- Web ref. for surface lecture notes
- Foord group
  http://www.chem.ox.ac.uk/researchguide/jsfoord.html
- Click on “group web pages” and “teaching”

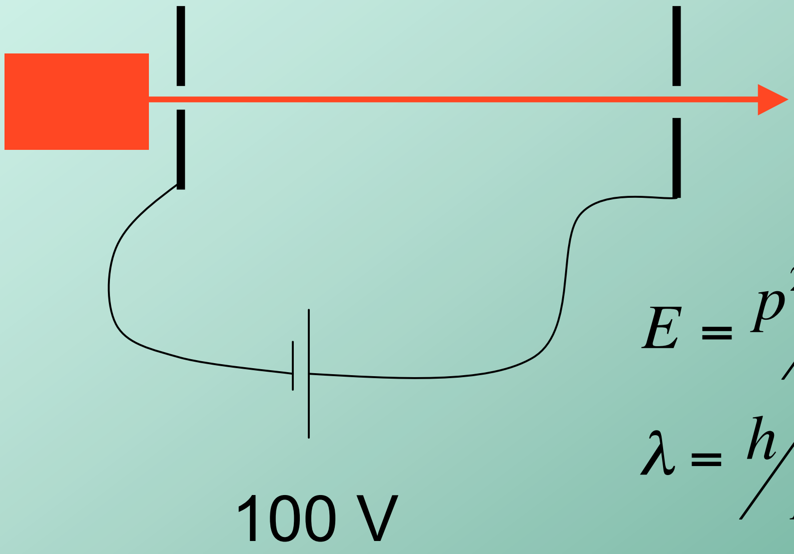
Surface Structure Determination

- Conventional XRD of little use since measures “bulk” properties

- Two particularly important surface structural probes
  - Low energy electron diffraction (LEED)
  - Scanning tunneling microscopy (STM)

LEED

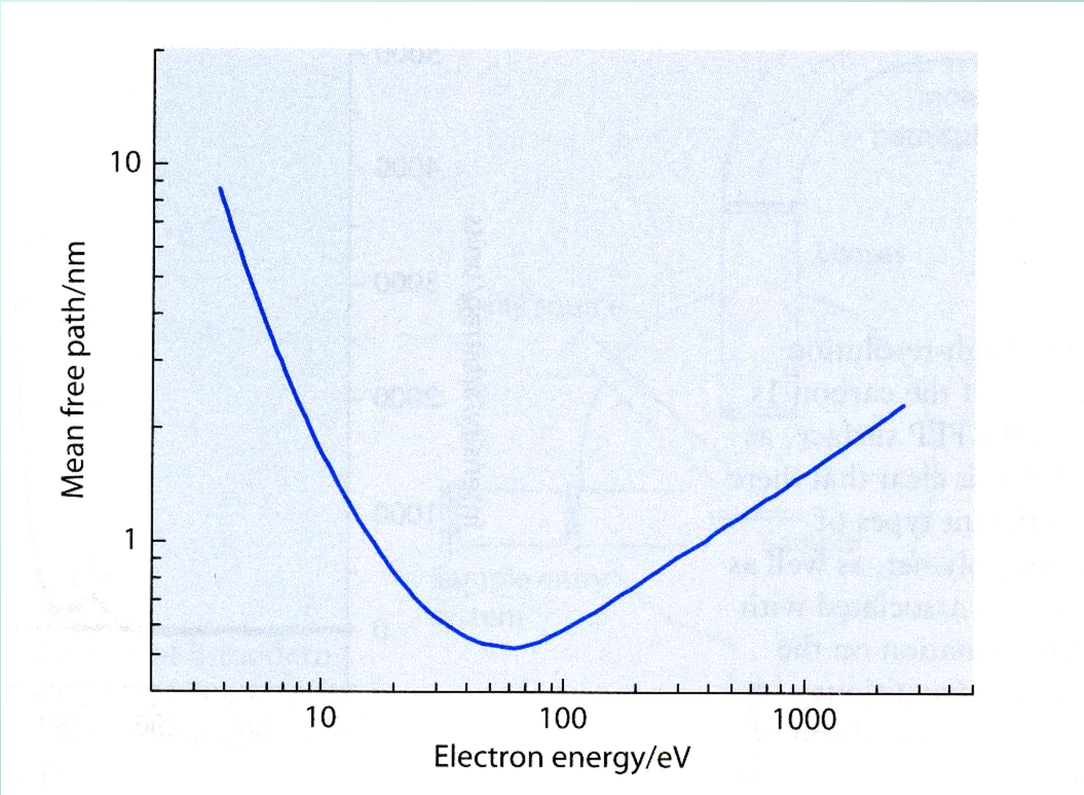
- Consider a beam of low energy electrons formed by acceleration through a voltage V, < 100 V

