

Background

In 1990, Strohmeier published a simple method for estimating the oxide thickness on aluminium alloys using XPS [1]. Based on a uniform overlayer model, the calculation is straightforward and typically can be achieved from only a single measurement per sample where the oxidic and metallic peak intensities are recorded.

The method itself is adventitious as the method is applicable to any x-ray source and does not require any sample preparation such as ion etching. Despite being derived for aluminium oxides; the method can be readily applied can also be applied to other thin film (i.e. <10 nm) metal oxide/metal systems. The equation assumes the electrons giving rise to the photoelectron signals originate from similar photoelectron energies and therefore the maximum oxide thickness that can be measured using the method is limited to approximately three times the inelastic mean free path of the appropriate photoelectrons within the material of interest.

The Strohmeier Equation

The equation derived by Strohmeier is:

$$d = \lambda_{ox} \sin\theta \ln \left[\left(\frac{(N_m \lambda_m I_{ox})}{(N_{ox} \lambda_{ox} I_m)} \right) + 1 \right]$$

Where d is the oxide thickness, θ the photoelectron take-off angle, I_{ox} and I_m are the percentage areas of the oxide and metal peaks fitted from the high-resolution spectrum, λ_m and λ_{ox} are the inelastic mean free paths of the photoelectron for the metal and oxide and N_m and N_{ox} are the volume densities of the metal atoms in the metal and oxide.

Calculation of volume density Ratio (N_m/N_{ox})

The metal volume density for both metal and oxide is the respective density divided by the mass of the compound. By means of example, we consider Cu, CuO, Cu(OH)₂ and Cu₂O.

Species	Density (g cm ⁻³)	Molar Mass	N _x (x = m or ox)
Cu	8.93	63.53	0.141
CuO	6.39	79.55	0.080
Cu(OH) ₂	3.37	97.56	0.035
Cu ₂ O	6.14	143.09	0.086

Note that for the case of Cu₂O, the number of Cu atoms in the oxide must be accounted for, so the volume density (N_{Cu_2O}) calculation for this is given by [(6.14 x 2) / 143.09].

Species	N_m/N_{ox}
CuO	1.76
Cu(OH) ₂	4.03
Cu ₂ O	1.64

Table of volume density ratios for copper oxides and hydroxides. The values here are in excellent agreement with those published [2]

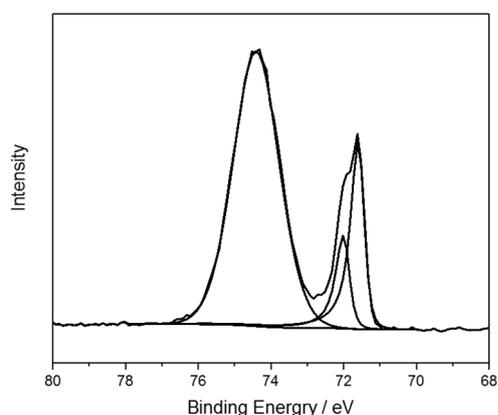
What if my surface contains oxides and hydroxides?

For this situation we assume a uniform mixture of oxide and hydroxide and take the weighted average of the oxide/hydroxide number densities and IMFP's as shown below:

$$d = \lambda_{ave} \sin \Theta \ln \left[\frac{N_m \lambda_m (I_{oxide} + I_{hydroxide})}{N_{ave} \lambda_{ave} I_m} + 1 \right]$$

Where I_{oxide} and $I_{hydroxide}$ are calculated by means of curve fitting the core-level spectra. Note that should you have different oxides present (e.g. CuO and Cu₂O) these can easily be added in to the equation above. An example of such analysis with nickel oxides/hydroxides can be found in reference [3].

Example – Aluminium Oxide/Aluminium



Using the system discussed by Strohemier and using the associated values [1], the oxide thickness in the given example is calculated to be 4.4 nm (44 Å).

References

[1] B. R. Strohmeier, Surf. Interface Anal., 1990, 15, 51

[2] M. C. Biesinger, In Press, (DOI: 10.1002/sia.6239)

[3] M. C. Biesinger, B. P. Payne, L. W. M. Lau, A. Gerson, R. S. C. Smart, Surf. Interface Anal., 2009, 41, 324.