Spectroscopic Determination of Work Functions

Piero Pianetta, EE & SSRL
Stanford University

Definition of parameters
Photoemission Determination
Kelvin Probes
Definition of Parameters

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

- Vacuum level
- Metal
  - $q\Phi_M$
  - $E_F$
- Semiconductor (n-type)
  - $q\Phi_S$
  - $E_{CBM}$
  - $E_{E_F}$
  - $E_{VBM}$
  - $E_g$
Photoemission of valence electrons

\[ E_{k(\text{max})} = h\nu - q\Phi_M \]

\[ E_{k(\text{max})} = h\nu - qX - E_g \]

\[ \text{EF} \]

\[ \text{Metal} \]

\[ \text{Vacuum level} \]

\[ q\Phi_M \]

\[ \text{EvBm} \]

\[ \text{Semiconductor (n-type)} \]

\[ \text{EF} \]

\[ \text{ECBM} \]
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

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

At the cut off, $E_{\text{kin}}(\text{min}) = \Phi_{\text{sample}} - \Phi_{\text{analyzer}}$

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

Indium tin oxide is conductive resulting in a Fermi level

Hel 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

Park et al., APL 68, 2699 (1986)
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.) (b) Angle-resolved photoelectron spectra for a clean and a contaminated Si(111) surface. Azimuthal angle $\phi = 0$ corresponds to the [11\(\overline{2}\)] crystal direction. (After Rowe, Traum, and Smith.)
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:

$$\Phi_{\text{sample}} = \Phi_{\text{cantilever}} + \text{CPD}$$

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

Sadewasser, APL 80, 2979 (2002)
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.