Journal of Surface Analysis Vol.1, No. 3, 1995

Q & A

Work Functions and Electron Spectroscopy

M P Seah
National Physical Laboratory
Teddington, Middlesex TW11 0LW, UK

In a recent article [1] Sekine presents some interesting aspects of the problems of work functions in electron spectroscopy, and, in particular, for XPS. In his "Summary of the Issue" he defines work function and since that definition is essentially the same as my understanding of the term I, have attempted some discussion of his two question points below. Furthermore, I have added a third point which seems to me to be related. Some interesting comments have already been supplied by Ichimura [2]. For the benefit of English readers the question points are shown in bold below.

Q1) When conductors with different work functions are in contact, electrons move at the conduction level and both the Fermi levels are equalised to a potential which may be in between the two previous levels, as shown in Fig 1 [1]. Then, do the work functions, ϕ_s, ϕ_a change before and after the contact? (If the contact of materials of different work functions induces electron movement in order to keep the two Fermi levels at an equal potential, does it influence the electric structure of the surface ...?) If so, the observed binding energy will include an error due to this effect.

A1) When conductors are joined their Fermi levels are aligned by a small charge transfer. If, in Fig 1 [1], the sample is at ground and the spectrometer is brought into contact with the sample then the spectrometer's Fermi level aligns with that of the sample, ie ground. If, however, the sample and spectrometer are joined but isolated from everything else, the final Fermi level will be at an energy which depends on the charges and capacities involved but will be, as noted above, between the two previous levels.

When contact is made the work functions remain unaltered. For polycrystalline solids the different crystals may be imaged at very high spatial resolution in instruments with UV light sources using any one of the emission signals which are work function dependent (eg the Siemens' Metioscope). The work functions of each crystallite is the same as that of an isolated larger crystal of the same orientation. Thus, the work functions do not change either before or after the contact.

Q2) Even the same materials of different crystal orientations sometimes show different work functions. For example, for Cu, they are 4.59, 4.98 and 4.48 eV for the (100), (111) and (110) surfaces, respectively. The question is whether the binding energies of such samples are shifting or not, as illustrated in Fig 2 [1].

If the small changes of work functions and/or binding energies do not occur or can be ignored, we will be able to perform accurate analysis by adjusting the spectrometer offset to remove the analyser work function. If not, we must consider the extra small error. As we try to improve the accuracy of surface analysis, we sometime find such new items which we have not considered before.

A2) Sekine [1] is correct that different crystal faces have different work functions and that the different faces are important. For atoms deep within the bulk it does not matter whether the photoelectron trajectories from those atoms exit from the solid via one face or another before passage into the spectrometer. The electron energy must be conserved and so, through either face, the energy is given as the bulk binding energy referred to the Fermi level, the latter being measurable within the same experiment. We may probably treat all atoms except the outermost atom layer as being bulk atoms within this context. For single crystals the changes in the electronic structure for the outermost layers do lead to what has been termed "surface core level shifts". This is an effect treated in the Discussion section of our original binding energy calibration work [3] and is an effect seen most strongly for clean, annealed and ordered low index single crystal faces. Many films of face centred cubic metals evaporated onto glass show very strong (111) texturing and this probably explains Citrin *et al's* [4] observations on clean Cu, Ag and Au. Their measurements show, essentially, that a peak occurs due to the bulk atoms together with a further peak, at lower binding energy, due to the atoms in the surface layer. This latter peak is similar in shape but is at only 12% of the intensity of the bulk peak for normal emission. At an emission angle of 60° from the surface normal the relative intensity of the surface peak rises, as expected, to some 20%. For the Au $4f_{7/2}$, Cu $2p_{3/2}$ and Ag $3d_{5/2}$ peaks the shifts seen were 0.389 eV, 0.241 eV and 0.076 eV, respectively. Depending on the analyser resolution, these effects could lead to shifts in the overall peak, for emission angles of less than 60° to the surface normal, of 0.03, 0.03 and 0.01 eV, respectively. Although this is very small, for this reason we recommended in our work the use of argon ion sputtered finely polycrystalline foils with average surfaces that were high indexed, rather than evaporated films on substrates such as glass or silicon. In all the published work no surface core level shifts have been observed for high index crystal surfaces and, even for low index surfaces, the effects are lost by sputter cleaning.

Thus, in summary, Sekine [1] is correct that there are effects which are sufficiently strong to be observable in carefully conducted experiments. However, these are not effects with which we need be particularly concerned provided we use polycrystalline foils for calibration.

Comment 3) A third interesting topic which involves the same field is that of the analyser work function. The ability of the spectrometer to deflect electrons depends on the potential in the vacuum and so is sensitive to the work functions of certain of the metal electrodes. Normally these work functions are stable and are combined into the overall "spectrometer work function". Commercial systems have coated electrodes to reduce any variability either with time or with distance across the electrode. This is particularly important in both high resolution electron energy loss and ultraviolet photoelectron spectroscopies. In XPS, significant effects, ie shifts of 0.1 eV, could occur for uncoated electrodes after a bake-out or after admission of reactive gases. To the authors' knowledge there is no adequate published data to show if this can be a problem in any particular instrument.

Acknowledgements

The author would like to thank Dr Sekine for his assistance with translations and comments.

References

[1] T Sekine, J. Surface Analysis 1, 43-44 (1995).

[2] S Ichimura, J. Surface Analysis 1, 264-266 (1995).

[3] M T Anthony and M P Seah, Surface Interface Anal. 6, 95-106 (1984).

[4] P H Citrin, G K Wertheim and Y Baer, Phys. Rev. B 27, 3160-3175 (1983).