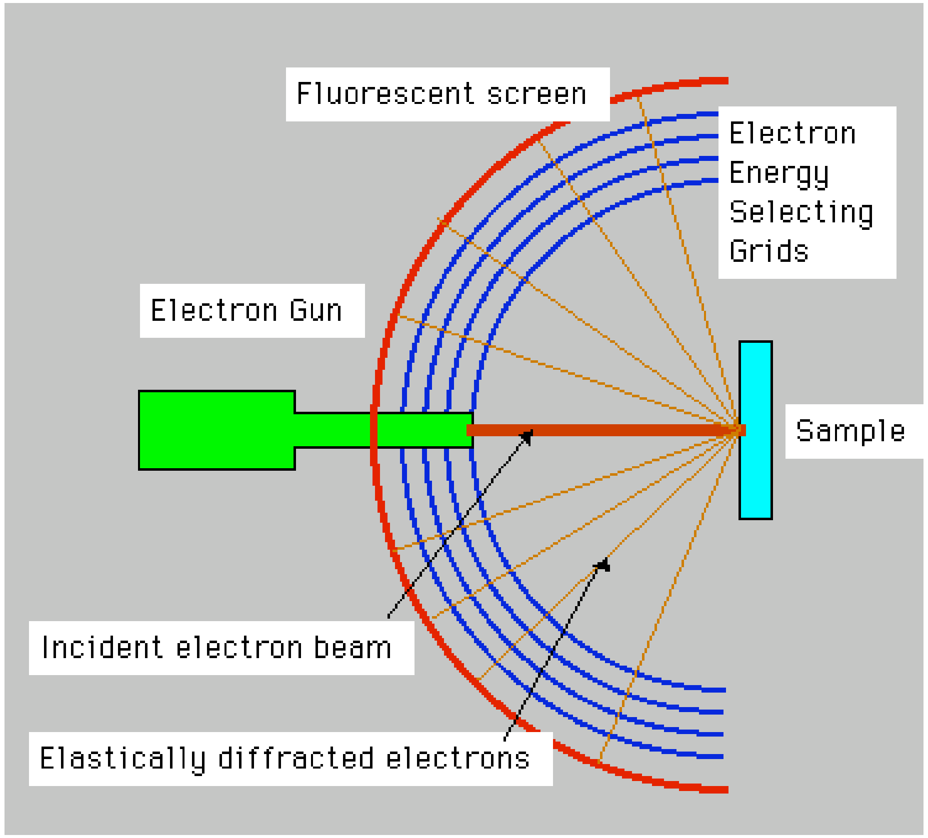


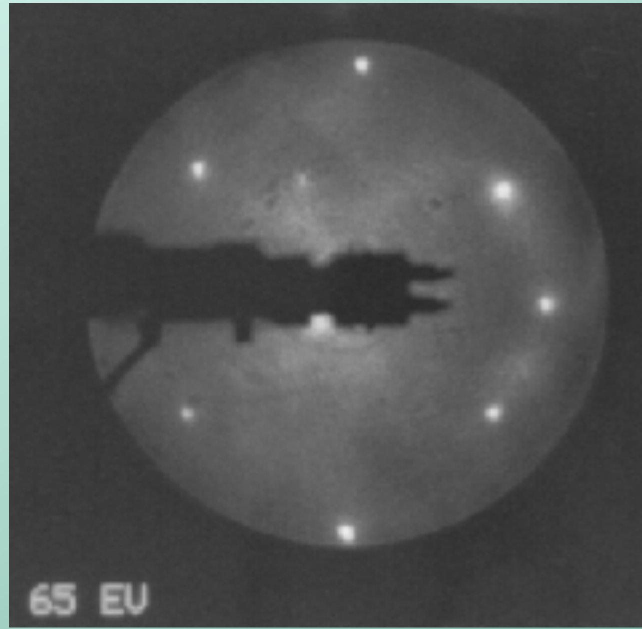
$$E = \frac{p^2}{2m} = eV \Rightarrow p = \sqrt{2meV}$$

