Spectroscopic Determination of Work Functions

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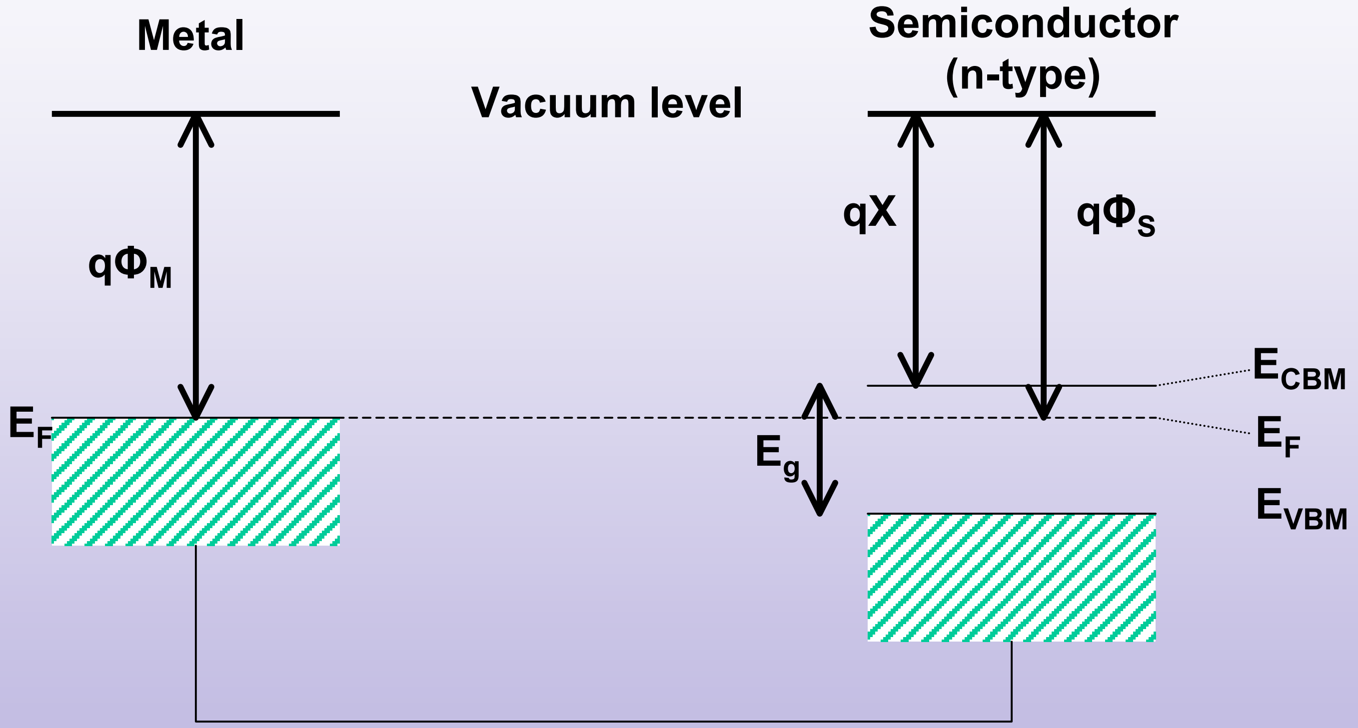
