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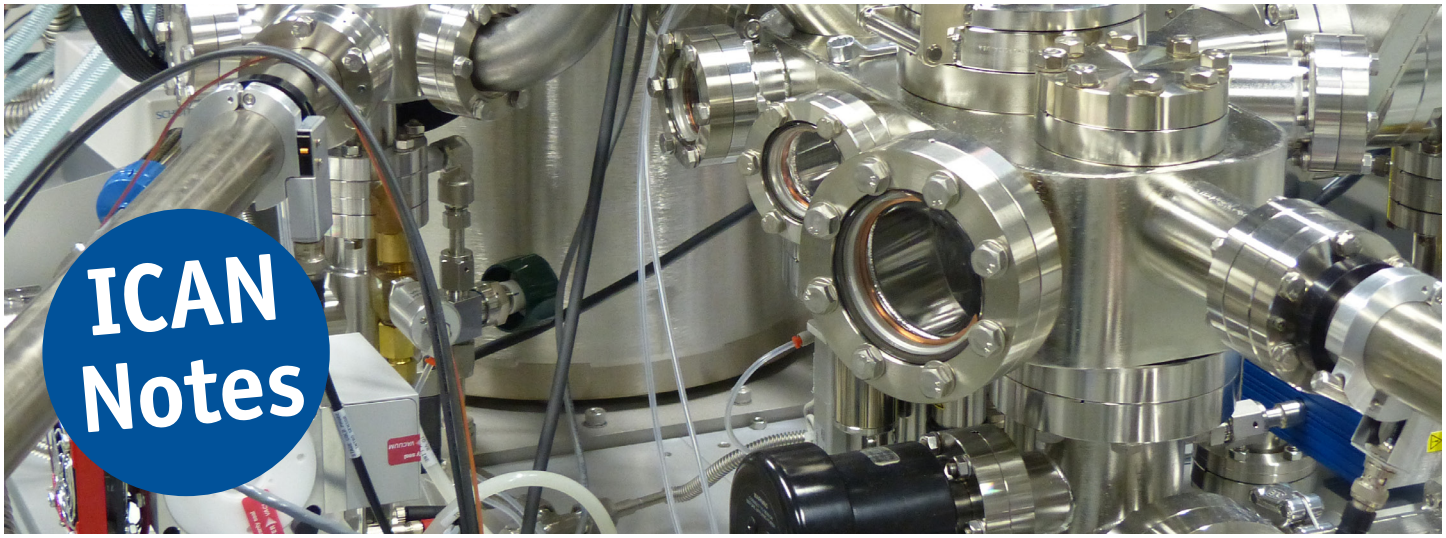

Angle Resolved XPS - ARXPS

by Ulrich Hagemann* - Interdisciplinary Center for Analytics on the Nanoscale (ICAN)

The three-step model of photoemission breaks down the quantum-mechanical process of the absorption of a photon and the emission of an electron into subsequent processes of excitation in the solid, transport to the surface, and transmission through the surface barrier into the vacuum [1]. Hereby, the number of excited photoelectrons that reach the sample decreases exponentially with the depth of the emitting atom relative to the surface. The corresponding depth-dependent yield can be described as

$$Y_a = Y_0 e^{-a/\lambda_{\mathrm{IMFP}}}$$

where Y_a is the electron yield after the electron beam had to travel the distance a through the sample, and λ_{IMFP} is the inelastic mean free path (IMFP) of the excited electrons [1]. The IMFP depends mainly on the kinetic energy of the electron and follows the famous universal curve [2] that is roughly element-independent. In the kinetic energy range of photoelectrons excited by X-rays (~200 – 1200 eV) the IMFP is on the order of a few nm. The equation for Y_a predicts that when photoelectrons have to travel three times the IMFP to reach the sample surface, only about 5% of those originally excited will do so.