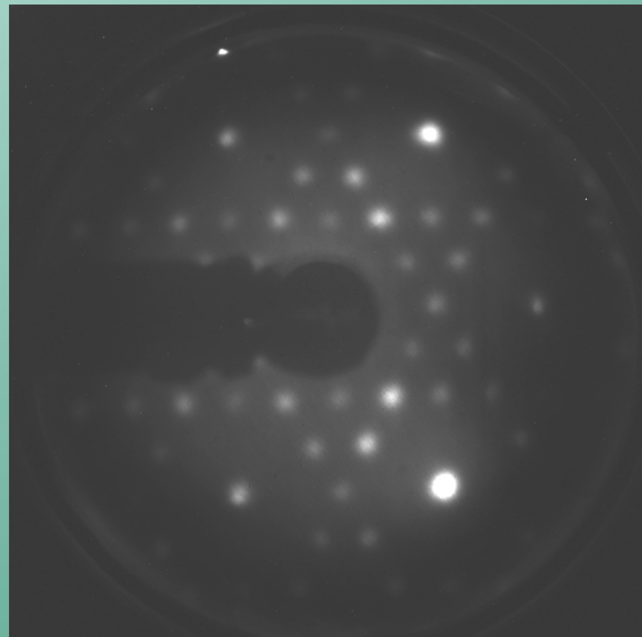
$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2meV}} \approx \textit{atomic separations}$$

- The elastic mean free path of slow electrons in solids is only a few atomic layers, so elastic electrons remain near the surface.





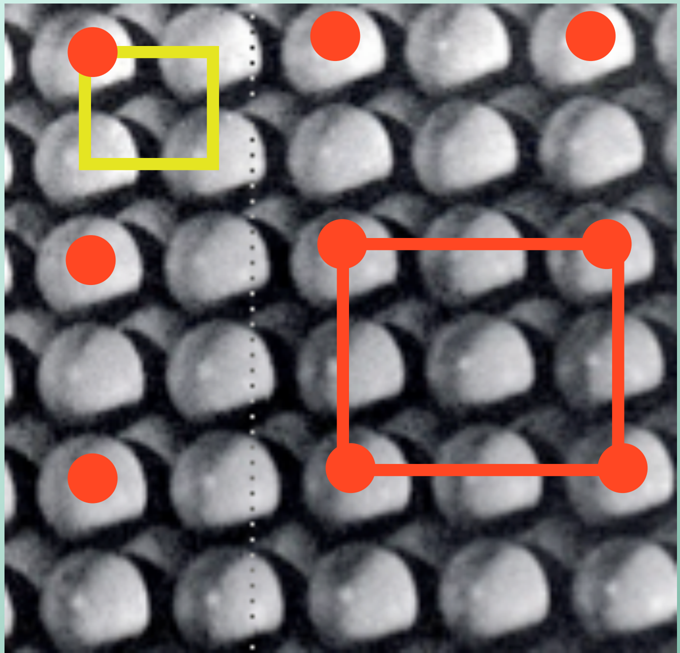




- Low energy electrons impinge on single crystal surface in vacuum
- Elastically backscattered diffracted beams are produced and imaged on phosphor-coated screen

Information obtained

- Spot positions yield the dimensions of the surface unit cell from a clean atomically ordered surface…..