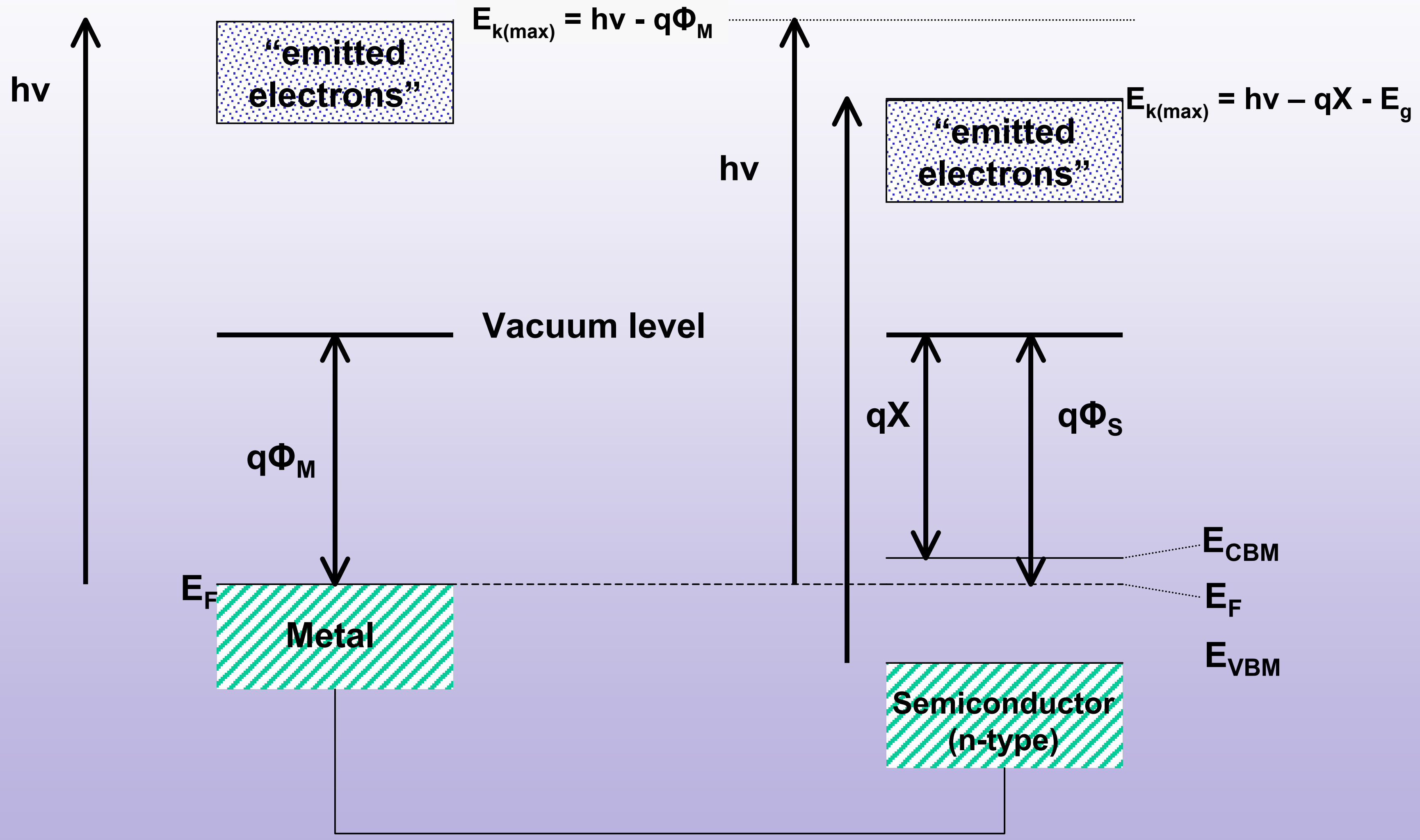
Definition of parameters
Photoemission Determination
Kelvin Probes