In XPS it is usually assumed that the signal from electrons that travelled a distance of $l \approx 3 \cdot \lambda_{\mathrm{IMFP}} \approx 10$ nm through the solid is still detectable. This traveling distance equals the maximal attainable information depth $l = d_{\max}$. However, the traveling distance does not equal the information depth d in all cases. Figure 1 illustrates how a tilt of the sample relative to the analyser affects the correlation between the electron emission angle α, the information depth d and the traveling distance l. The analyser is positioned in the direction of the red arrow above the sample surface. For the case shown in Fig. 1a, the analyser dominantly detects electrons that are being emitted along the sample surface's normal, and the information depth is $d = d_{\max} = 3 \cdot \lambda_{\mathrm{IMFP}}$. If the sample is tilted, like in Fig. 1b the relative angle between the analyser and the sample surface is changed, and the detected electrons must have left the sample under a much smaller angle. However, as λ_{IMFP} in the sample is usually unchanged, the resulting information depth d is decreased as

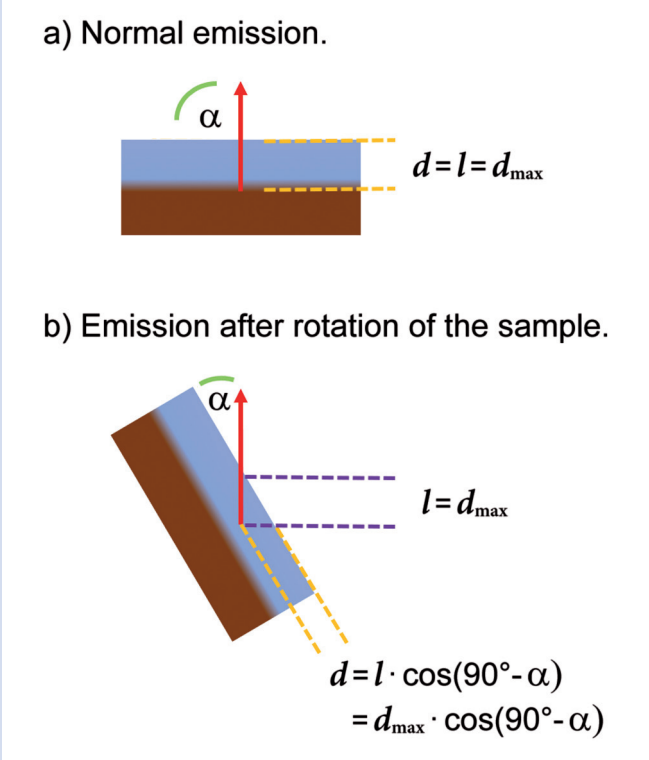

Figure 1: Correlation of the emission angle α and the resulting information depth d.

$$d = d_{\max} \cos(90° - \alpha).$$

Hence, recording XPS spectra at different sample tilt angles yields spectra with different information depths. This allows for a thickness determination of ultrathin films or layered structures of a few nm thickness while still obtaining chemical state information (and without destroying the surface).