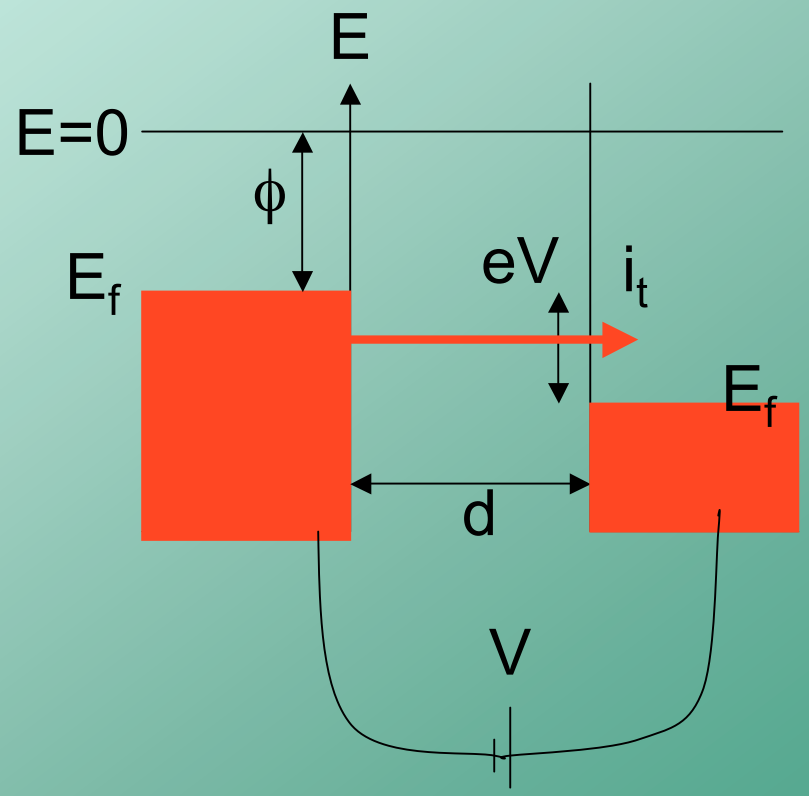
As well as that describing the spatial distribution of the adsorbates if they are present and distributed over the sites in an ordered manner

- Spot intensity analysis can be used to determine atoms and their positions within the unit cell e.g. molecular structure of the adsorbate (cf XRD)

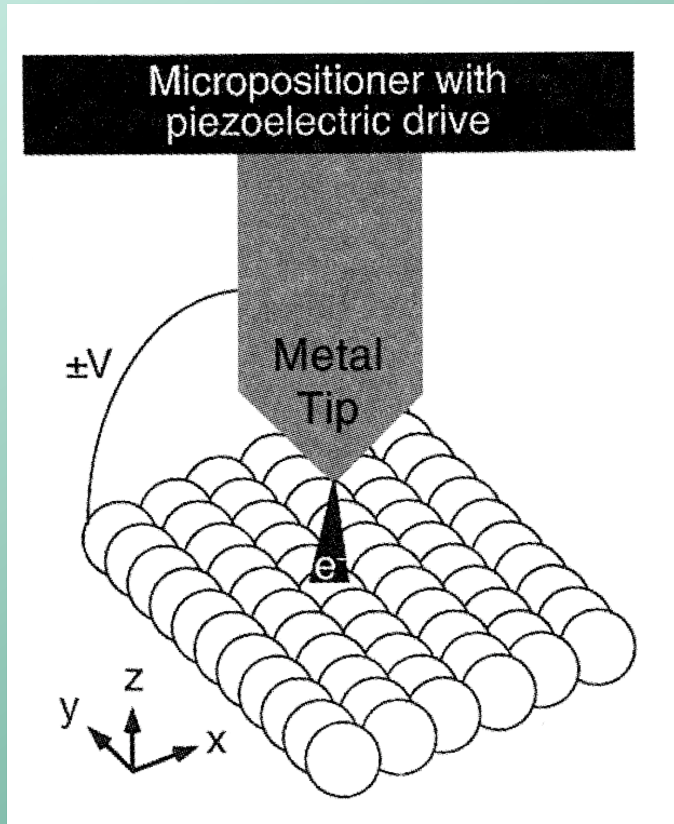
- However scattering of slow electrons is more complicated than X-rays, making analysis more complicated, and reducing complexity in structures which can be analysed.

