Technical Note #6

Angle Resolved XPS (ARXPS)

Introduction

It is well established that x-ray photoelectron spectroscopy (XPS) is a surface sensitive technique due to the finite distance a photoelectron can travel without collision – the inelastic mean free path (IMFP, λ).

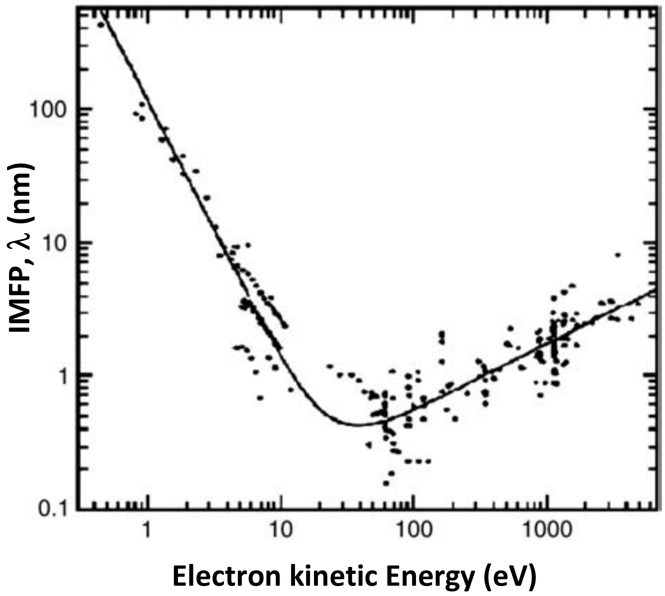

Figure 1: 'Universal curve' taken from ref [1]

As the so-called 'universal curve' shows (figure 1), photoelectrons with a kinetic energy in the 10 – 10^3 eV range have an IMFP in the range of 1-3.5 nm. [1]

The sampling depth of XPS, is defined by the quantity 3λ, which is the depth at which 95% of all signal originates from, so typically the XPS sampling depth is up to *ca.* 10 nm.

Since these electrons can only travel a given distance through a material before an interaction resulting in an energy loss occurs, by varying the angle at which the electrons are detected from the surface, we can enhance the surface contribution.

Therefore, by changing the tilt of the sample stepwise from say 0° to 75°, surface sensitivity can be increased by the reduction in the XPS information depth. This is shown graphically in figure 2.

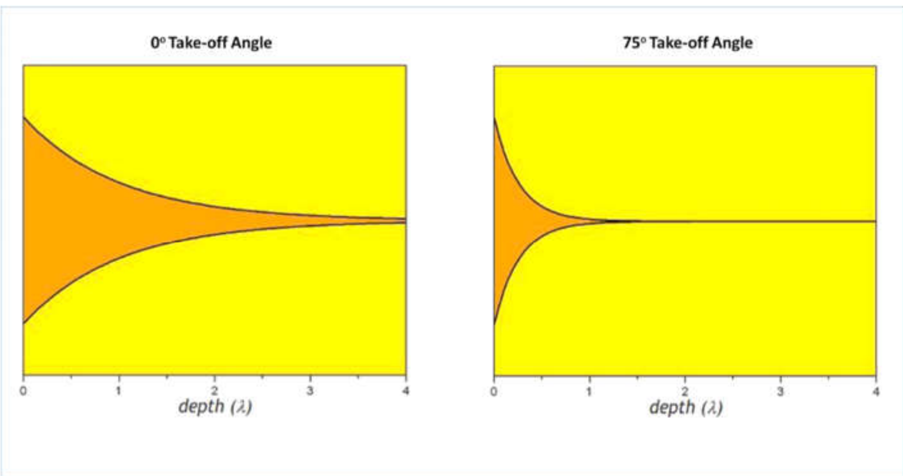

Figure 2: The variation of information depth as a function of take-off angle. Adapted from [2]

Increasing Surface Sensitivity

Angle resolved XPS (ARXPS) can be achieved by two methods.

1) Tilting the samples with respect to the analyser, or,
2) Parallel acquisition of all angles simultaneously (PAR-XPS)

The first of these is typical for the majority of spectrometers and relies on a known axis of rotation for the sample holder so that the same spot is analysed regardless of angle, whilst the latter is unique to the Thermo Scientific Theta Probe PAR-XPS instrument. The Therat Probes utilises an electrostatic lens with a 60° angular acceptance to maximise sensitivity, and with the axis of the lens is 50° from the sample normal, this enables electron collection between 20° and 80°.

Examples of both rotation and parallel acquisition these methods are shown in figure 2.

