3 Photoelectron Spectroscopy (XPS and UPS), Auger Electron Spectroscopy (AES), and Ion Scattering Spectroscopy (ISS)

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3.1 INTRODUCTION

The most commonly used surface spectroscopic techniques are x-ray photoelectron spectroscopy (XPS), ultraviolet photoemission spectroscopy (UPS), Auger electron spectroscopy (AES), and ion scattering spectroscopy (ISS). XPS and UPS are similar techniques and can be grouped under photoemission spectroscopy (PES). All four techniques are used widely for the study of solid surfaces both in fundamental scientific studies and in applied studies of polymers, ceramics, heterogeneous catalysts, metals and alloys, semiconductors, nanoparticles, biomaterials, etc. They can provide information about composition, chemical state, electronic structure, and geometrical structure. Detailed reviews have been presented previously [1,2].

3.2 PHYSICAL PROCESSES

In this section, the underlying physical processes are outlined and the nature of the information provided by the resultant spectra is discussed.

3.2.1 PHOTOEMISSION

In PES, either x-rays (XPS) or UV photons (UPS) strike the surface of a sample in an ultrahigh vacuum (UHV) environment. Electrons are emitted as shown schematically in Figure 3.1A. The emission process has been described by Berglund and Spicer [3] in a three-step model, in which the first step involves absorption of an x-ray or UV photon and promotion of an electron from its ground state to the final state above the fermi level. The final state lies within the potential field of the solid.

![Figure 3.1](https://example.com/fig3.1.png)

**FIGURE 3.1** Schematic diagrams of the (A) photoemission, (B) Auger, and (C) fluorescence processes.
and satisfies the Schrödinger equation for that field. The second step is transport of the electron to the surface, and the third step is escape of the electron into the vacuum. Since the electron is generated within the potential of the solid, its wave function contains contributions from the solid even after it has escaped into the vacuum. In PES, the kinetic energies (KEs) of the emitted electrons are measured using an electrostatic charged-particle energy analyzer, from which their electron binding energies (BEs) can be calculated from the following equation:

\[ E_b = h\nu - E_k + \Delta\phi \]  

(3.1)

where

- \( E_b \) is the electron BE in the solid
- \( h\nu \) is the energy of the incident photon
- \( E_k \) is the electron KE
- \( \Delta\phi \) is the difference in work function between the sample and the detector material assuming that there is no charge at the sample surface

Typical XPS and UPS spectra are shown in Figures 3.2 and 3.3, respectively. The characteristics of these spectra are discussed below, as are the photon sources and energy analyzers used to perform PES.

**FIGURE 3.2** XPS survey spectra obtained from (A) an AgO sample after a 130°C anneal for 30 min and (B) an Ag₂O sample after a 300°C anneal for 30 min. (From Hoflund, G.B., Hazos, Z.F., and Salaita, G.N., *Phys. Rev. B*, 62, 11126, 2000.)
FIGURE 3.3  HeII UPS spectra of CO adsorbed on transition metals. The two peaks below 8 eV, in the group labeled P2, are induced by CO adsorption. The structure above 8 eV, P1, which varies from metal to metal, is due to emission mainly from the metal d-orbitals. For comparison, the photoelectron spectra of Ir4(CO)12 and gas-phase CO are shown. (From Gustafsson, T. and Plummer, E.W., Photoemission and the Electronic Properties of Surfaces, John Wiley & Sons Ltd., Chichester, U.K., 1978.)

3.2.2 AUGER EMISSION

The process of Auger emission is multistep, as shown in Figure 3.1B. The first step is the production of a core hole by ejection of a core electron as a result of interaction with either incident electrons or photons. The second step involves an electron in a shallower energy level undergoing a transition to fill the core hole. The energy difference is then available to a third electron, which is ejected as the Auger electron. Thus, the AES process involves three different electrons in two or three different energy levels, and the KE of the Auger electron produced from, for example, K, L1, and L2 electrons is given by

\[ E_{AE} = E_K - E_{L1} - E_{L2} - \Delta \]