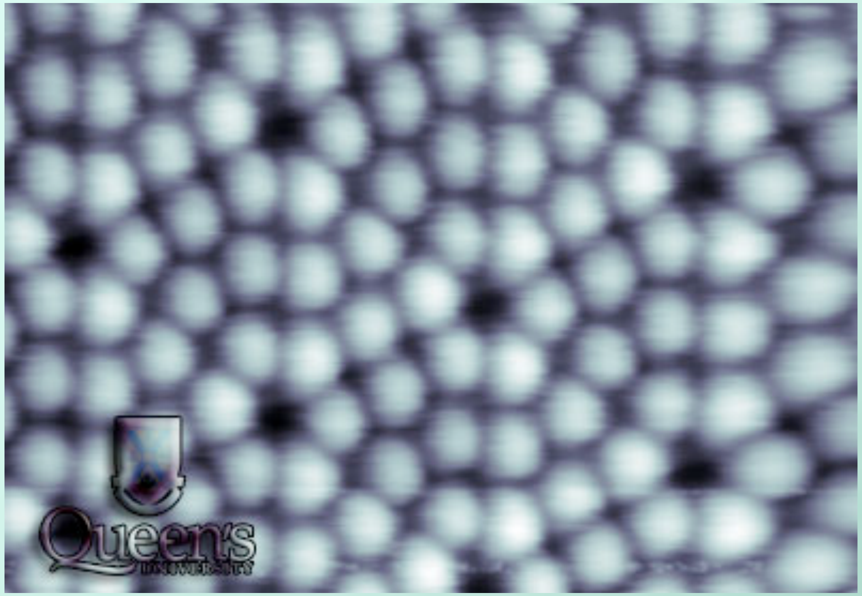
Scanning Tunneling Microscopy (STM)

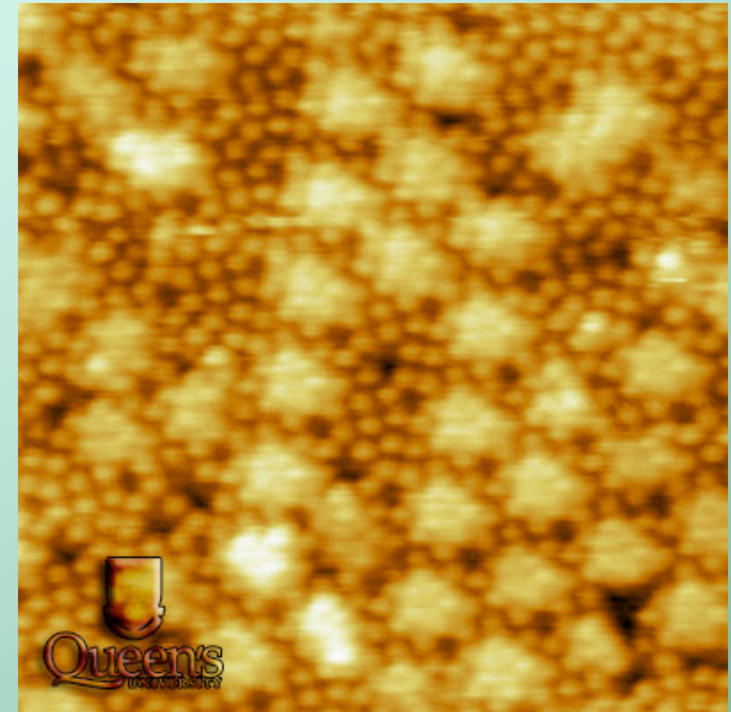
- Consider 2 metals in close proximity, with an applied electrical bias
- Current develops due to electron tunneling
- Magnitude is a *very* sensitive measure of d



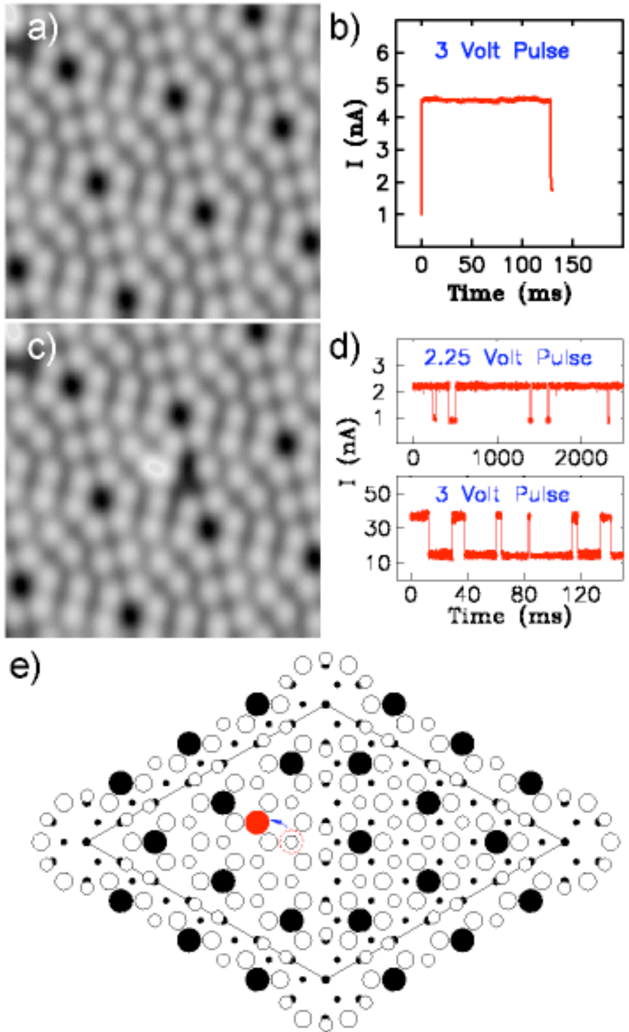
- Scan tip over surface at constant tunnelling current
- Record z (height) as a function of x,y (lateral position)
- Image reveals the atomic corrugation
- Direct determination of local surface structure





