17.2.3 The appearance potential spectroscopies

These are electron spectroscopies based on the principle of measuring the threshold energies for the creation of excited states of matter. They range from inelastic electron tunnelling spectroscopy, concerned with the thresholds for the excitation of molecular vibrations at energies less than 500 meV, to the nuclear resonance capture spectroscopies at energies greater than 1 MeV. A particular feature is that no energy analysis of the decay of the excited states is required. It is the energy of the exciting particle that is recorded. The appearance potential spectroscopies used in surface studies all employ differentiation to separate the structure due to threshold excitation from the background of primary and scattered electrons.

Soft X-ray appearance potential spectroscopy (SXAPS)

In this technique, also known as *X-ray Appearance Potential Spectroscopy* (*XAPS*) or *Electron excited X-ray Appearance Potential Spectroscopy* (*EXAPS*), core holes are produced by an electron beam incident on the surface. As the energy of this electron beam is increased each threshold for the production of a core hole by electron excitation or ionization is marked by a sudden 'appearance' of soft X-ray fluorescence characteristic of the energy level concerned. These characteristic soft X-rays are superimposed on a large bremsstrahlung background and at each threshold there is a step in the total X-ray flux.

Incident: Variable energy electrons (100-2000 eV); beam diameter: 10 mm; angle of incidence: approx. normal to surface.

Detected: Soft X-ray photons. (approx. 50-1000 eV. No X-ray analysis. Total X-ray flux recorded. Angle of exit: almost all photons within the maximum 2π steradian are collected.

Spectrum: Total X-ray flux vs. primary electron energy (excitation energy).

Auger-electron appearance potential spectroscopy (AEAPS)

This spectroscopy is also known as *Electron-Excited Auger-Electron Appearance Potential Spectroscopy* (*EAAPS*) or *Incident Energy Modulation Method Spectroscopy* (*IEMM*). As in *SXAPS*, core holes are produced by an electron beam incident on the surface. As the energy of this electron beam is increased the threshold for the production of a core hole by electron excitation or ionization is reached. At the threshold for core hole production there is a sudden 'appearance' or increase in both the X-ray fluorescence yield and secondary electron current. The additional photons and Auger electrons produced at the core hole threshold are isotropically directed unlike the background of quasielastically reflected electrons and inelastically scattered electrons which in the latter case tend to be directed in the forward direction into the bulk of the sample. These soft X-ray photons and Auger electrons can produce further secondary electrons so the secondary electron current is greater after the threshold than before it.

Incident: Variable energy photons (100-2000 eV); beam diameter: 10 mm; angle of incidence: approx. normal to surface.

Detected: Secondary Auger electrons (50-1400 eV); angle of exit: usually 2π steradian.

Spectrum: Auger electron current vs. primary electron energy (excitation energy).

Disappearance potential spectroscopy (DAPS)

As with SXAPS and AEAPS core holes are created by a variable energy electron beam. At the threshold of excitation the electrons in the primary beam, which create the core hole, *disappear* from the beam. In DAPS it is the attenuation of the primary beam which is studied. As secondary processes do not contribute to this attenuation DAPS observes the excitation directly without any interference from the decay processes. The attenuation of the primary beam is small ($\sim$1 in 10^3).

Incident: Variable energy electrons (50-2000 eV, modulated with 0.1-1.0 volt a.c. at 6-10 Hz); beam diameter: 2-10 mm; angle of incidence: approx. normal to surface.

Detected: Attenuation of primary electron beam (ca. 1 in 10^3).

Spectrum: Electron current at sample (target current) vs.
primary electron energy (excitation energy).

Total (or target) current spectroscopy (TCS)

In TCS a beam of low energy electrons varied over the range 0-15 eV is incident on the surface and the threshold of secondary electron processes are recorded by monitoring the current to the target rather than by energy analysis of the secondary electrons. TCS is thus similar to DAPS but should not be confused with it. TCS is a very low energy technique and all the secondary electrons originate from the valence band whereas DAPS is a higher energy, core ionization technique. The TCS signal is displayed as a function of increasing energy, starting at zero incident energy. Thus, the low energy part of the spectrum is not influenced by the higher energy loss processes which take place simultaneously and which are observed in some of the other low energy techniques, for example EELS. TCS seems particularly suited to the study of work functions, chemisorption, physisorption and excitons.

Incident: Variable energy electrons, 0-15 eV (modulated at 430 Hz, 0.15 eV); angle of incidence: normal to surface.

Detected: Change in target electron current (ca. 1 in 10^3).

Spectrum: First derivative of target current with respect to incident electron energy vs. incident electron energy.

X-ray excited electron appearance potential spectroscopy (XEAPS)

This is a variable photon energy photoelectron spectroscopy. Monochromatic synchrotron radiation is incident on a surface and the photoelectron yield recorded as the frequency is varied. The XEAP spectrum shows distinct threshold peaks for core ionization processes.

Incident: Variable energy photons (100-1000 eV, synchrotron radiation); flux: medium to low; angle of incidence: not critical.

Detected: Electrons (approx. 0 eV to within a few eV of photon energy).

Spectrum: Photoelectron current (total yield) vs. photon energy.

Extended (electron) appearance potential fine-structure analysis (EAPFS)

This technique is based on the analysis of the fine structure close to the threshold for the excitation of a core electron by a variable energy electron beam. Thus, in terms of experimental technique EAPFS is similar to AEAPS and DAPS.

Incident: Variable energy electrons (200-2000 eV); angle of incidence: approx. normal to surface.

Detected: Elastically scattered electrons; angle of exit: 20-80° (not critical).

Spectrum: Second derivative of the elastic electron current with respect to the incident electron energy vs. incident electron energy.

Inelastic electron tunnelling spectroscopy (IETS)

An experimental technique measuring the junction tunnelling current as the applied potential difference is varied from zero to about one volt. In practice an audio frequency modulation voltage is applied to the junction in parallel with the applied potential difference and the tunnel current derivative is detected with a phase-sensitive lock-in amplifier. This signal is then differentiated to give the second derivative of the tunnelling current, which is plotted against applied potential difference, to give the inelastic electron tunnelling spectrum.

Incident: Variable energy electrons (0-1 eV) temperature: ≈ 1 K.

Detected: Tunnelling current.

Spectrum: Second derivative of tunnelling current with respect to applied junction voltage vs. junction voltage.