Definition of Parameters



Metal and semiconductor connected by a wire
Fermi levels line up → Determine Semiconductor E_F

Photoemission of valence electrons

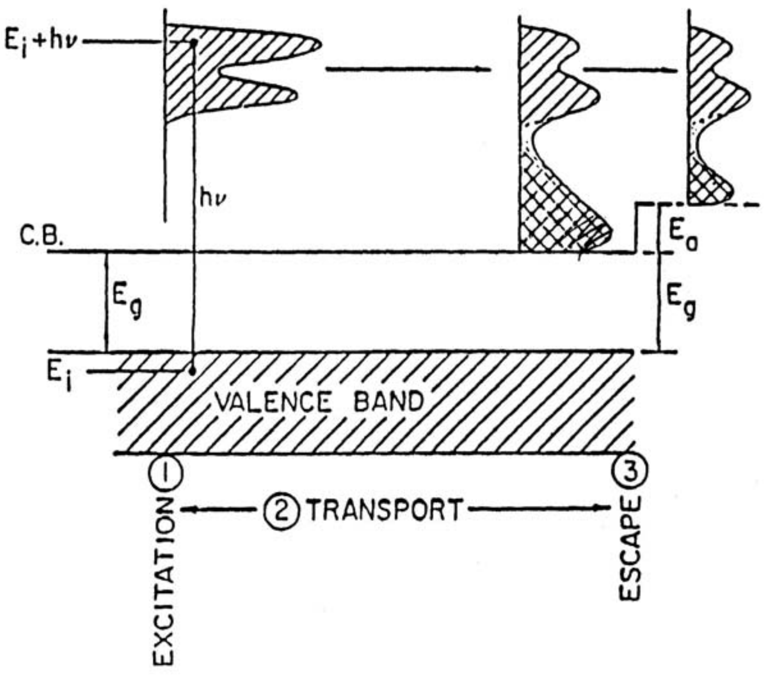


Photoemission Process

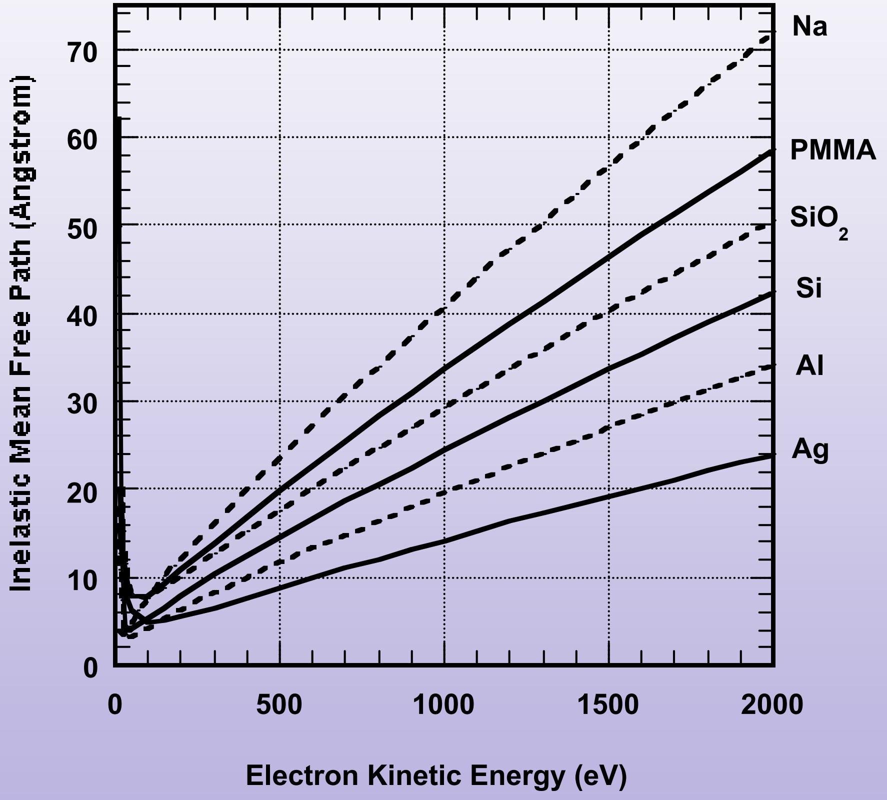
Electrons are excited within the solid
Scatter on their way to the surface