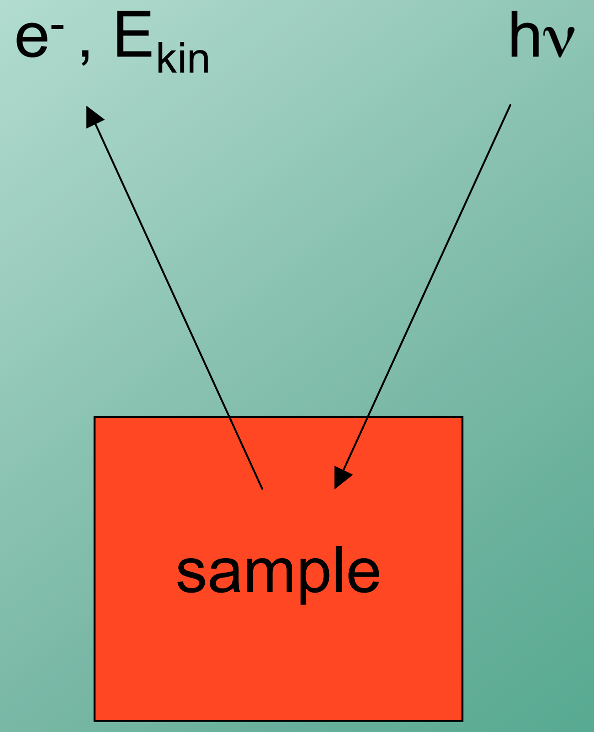


Reversible Displacement by Tunneling Electrons



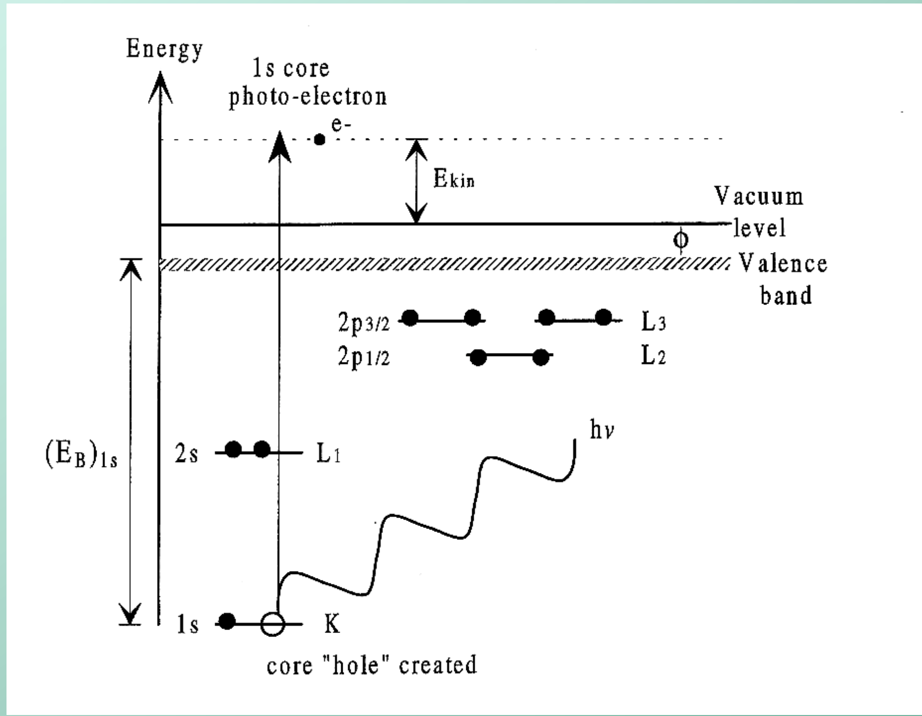
Surface composition

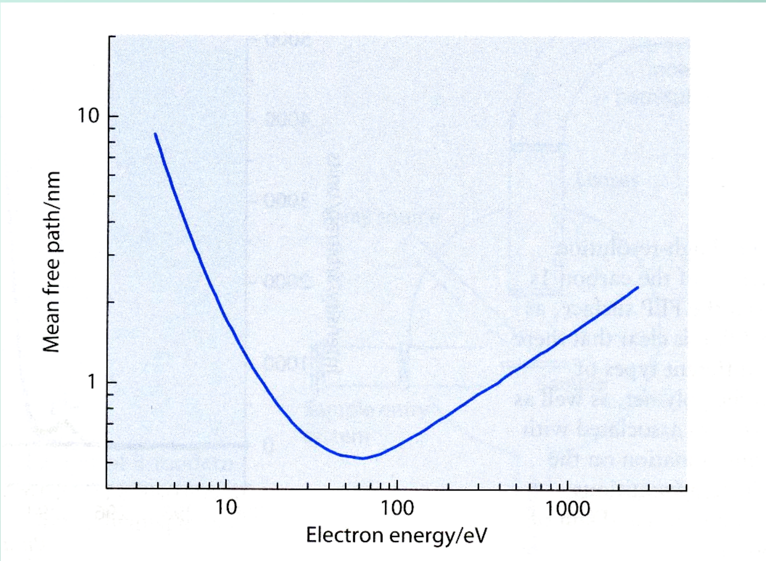
- Photoelectron spectroscopy (PES)
- uses X-rays (XPS)