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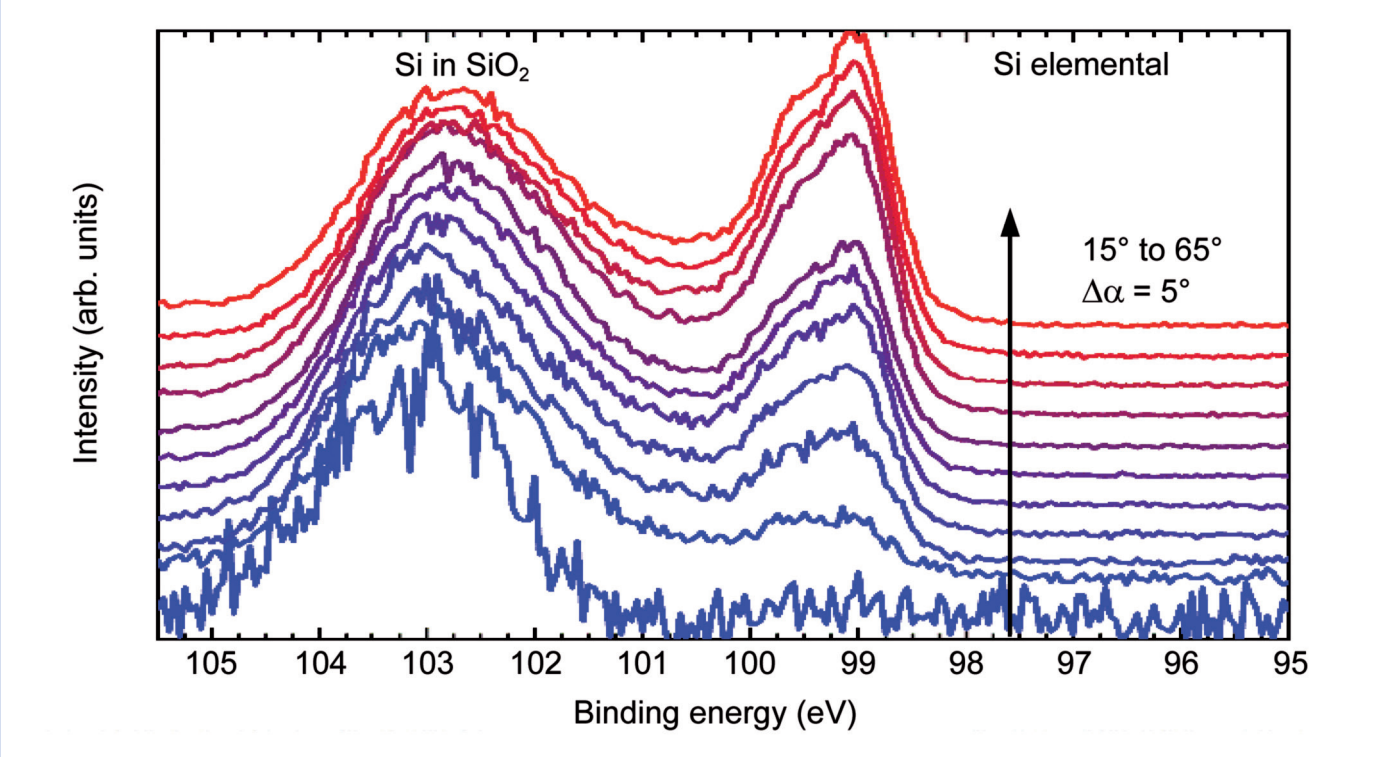

Figure 2: Si 2p spectra of a thin SiO_2 film on a Si substrate.
The emission angle is changed in steps of 5° between 15° and 65° from bottom to top, illustrated by the color change from blue to the red.

Figure 2 shows XPS scans of the Si 2p region of a thin SiO_2 layer on a silicon substrate. The emission angle α is gradually changed in 5° steps from 15° (blue curve) to 65° (red curve). The dominant photoelectron signal at 15° emission angle and ~103 eV binding energy corresponds to oxidized Si. The elemental Si signal at around 99 eV binding energy is barely visible at a detection angle of 15°. Upon increasing the emission angle towards normal emission, the elemental Si peaks appears and becomes stronger, while the corresponding signal from oxidized Si becomes weaker in comparison. From this data, the SiO_2 layer thickness can be calculated to be about 1 nm.

This example demonstrates that ARXPS is a powerful technique to determine a layer thickness, but it is important to note that this technique cannot be applied to all types of samples. Rather, some requirements of the sample structure have to be fulfilled and some assumptions have to be made for the analysis of the results:

(i) The sample must have a rather flat surface.
(ii) Layers on the sample must be continuous. If the covering layers consist of islands smaller than the beam diameter, the data interpretation is likely flawed.
(iii) The electron attenuation lengths are considered to be constant within each layer of the sample and are assumed to be independent of the detection angle.
(iv) The density of atoms is assumed to be constant within each layer.
(v) The X-ray intensity is presumed to be constant in the analysed volume.

In conclusion, ARXPS provides a non-destructive depth-profile of the topmost few layers (about 10 nm) of a sample surface. It allows the determination of the thickness of oxide films, the order of multilayer structures, and elemental gradients at the surface.

References

[1] S. Hüfner. *Photoelectron Spectroscopy*. Springer Series: Advanced Texts in Physics. Springer-Verlag, Berlin, Heidelberg, 2003.
[2] M. P. Seah and W. A. Dench. *Quantitative electron spectroscopy of surfaces: a standard data base for electron inelastic mean free paths in solids.* Surf. Interface Anal. 1, 2 - 11, 1979.

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