Three-step Model

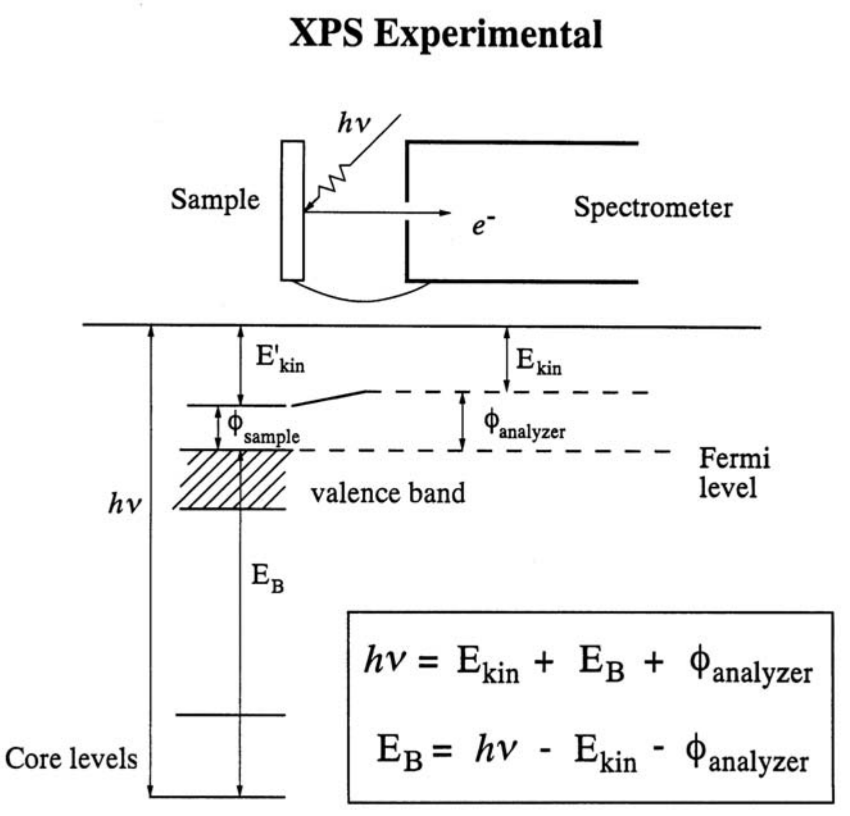
Spicer, Phys. Rev. 112, 114 (1958)



$$P(E,\omega) \times L(E) \times T(E) = I_p(E,\omega)$$

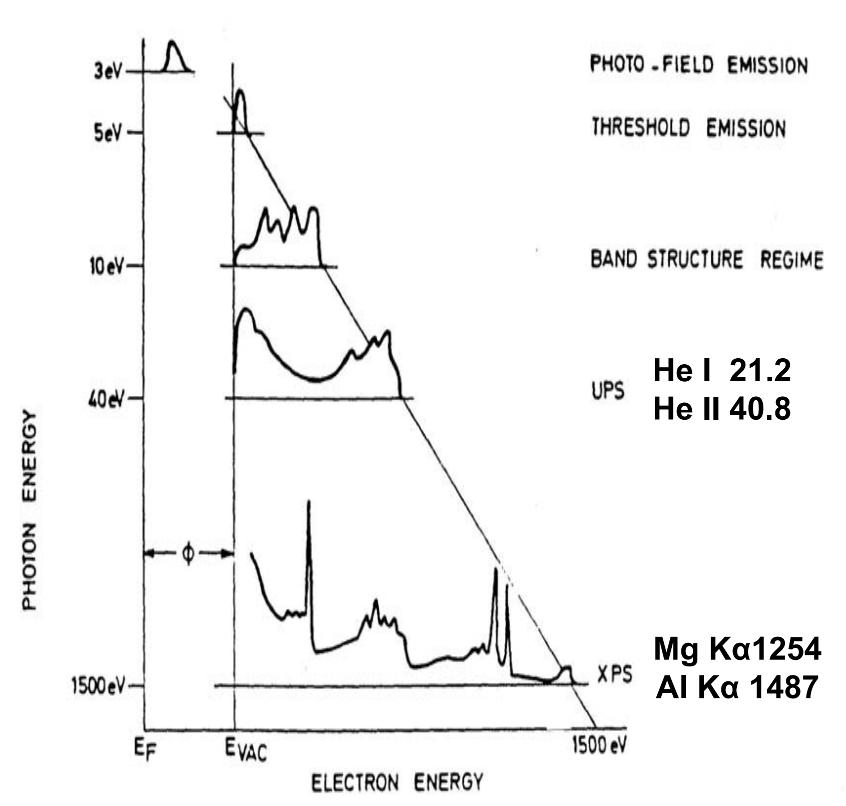


Photoemission Practical Aspects



$$h\nu = E_{kin} + E_B + \phi_{analyzer}$$

$$E_B = h\nu - E_{kin} - \phi_{analyzer}$$



At the Fermi level, $E_B = 0$ and $E_{kin}(\max) = h\nu - \Phi_{analyzer}$
At the cut off, $E_{kin}(\min) = \Phi_{sample} - \Phi_{analyzer}$

$E_{kin}(\max) - E_{kin}(\min) = h\nu - \Phi_{sample}$ (negative sample bias forces electrons into analyzer)