- contrasts to ultra-violet PES
- the more energetic photons ionise core-levels



Measure photoelectron current as a function of E_{kin}

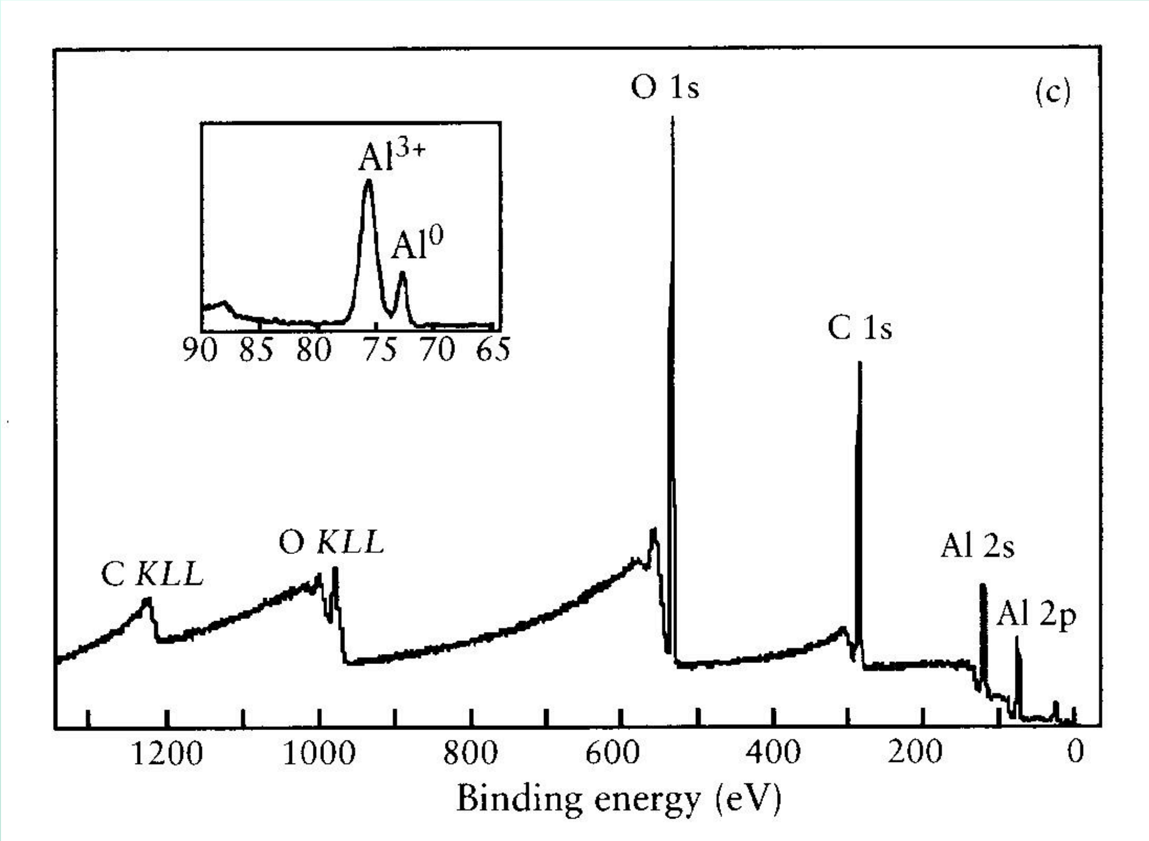
- For hν~1000 eV, E_{kin}<1000 eV.
- So sampling depth ~1.5 nm





