XPS Analysis of Small Particles by Proximal X-Ray Generation

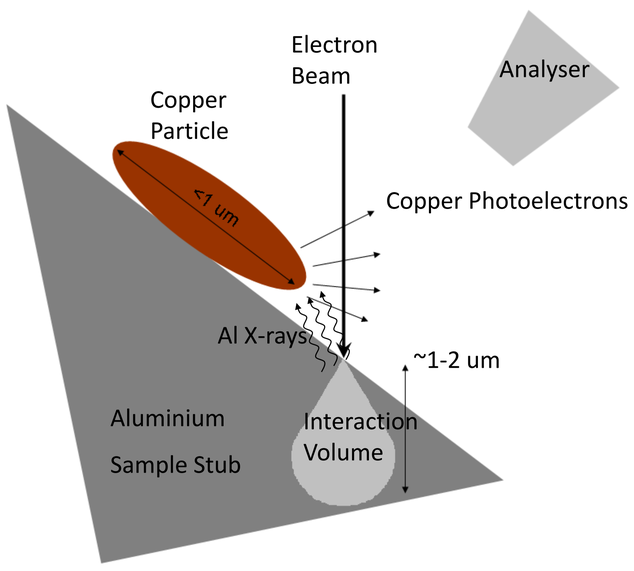
J. E. Castle, R.Grilli and C.F. Mallinson

Department of Mechanical Engineering Science, University of Surrey, Guildford, Surrey, GU2 7XH, U.K.

Corresponding author: j.castle@surrey.ac.uk

Introduction With the increasing interest on the health and safety issues associated with the use of, and emission of, small particles, particularly those which are able to evade the body's natural defences, there is a need for the chemical analysis of sub-micron sized particles. Analysis of particles is typically carried out by Auger electron spectroscopy (AES) or by secondary ion mass spectrometry (SIMS). X-ray photoelectron spectroscopy (XPS) has ability to identify chemical states with an ease that is not found in AES or SIMS: we have now explored the possibilities for generation of characteristic photoelectrons from a particle using Al Kα X-rays from the substrate on which it is mounted in a scanning Auger microscope.

Figure 1 Sample Geometry



The electron beam strikes the aluminium close to the particle, generating X-rays that in turn, excite photoelectrons from the sample to be analysed.

Experimental

All work described in this presentation was carried out on the Microlab 350 Scanning Auger Electron Microscope (Thermo Scientific, UK) in the Surface Analysis Laboratory at the University of Surrey. This instrument has high spatial resolution (12 nm) with simultaneous EDX analysis.

In order to minimize beam damage of the particle under examination, the sequence of analysis was; 1) location of the object on the Al support using the low current SEM mode of the microscope, 2) high-current generation of Al Kα x-rays from the support at a point well clear of the particle of interest and 3) movement of the X-ray source so as to envelope the object or particle without it being exposed directly to the electron beam. To facilitate this sequence the X-ray intensity can be monitored using the EDX detector but this was not employed in the work presented here.

Having located the feature for XPS analysis using the normal 'SEM' setting the aperture was withdrawn to give the maximum possible beam current, ca.50 nA at an operating potential of 15 kV, and the sample holder tilted towards the analyser entry lens.

Figure 2. Preliminary Result

As a proof of concept an aluminium foil supporting a copper mounting grid from a transmission electron microscope was placed on a conventional stainless steel stub. The resultant spectrum is shown, in figure 2, as obtained (a) and after subtraction of a linear background and conversion to binding energy (b), the two peaks revealed are in the appropriate place and ratio for the 2p components of copper.

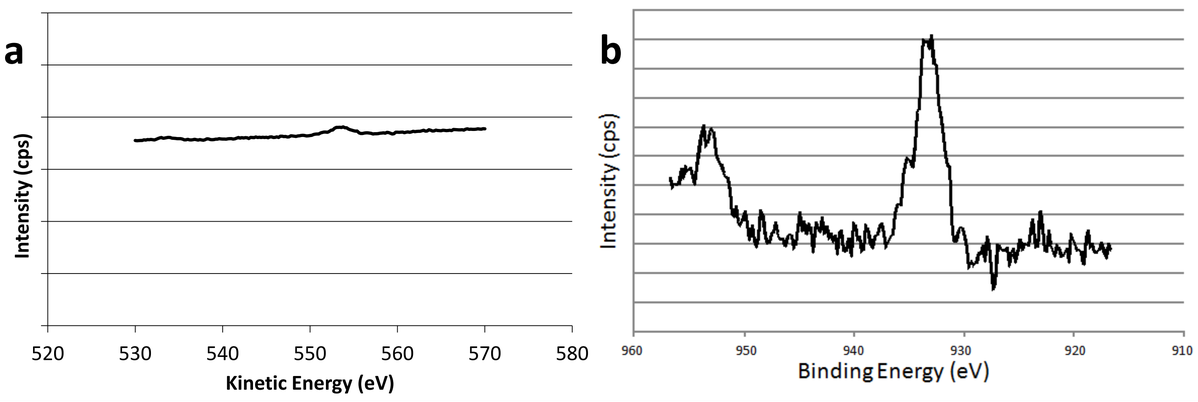


Figure 3 Precipitated copper powder:

To give some idea of the possibilities for obtaining chemical state from small particles a small amount of precipitated copper powder was sprinkled onto a polished aluminium stub. Figure 3a shows a particle of this powder resting on the stub. It is approximately 4 µm in width and the location of the electron beam is marked by the yellow cross near the top of the image. The resulting $Cu2p_{3/2}$ peak obtained using a CRR of 4 is shown in Fig.3b whilst Fig.3c shows the same region using a CRR of 10 to give improved resolution.