Example of Photoemission Measurement

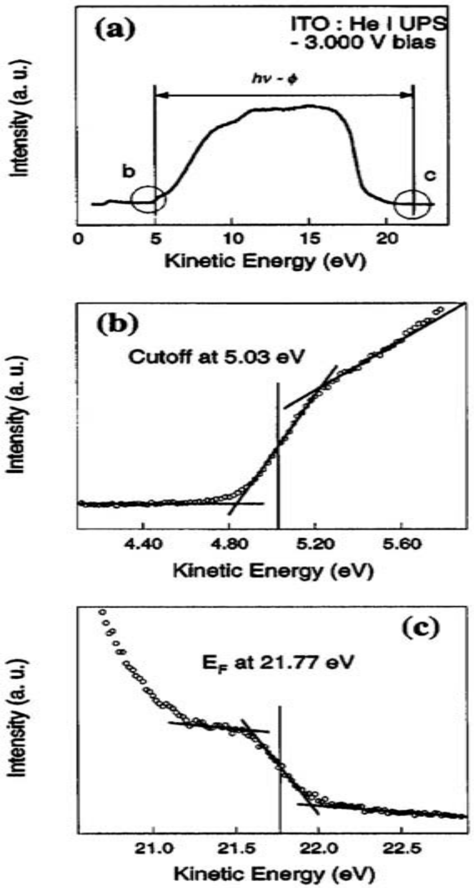


FIG. 1. (a) Shows a typical He I ($h\nu$=21.22 eV) UPS spectrum of ITO taken with −3.000 V bias applied to the sample. Also shown is inelastic cutoff (circle b) and Fermi edge (circle c). The relation between spectrum width $h\nu$, and work function ϕ is illustrated. (b) Shows a detailed spectrum of inelastic cutoff region. It also shows the cutoff energy with a vertical bar; (c) is similar to (b), but shows Fermi edge region.

Park et al., APL 68, 2699 (1986)

Indium tin oxide is conductive resulting In a Fermi level

HeI line from a discharge lamp provides a highly accurate photon energy

3 V sample bias shifts low energy cut off above analyzer work function

Width of spectrum measured at cut off points—not sharp due to finite analyzer resolution and room temp measurement

For conductive samples with poorly defined Fermi levels, measurements still possible by using the Fermi level from a gold sample in electrical contact