where \( E_K \), \( E_{L1} \), and \( E_{L2} \) are the BEs of electrons in the K, L1, and L2 energy levels, respectively, and \( \Delta \) is a complicated term containing both the sample and spectrometer work functions, as well as many-body corrections that account for energy shifts during the Auger process and other electronic effects. The \( \Delta \) term is usually small (<10 eV) and varies with chemical state. The initial core hole can also decay by x-ray fluorescence, in which an electron in a shallower level drops into the core hole with emission of an x-ray photon as shown in Figure 3.1C. The probability of decay via an Auger
process is greater for light elements than that via fluorescence, as shown in Figure 3.4 for K-shell electrons [6]. Auger processes occur for all elements except hydrogen and helium, which have no or insufficient outer electrons. As can be seen from Equation 3.2, the Auger KE does not depend on the primary beam energy, and the threshold energy for the transition is that required to produce the core-level hole. A typical Auger spectrum in both the $N(E)$ and $dN(E)/dE$ modes, recorded from a polycrystalline Ag surface, using 1 keV primary electrons, is shown in Figure 3.5 [7].

### 3.2.3 Ion Scattering

In ISS, an incident flux of monochromatic inert-gas ions (typically of energies 500–2000 eV) impinges on a solid surface, followed by energy analysis of the ions scattered from the surface at
some preselected angle, as shown schematically in Figure 3.6. The ion–solid interactions can be approximated as elastic binary collisions between the ions and the individual atoms in the solid. This approximation works quite well because the collision times are short (10^{-15} to 10^{-16} s) compared to the time constant of a characteristic lattice vibration (10^{-13} s). The ion therefore strikes a surface atom and leaves the surface region before the recoiling atom has time to interact with the solid. The conservation of energy and momentum in the binary scattering process can be written as

\[ E_o = E + E' \]  
(3.3)  
\[ M_o V_o = M_o V_s \cos \theta + M_s V' \cos \phi \]  
(3.4)  
\[ 0 = M_o V_s \sin \theta - M_s V' \sin \phi \]  
(3.5)

and combined to yield

\[ \frac{E_s}{E_o} = \left( \frac{M_o}{M_o + M_s} \right)^2 \cos \theta \pm \left[ \frac{M_s}{M_o} \right]^2 \left[ \sin^2 \theta \right]^{1/2} \]  
(3.6)

The symbols in these equations are specified in Figure 3.6. In Equations 3.3 through 3.6, \( E_o \) is the KE of the incident inert-gas ion (set by the ion source), \( E \) is the KE of the scattered ion measured with an electrostatic energy analyzer, \( M_o \) is the mass of the primary ion (selected by the choice of inert gas), and \( \theta \) is the scattering angle determined by the experimental geometry. The variables are all known so that \( M_s \), the masses of the surface atoms, can be determined from the positions of the peaks in the ISS spectrum. If \( M_s/M_o > 1 \), then only the plus sign in Equation 3.6 applies and each target mass gives rise to a single peak in the spectrum of scattered intensity as a function of \( E/E_o \). If \( M_s/M_o < 1 \), then both signs apply, subject to the constraint

\[ \frac{M_s}{M_o} \geq \sin \theta \]  
(3.7)

and each target mass gives peaks at two energies in the above spectrum. ISS spectra obtained from a higher alcohol synthesis catalyst are shown in Figure 3.7 [8].
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3.3 SPECTRAL FEATURES

3.3.1 PES/XPS

XPS survey (also called wide scan) spectra obtained from Ag₂CO₃ before (a) and then after annealing at (b) 350°C, and (c) 500°C, each for 10 min in vacuum, are shown in Figure 3.8 [9]. In (A), many peaks are present, including the 3s, 3p, 3d, 4s, and 4p Ag peaks, as well as those of O 1s and C 1s. All these peaks arise from direct photoemission processes from core levels as shown in Figure 3.1A. A very small Na 1s peak can also be seen due to a low level of Na contamination. Tables of the BEs of core-level electrons are given in several references [10–12], so if an unknown peak is apparent at a particular BE, it can be identified. Ag and O Auger peaks are also present in Figures 3.2 and 3.8, produced by the process shown in Figure 3.1B, because core holes created by x-rays can also decay by an Auger process. Since the principal electronic shells usually contain electrons of different energies due to multiplet splitting, an Auger feature arising from the ionization of a particular core level consists of multiple peaks. Another feature in Figures 3.2 and 3.8 can be seen at and just above a BE of 0 eV. This is the valence band (VB) photoemission spectrum, due to the valence electrons of each element present. Its position and shape result from the chemical interactions (bonding) of the various elements.