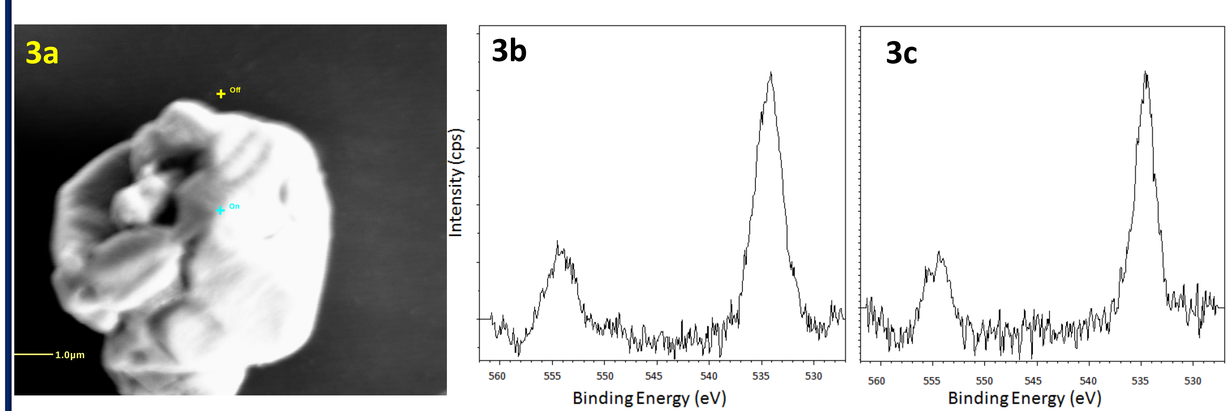


Figure 4. Measurement of Auger Parameter

A further, smaller, particle of copper was selected, as shown in Figure 4a. Both Cu *LLM* and Cu 2p regions were acquired, Figures 4b and c. Using this data and values from other similar particles after a range of treatments, the Auger Parameters are as given in Table 1

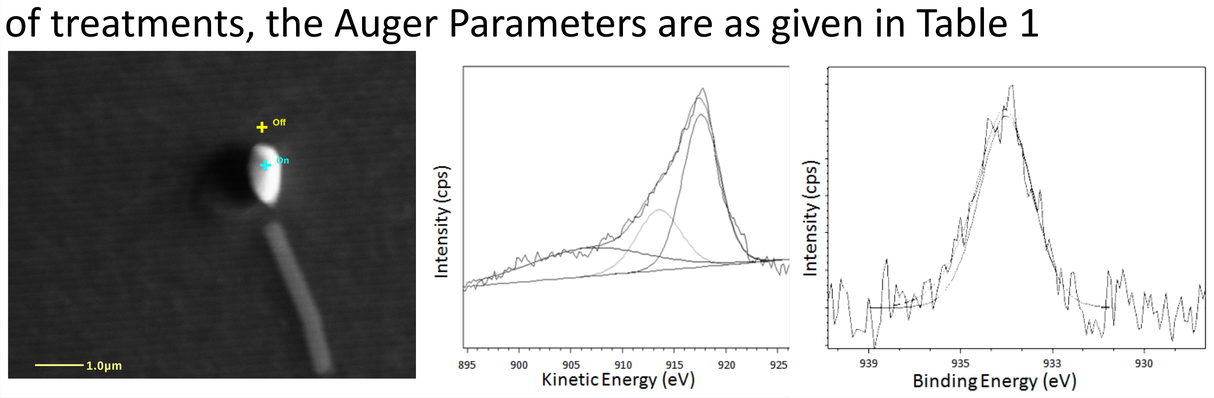


Table 1 Data and Auger Parameter

Treatment	Cu $L_3M_3M_3$ (KE)	Cu 2p (BE)	AP
Etched	917.2	934.5	1851.7
Unetched	917.9	934.0	1851.9
120° oxidation particle 2	917.6	934.4	1852.0
120° oxidation particle 3	917.9	934.0	1851.9

Discussion This work has demonstrated the feasibility of XPS analysis using locally generated Al Kα radiation. Both photo and Auger-electron signals can be obtained from a single, sub-µm, particle and thus chemical state identification by means of the Auger parameter is possible. The values for the copper particles used in this proof of concept are very close to the reported value for Cu(II)O of 1851.5 eV. However, in none of the analyses was there significant evidence of a divalent shake-up satellite. We thus conclude that the particles are in the metallic state (Cu metal, AP; 1851.2 eV). Either the oxide was too thin or the shakeup does not develop on small particles or it points to some degree of beam damage. In this work we were careful not to allow the electron beam to dwell directly on the particle. However it is possible that the aluminium became hot and enabled reduction of oxide on the copper particle. Work is continuing to optimise the method.

Conclusion: It is feasible to use a scanning Auger microscope for XPS analysis of nano-particles by proximal excitation of x-rays.