Adsorption changes work function

Silicon Surface States

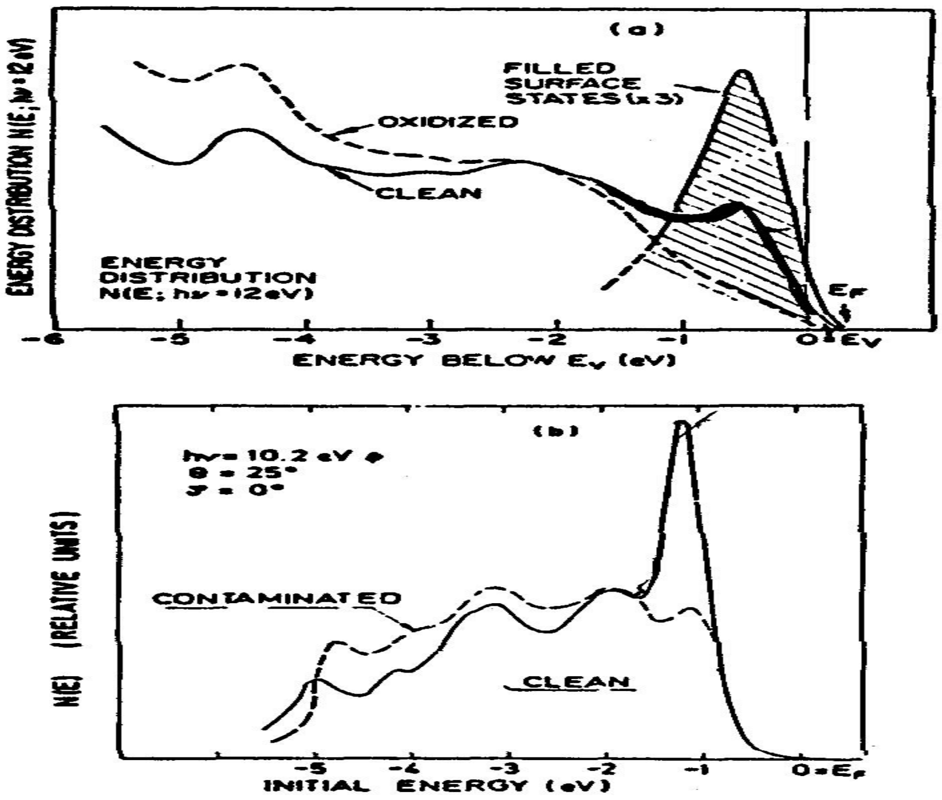
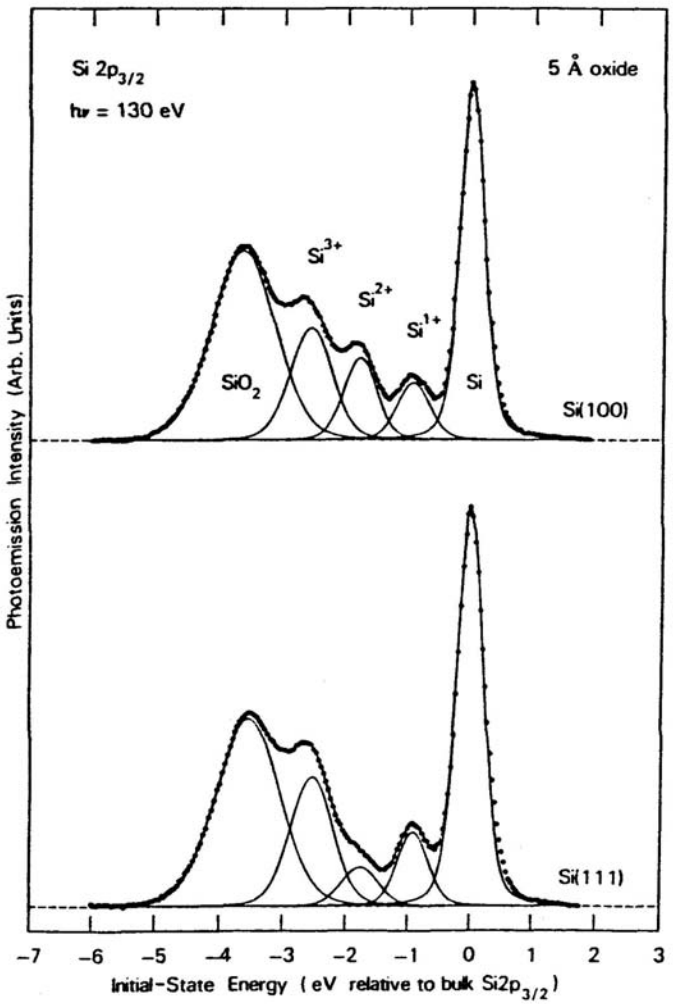
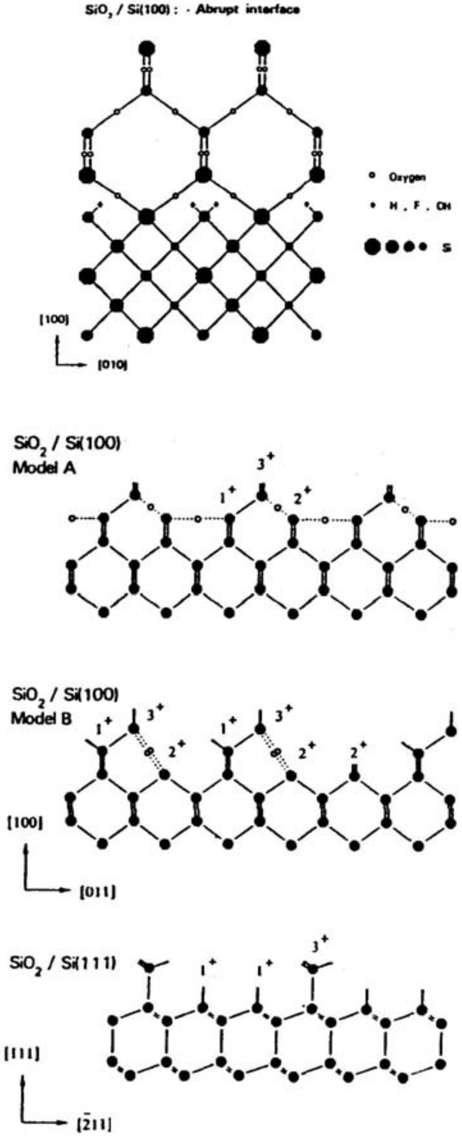