Unmonochromatized x-ray sources contain several x-ray lines, each of which can cause core-hole ionization, giving rise to satellite peaks in an XPS spectrum. These satellite peaks can be removed using a monochromator, but this reduces the x-ray flux and, hence, the photoemission

![ISS spectra obtained from an aged catalyst after (A) insertion into the analysis chamber and after sputtering with 1 keV He⁺ for (B) 5 min, (C) 10 min, and (D) after a further 15 min using a 1:1 He⁺ and Ar⁺ gas mixture. (From Hoflund, G.B., Epling, W.S., and Minahan, D.M., J. Elect. Spec. Rel. Phenom., 95, 289, 1998.)](image-url)
signal strength. The satellite features appear at BEs lower than those of the primary peaks and are of considerably lower intensity (<10%) [10]. Structure is also apparent at BEs slightly higher (0–50 eV) than those of primary features, due to two types of electron energy loss processes: (1) excitation of plasmons and (2) production of inter- and intra-band transitions.

According to Equation 3.1 for a conductor, a raw spectrum should be shifted in energy by \( \Delta f \) in order to be able to plot \( N(E) \) versus BE. If \( \Delta f \) were to be known from the work functions of the sample and detector material, then the process would be simple. Where \( \Delta f \) is not known, which is invariably the case, the calibration shift can be made using a peak that corresponds to a given (known) chemical state. Most samples exposed to air accumulate hydrocarbon contamination resulting in a significant C 1s peak. The magnitude of the shift required is then often determined by assigning the BE of this C 1s peak to a value of 285.0 eV, but it is essential that this assignment be checked against the BEs of other peaks in the spectrum, to ensure they make sense chemically. If they do not, then differential charging is probably occurring, and the data must be retaken using charge compensation techniques. For insulating samples, the surface may charge to some arbitrary potential, which cannot be correlated with any physical or chemical variables.

Damage phenomena must always be considered when using surface techniques. XPS produces the least damage because x-rays interact weakly with a solid, but in conventional XPS, the close proximity of the sample to the source itself can cause thermal damage. Damage can occur by several
processes including bond breakage, and emission of particles by photon-stimulated desorption. The possibility of damage can be established by recording sequential spectra as a function of irradiation time. If the spectra change during the sequence, then damage has occurred, and the data collection parameters need to be changed to minimize it.

3.3.2 PES/UPS

In UPS, UV photons, rather than x-rays, are used as the excitation source. In many laboratories, UV sources at fixed energies, for example, HeI and HeII at 21.21 eV and 40.82 eV, respectively, are still used, but more information can be obtained with the help of the variable photon energy provided by a synchrotron (see also Chapter 7). As in XPS, the KEs and signal strengths of the photoelectrons are measured. Similar features are observed using either XPS or UPS to examine the VB, but their relative intensities differ due to variations in the ionization cross-section with photon energy. Another important difference is that the overall intensity of the VB photoemission signal is much greater in UPS than in XPS, because in the former the photon energy is of similar magnitude to that of the energy required for the excitation process (i.e., the Einstein Golden Rule). Since photoelectrons are initially elevated from a filled to an unfilled level, the structure of the density of states (DOS) influences the UPS signal; thus, although UPS occurs by the process shown in Figure 3.1A, and obeys Equation 3.1, the photoemission signal is modulated by the DOS of the unfilled levels just above the fermi level. The UPS VB spectrum therefore reflects a joint DOS. Since the unfilled DOS is much extended at energies far above the fermi level, and is essentially continuous there, such modulation is not a consideration in XPS.