$$E_{kin} = h\nu - E_b^{core}$$

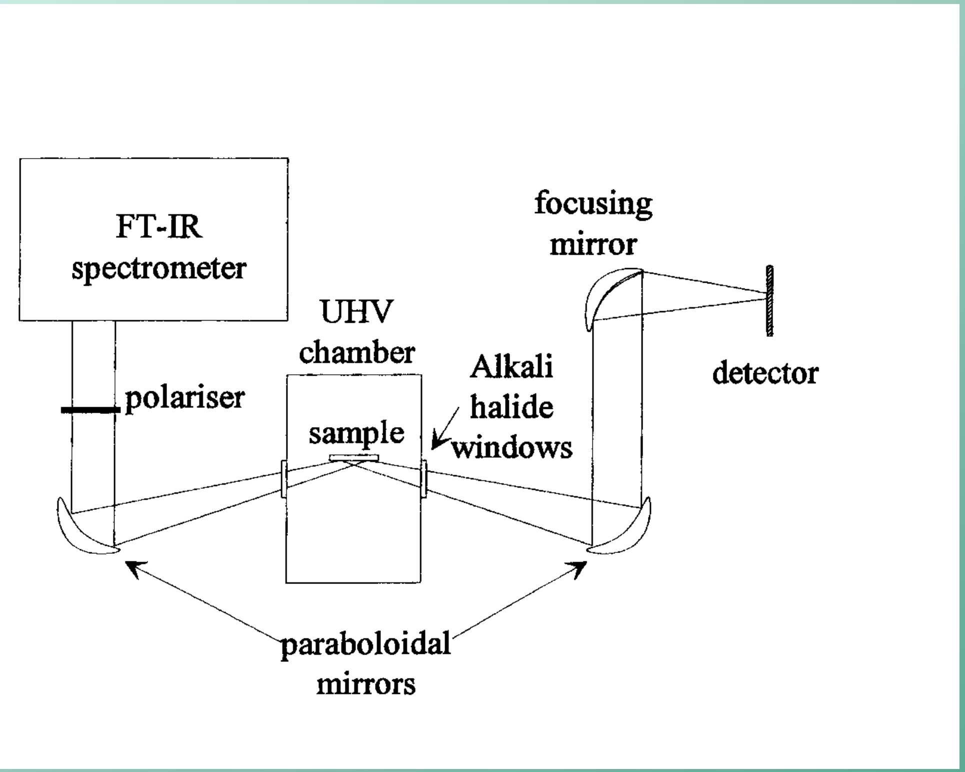
E^{core} is characteristic of the emitting atom



- XPS peaks are denoted by emitting atom and core level
- Provides analysis of the surface region

Adsorbates

- Vibrational spectroscopies on adsorbed layers
- E.g. Reflection-absorption IR



- Electron energy loss spectroscopy
  - Measure kinetic energy of scattered electrons from surface, for a fixed incident energy
  - See various distinct energy losses, corresponding to vibrations excited by incident electron

$$h\nu^{vib} = E^{incident} - E^{scattered}$$