Figure 11.4 (a) Angle-integrated photoelectron energy distribution spectra taken with a cylindrical mirror analyser for clean and contaminated Si(111) (2 × 1) surfaces. The difference curve of the two spectra depicts the optical density of intrinsic surface states. (From Eastman and Grobman[43].) (b) Angle-resolved photoelectron spectra for a clean and a contaminated Si(111) surface. Azimuthal angle $\phi = 0$ corresponds to the $\langle 11\bar{2} \rangle$ crystal direction. (After Rowe, Traum, and Smith[50])

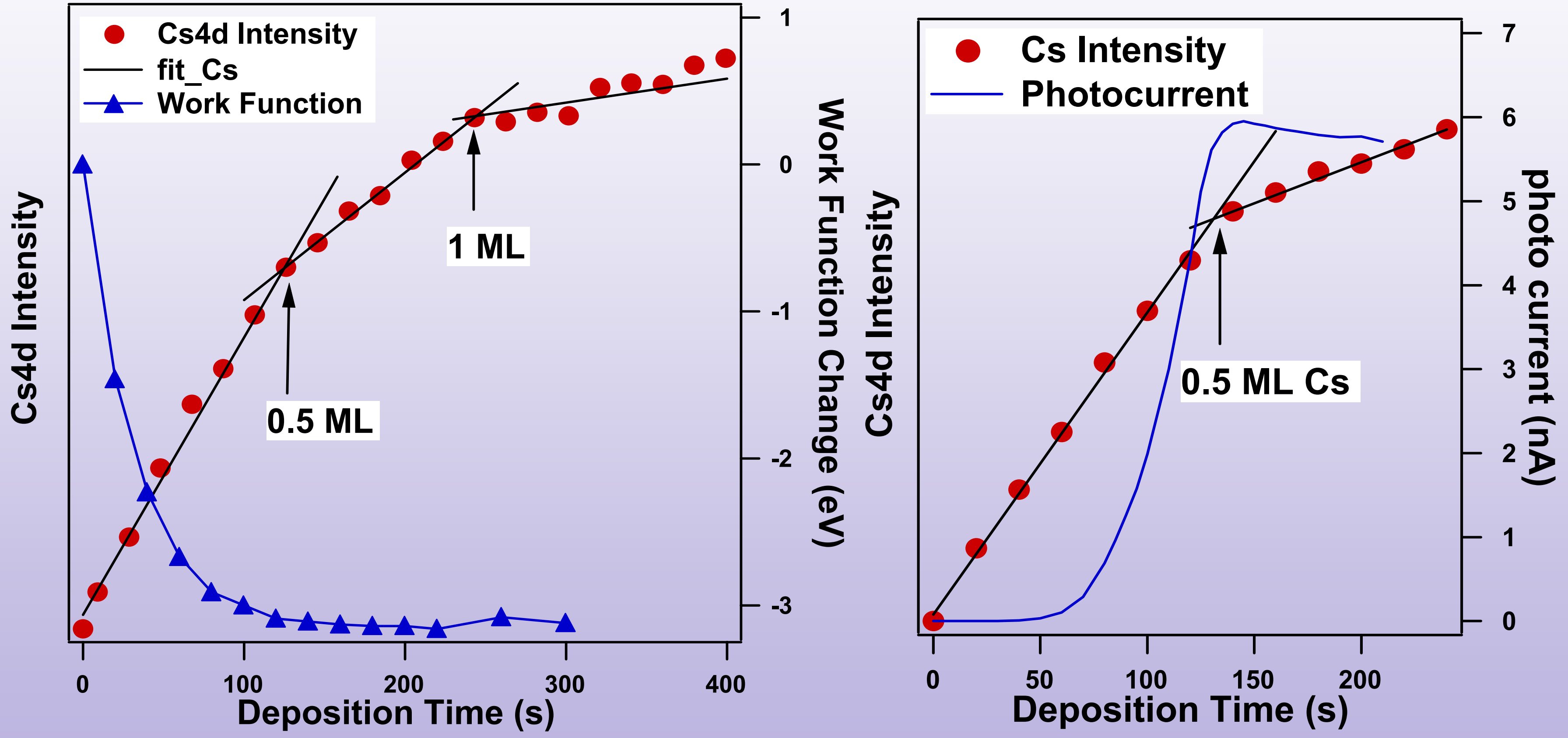
Si 2p Chemical Shifts with Oxidation





Himpsel et al.

Work function and photocurrent dependence of InP surfaces with Cs coverage



Y. Sun, Ph.D. Thesis, Stanford University, 2002

Kelvin Probe Force Microscope

Conductive AFM tip, ac voltage applied to sample results in an oscillating electrostatic force between tip and sample. Compensate force with a dc bias that matches the contact potential difference (CPD) between tip and sample.

Work function of cantilever is calibrated and then:

Φsample = Φcantilever + CPD

Analogous measurements can be performed with conventional Kelvin probes at mm spatial resolutions.

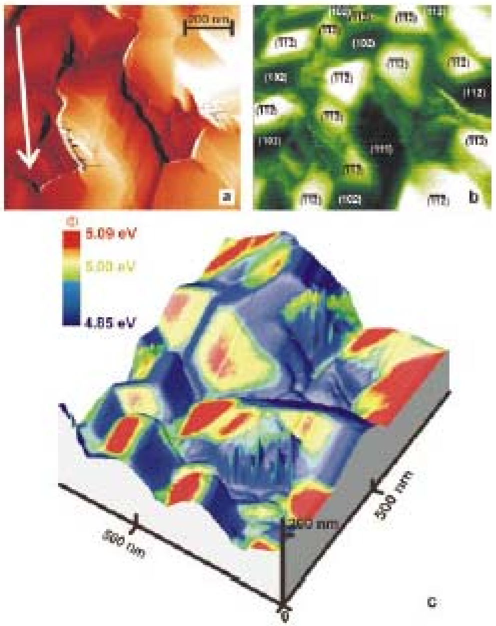


FIG. 1. (Color) KPFM measurement of a $CuGaSe_2$ thin film grown on a freshly cleaved single crystalline ZnSe(110) substrate. (a) The topography image shows distinct crystal facets on the (220) oriented $CuGaSe_2$ film. The