In a synchrotron, the photon energy can be scanned using a monochromator. The initial (i.e., filled) DOS can be recorded by choosing a particular unfilled level (i.e., at a fixed KE) and by scanning the photon energy. The final (i.e., unfilled) DOS, on the other hand, can be obtained by scanning both photon and KE. Figure 3.9 shows the filled and unfilled DOS from the surface of α-quartz [13], recorded in this way. If 21 eV photons had been used, the feature at −10 eV would have been significantly reduced due to the low population of the unfilled DOS at 11 eV. The nature of the orbitals and their related selection rules also influence the intensities in the joint DOS.

![FIGURE 3.9](image-url)  
UPS can be used to obtain various types of information, the most obvious being VB electronic structure, as described above. Valence electrons are responsible for the chemical bonding that holds atoms together to form a solid; various quantum mechanical methods can be used to calculate the bonding structure, in particular the VB DOS, thus providing a direct means of comparison of calculated results with experimental data. Both crystalline and amorphous solids can be studied. Using angle-resolved UPS and synchrotron radiation, the complete band structure of single-crystal surfaces can be mapped along different crystal directions. An illustration of this approach is given in Figure 3.10, in which the band structure of a Be(0001) surface has been mapped out in the $\Delta$ direction [14]. Comparison is shown with the results of a calculation using an \textit{ab initio} self-consistent pseudopotential method in the local-density formalism. The agreement between the calculated and experimental results is quite good except near the plasmon threshold. Another important application.

\begin{figure}[h]
\centering
\includegraphics[width=0.7\textwidth]{figure3.10.png}
\caption{Calculated and experimental band structure of Be(0001) along $\Delta$. The thicker lines denote final states, which have large plane-wave components along $\Delta$. The dashed line is the corrected initial state used to determine the final state. Note that the vertical scale changes at $E_F$. (From Jenson, E., Bartynski, R.A., Gustafsson, T., Plummer, E.W., Chou, M.Y., Cohen, M.L., and Hoflund, G.B., \textit{Phys. Rev. B}, 30, 5500, 1984.)}
\end{figure}
of angle-resolved UPS, using synchrotron radiation, is the determination of bonding orientation of adsorbates on single-crystal surfaces [5,15].

### 3.3.3 AES

An Auger spectrum, in the derivative, \( dN(E)/dE \), mode, recorded from a sputter-cleaned Ni/Cr alloy foil, is shown in Figure 3.11 [16]. In the integral mode, Auger features appear as small peaks riding on a large background of inelastically scattered electrons, as seen in the lower two spectra in Figure 3.5. Differentiating the \( N(E) \) spectrum either electronically or numerically accentuates the Auger features relative to the background, which, as can be seen in Figure 3.5, is of much greater intensity. Ni and Cr features are present in Figure 3.11 at both low (<200 eV) and high KEs (>400 eV). The low KE features involve one or two valence levels in the Auger process, while those at high KE arise from three core levels. As with XPS, AES peaks can be identified from their KEs, using reference manuals [12,17–19]. When assigning a particular peak to an element, it is vital to check that all the other Auger peaks belonging to that element are present in the spectrum and with the correct relative intensities.

Damage is a very important consideration in AES since many types of sample are susceptible to electron-beam damage by a variety of processes. Such damage can be minimized by using a low

![Figure 3.11](https://example.com/figure3.11.png)

**FIGURE 3.11** Auger spectra obtained from (A) cleaned Ni/Cr surface and (B) after room temperature exposure to 100 L of oxygen. (The Langmuir [L] is not an SI unit, but remains in common usage. 1 L is defined as a dose corresponding to one monolayer coverage for a sticking coefficient of unity.) (From Hoflund, G.B. and Epling, W.S., *Chem. Mater.*, 10, 50, 1998.)
electron-beam flux coupled with pulse counting. For a homogeneous sample, the electron beam may be rastered across the surface to minimize beam exposure. As with XPS, damage can be detected in AES by recording sequential spectra and looking for differences, as a function of electron-beam exposure.

### 3.3.4 ISS

ISS spectra recorded from an higher alcohol synthesis (HAS) catalyst are shown in Figure 3.7. They exhibit a variety of peaks arising from different elements including O, Na, Cl, Zn, Al, P, K, and Ti. Each peak lies at an $E/E_0$ value close to that predicted by Equation 3.6.

