

### 17.7.2 Characterisation of surface elemental composition

#### **X-ray photoelectron spectroscopy (XPS or XPES) See 17.2.1.2**

The value of the binding energy of the electron for a particular photoelectron provides an elemental identification of the atom from which the electron was emitted and is particularly sensitive to the chemical environment through a "chemical shift" effect. This is associated with different atomic environments and is of considerable practical value in XPES. The chemical shifts arise from the sum of two effects, namely, a difference in the relaxation referred to above and a shift in the orbital energy due to the changed chemical environment.

The low escape depth for photoelectrons in solids means that XPES is a surface sensitive technique, about 20% of the measured signal intensity (the precise fraction depends on the material and the electron kinetic energy) arising from the outermost atomic layer of the sample. The measured photoelectron intensities can be related to the concentration of emitting atoms in the surface region and a relationship which has been extensively and successfully used, for instance for an adlayer, is the equation

$$\frac{Y_m}{Y_s} = \frac{\mu_m M_m \Theta}{N_A \mu_s \rho \lambda \cos \phi}$$

in which  $\Theta$  is the adatom surface coverage,  $Y_m$  the integrated photoelectron signal from a particular subshell of the adatom,  $Y_s$  the integrated signal from the relevant subshell of the substrate,  $\mu_m$  and  $\mu_s$  are the subshell photoionisation cross-sections for the adatom and substrate respectively,  $M_m$  and  $\rho$  are the molecular weight and density of the substrate, respectively,  $\lambda$  is the electron escape depth in the substrate for the particular substrate subshell photoelectrons,  $\phi$  is the angle of electron collection with respect to the sample normal and  $N_A$  is Avogadro's constant.

Various corrections have to be made to the signal intensities; the values of  $\mu$  and  $\lambda$  are now available. Extensive use of the above relationship together with comparisons with other methods of estimating surface concentrations suggest an accuracy of up to  $\pm 15\%$ .

Calibration is usually performed with respect to the C1s level of carbon at a binding energy of 284.9 eV, or to the Au 4  $f_{7/2}$  level at 84.0 eV.

#### **Auger electron spectroscopy (AES) See 17.2.4.**

It should be emphasised that the Auger process is inherently more complex than XPES (a single electron process) since it involves three electrons. Nevertheless it is unquestionably

the most frequently used electron spectroscopic technique in surface analysis. By reducing the dimensions of the incident electron beam it is now possible to obtain a lateral resolution of less than 50 nm in the scanning Auger electron microscope (SAM). In addition, it is possible to combine its surface sensitivity with ion-etching, so that information on the chemical composition as a function of depth may be obtained. Other variations include the utilization of photoelectrons and Auger peaks to give an "Auger parameter" which has been shown to be sensitive to the oxidation state of a given element. In general, electron-induced Auger spectra do not provide unambiguous information on the nature of adsorbed molecules in view of their sensitivity to electron beam-induced dissociation. However, fingerprint spectra for surface species can be obtained if care is taken in minimising the current in the electron beam with maximisation of the area of incidence. More important for adsorbates from this point of view are photon-induced Auger spectra, where less damage occurs in the layer. Recently, the orientation of molecules on surfaces has been investigated via the angular distribution of Auger electrons excited with synchrotron radiation.

### **Secondary ion mass spectroscopy (SIMS) See 17.3.**

The erosion of a solid sample due to bombardment with energetic particles - a phenomenon known as sputtering - is used in this technique for the purpose of surface analysis. The outermost layers are sputtered by the impact of suitable primary ions with an energy up to a few keV. The resulting secondary ions, with positive or negative charge are analysed in a mass spectrometer. The relative abundance of sputtered species gives analytical data about the composition of the removed surface layer. SIMS is a very sensitive surface analytical tool. At low primary ion currents surface monolayer may exist for hours before being completely removed (static SIMS). On the other hand SIMS is also capable of elemental depth profile analysis (dynamic SIMS).

### **Laser microprobe mass analysis (LAMMA) See 17.3.**

The microprobe can be used in transmission or reflection mode. The transmission mode is used for the study of thin specimens of bulk materials. It allows the qualitative analysis of all solid materials which can be prepared as microparticles, films or thin sections. In the reflection mode, the surface of solid samples can be analyzed without any pretreatment. The diameter of the laser impact spot may be as small as 2 $\mu$ m. In general, two regimes of ion production are used. Low (under  $10^8$  W cm<sup>-2</sup>) power density is used where molecular information is desired; in this case the fraction of emitted species which is ionised is quite small. High (over  $10^9$  W cm<sup>-2</sup>) power density is used to obtain elemental compositions; in this case the fraction of emitted species ionised can approach 100%.

### **Thermal desorption spectroscopy (TPD) See 17.3.**

It is usually assumed that the rate of desorption of a surface species from a single binding state follows the Arrhenius equation.

A fairly good estimate of the activation energy can be made from the peak-maximum temperature,  $T_p$ , if the preexponential term is known. The activation energy for desorption can be determined without assuming a value of the preexponential factor for all orders of reaction by varying the heating rate ( $\beta$ ) over a wide range (two orders of magnitude) and plotting  $\ln(\beta/T_p^2)$  vs.  $1/T_p$ . Whether a species is adsorbed molecularly or dissociatively can often be inferred from the desorption reaction order.