color scale corresponds to height differences of 384 nm. The line gives the location of the linescan shown in Fig. 2. (b) Representation of the simultaneously measured work function (Φ =4.85...5.09 eV). The crystallographic orientation of the facets is assigned based on the angles to other facets and to the surface normal. (c) three-dimensional image merging the topography (as the 3D effect) and the work function represented by the color scale. The origin corresponds to the lower left corner in the 2D images.

Sadewasser, APL 80, 2979 (2002)

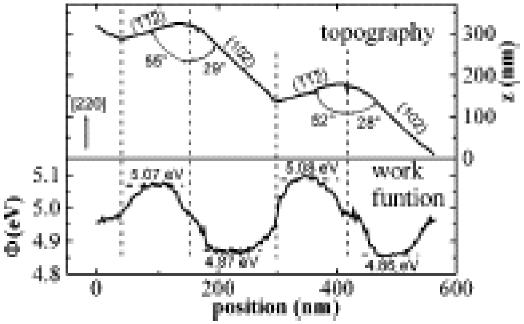


FIG. 2. Topography and work function along the line in Fig. 1(a). It is clearly seen that the work function assumes a constant value on the crystal facets. The orientation of the facets is indicated in the upper plot and was calculated from the angles of the facet to the surface normal and to other facets of the same grain.

Conclusions

Work functions of bare surfaces can be obtained with photoemission to obtain fundamental properties

Work functions affected by surface contamination, overlayers etc.

Use surface analytical results to understand interfaces on an atomic scale.

Photoemission has been used in thin multilayer systems to obtain band offsets using core levels for appropriate materials systems.

Scanning probe techniques can be used at both microscopic and Macroscopic levels.

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