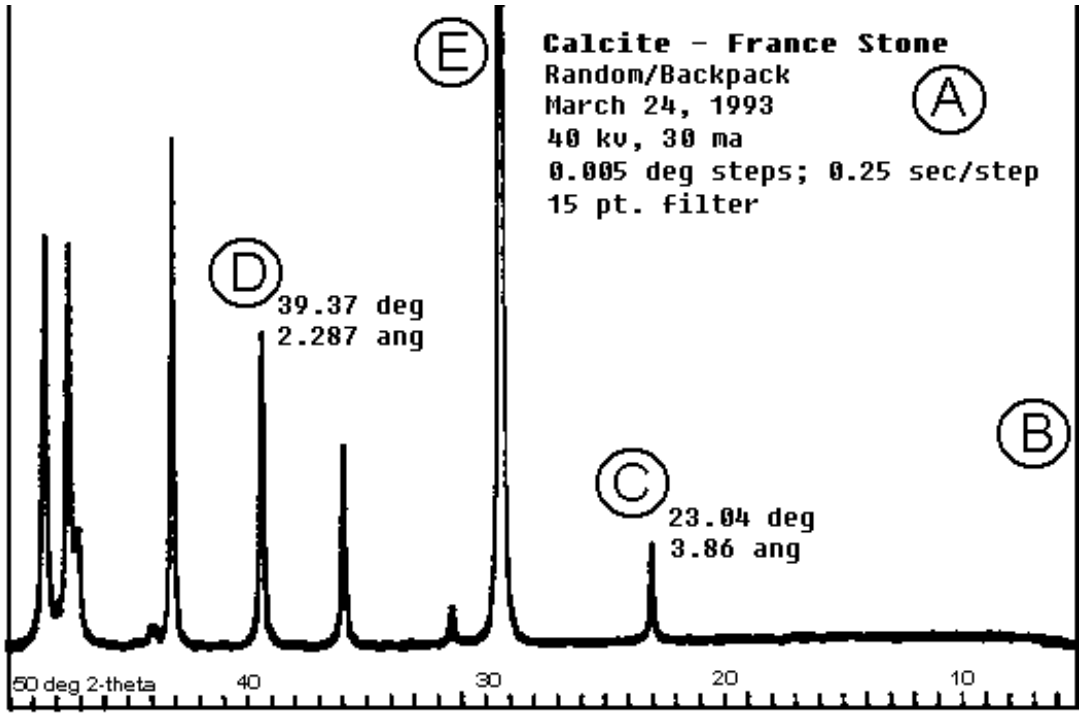
The peaks in a x-ray diffraction pattern are directly related to the atomic distances. Let us consider an incident x-ray beam interacting with the atoms arranged in a periodic manner as shown in 2 dimensions in the following illustrations. The atoms, represented as green spheres in the graph, can be viewed as forming different sets of planes in the crystal (colored lines in graph on left). For a given set of lattice planes with an inter-plane distance of d, the condition for a diffraction (peak) to occur can be simply written as





which is known as the Bragg's law, after W.L. Bragg, who first proposed it. In the equation, λ is the wavelength of the x-ray, θ the scattering angle, and n an integer representing the order of the diffraction peak. The Bragg's Law is one of most important laws used for interpreting x-ray diffraction data.

X-ray Diffraction (XRD)



Bragg's Law refers to the simple equation:

$$n\lambda = 2d \sin\Theta$$

derived by the English physicists Sir W.H. Bragg and his son Sir W.L. Bragg in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence (Θ, λ). The variable *d* is the distance between atomic layers in a crystal, and the variable lambda is the **wavelength** of the incident X-ray beam (see applet); n is an integer.