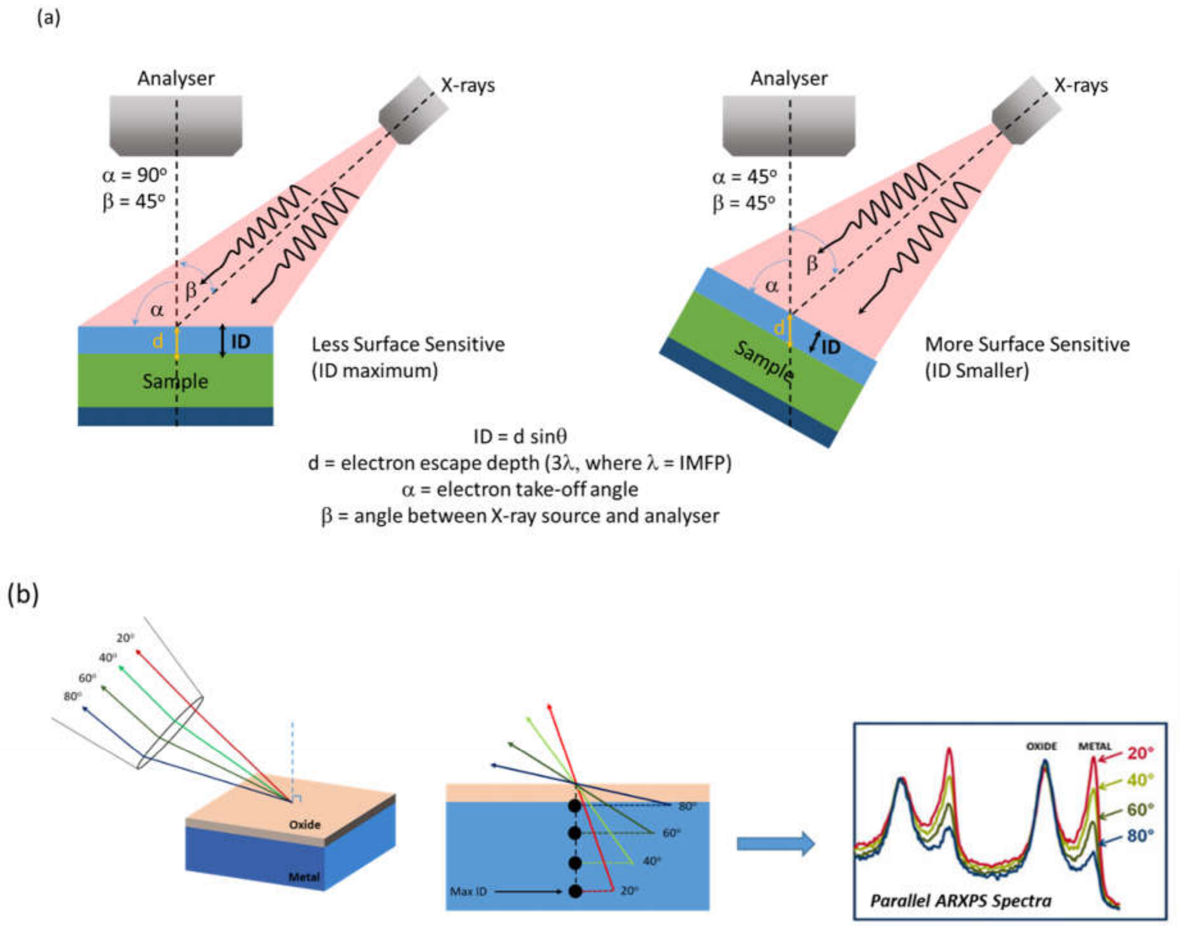

Figure 3: Angle-resolved XPS methods for: (a) rotation around a point and (b) Parallel ARXPS

Example of ARXPS in Practice

Figure 4 shows normal and grazing incidence spectra for the Nb(3d) core-level of a niobium containing alloy, which have been taken from a larger angle-resolved study.

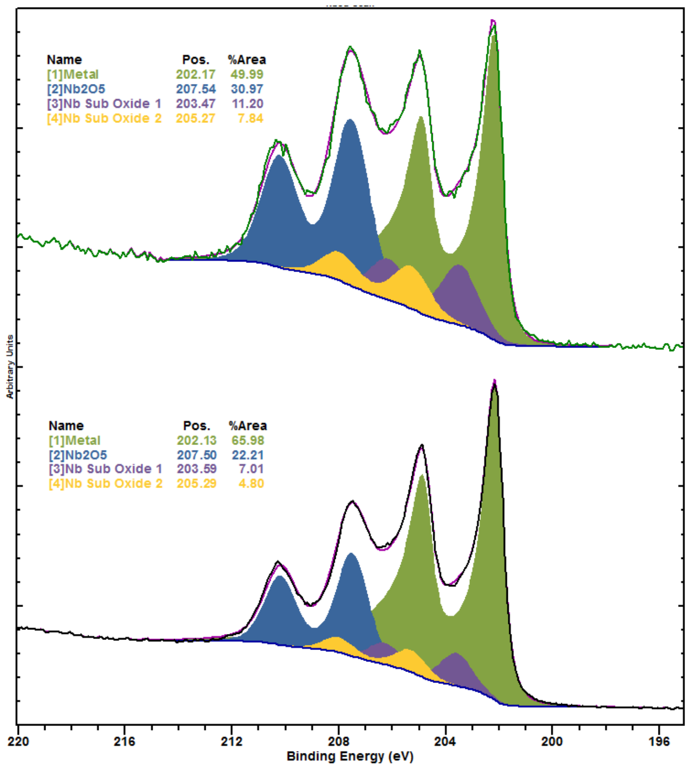

Figure 4: Nb(3d) core level spectra at 0° (bottom) and 70° (top) take off angles. Note the increase in the relative concentration of the oxide components to that of the metal at the grazing angle. Note also how the signal at the grazing angle is noisier than that taken at normal emission.

Summary

We have presented here a snapshot of the theory and methods of ARXPS, together with a simple example highlighting the improved near-surface information obtained from such angular experiments.

Purposely we haven't touched upon the intricacies in data analysis of ARXPS data for complex systems, instead using this note to serve as an introduction and for further discussion and background we recommend reading ref [2] and references therein.

References

[1] M.P. Seah, W.A. Dench, *Surf. Interf. Anal.*, 1 (1979) 2

[2] R. W. Paynter, J. Rel. Spec. 169 (2009) 1-9