Under the usual operating conditions, that is, light incident ion (He$^+$), relatively low incident ion energy (1–2 keV), and low incident ion current (10–50 nA), damage in ISS is negligible. However, when heavier ions are used, for example, Ar$^+$, often at higher energies, then there is a real danger of surface damage, which should be checked in a manner similar to that suggested for XPS and AES.

### 3.4 DEPTH SPECIFICITY

#### 3.4.1 PES/XPS/UPS

Both XPS and UPS are surface-specific techniques in that the information obtained originates within the outermost 6 nm. In both techniques, the incident photons penetrate deeply, and do not govern the depth specificity. The deciding factor is the attenuation length ($\lambda$) of the photoelectrons. The attenuation length is shown in Figure 3.12 as a function of photoelectron KE for elements, inorganic compounds, and organic compounds [20]. The probability of an electron traveling a given distance $x$ in a solid without scattering inelastically is given by

$$P(x) = ke^{-x/\lambda} \quad (3.8)$$

![Figure 3.12](image)

**FIGURE 3.12** Dependence of the attenuation length on the photoelectron KE for elements, inorganic compounds, and organic compounds. (From Seah, M.P. and Dench, W.A., *Surf. Interface Anal.*, 1, 2, 1979.)
where $k$ is a normalization constant. This equation and Figure 3.12 can be used to calculate the contributions to a given elemental peak for varying depths of the element beneath the surface. For any given element, the associated XPS peaks have different KEs and consequently different information depths. Over 90% of photo-emitted electrons originate from a depth less than $3l$, which defines roughly the depth specificity for a particular peak. The spectral features that have the greatest surface specificity are those with KEs near the minimum $l$ in Figure 3.12. For organic compounds such as polymers, this would be at about 18 eV, where $l$ is about 0.4 nm and the information depth about 1.1 nm, that is, between 5 and 8 atomic layers for most materials. For photoelectrons at higher KEs, around 1000 eV, from elements or inorganic compounds, $l$ is about 2.5 nm so that the information depth would be about 7.0 nm. Note that photoelectrons at very low KEs have low depth specificity. Photoelectrons emitted from the outermost atomic layers have the lowest probability of scattering inelastically so that they make the largest contribution to a peak. This contribution decreases exponentially with depth according to Equation 3.8.

XPS and UPS can be performed in angle-resolved modes in order to vary the information depth. For these modes, the only parameter that can be varied is the collection angle, as shown in Figure 3.13. If this collection angle is changed from normal to grazing by rotating the specimen (typically up to 80° off normal), a compositional profile can be obtained, with the help of various numerical procedures [21–23]. In UPS, variation of the collection angle can reveal differences in electronic structure and composition between the surface and the bulk. These differences include band bending and accentuation of some surface electronic states not allowed in the bulk electronic structure.

3.4.2 AES

The Auger electrons generated in AES obey the same scattering rules as do photoelectrons in XPS and UPS, and the Auger electrons in XPS. The difference in the technique is that both the KE and angle of incidence of the primary beam can influence the surface specificity. As the KE of the primary beam is decreased, the beam penetrates less deeply into the surface, thereby increasing the surface specificity. Also, if the incident angle of the primary beam is decreased from normal to grazing, the surface specificity is again increased, because although a grazing beam travels the same distance through a solid as would a normal beam, Auger electrons would then be originating nearer the surface, and the information depth decreases.

As in XPS and UPS, AES can also be used in the angularly resolved mode. There is more flexibility available in AES, because both the incidence and collection angles as well as the primary
beam energy can be altered, and all these influence the surface specificity [24]. An example is shown in Figure 3.14 [25]. The spectra shown there were collected, using a cylindrical mirror analyzer (CMA), from a Li-contaminated Ag sample after annealing in O₂. Spectrum (A) contains three prominent features due to Li, Ag, and O, and was collected in the conventional manner using a primary electron beam at normal incidence and a collection angle of 42° off normal. Spectrum (B) was recorded in a surface-specific mode using angles of incidence and collection of 45° and 7°, respectively, with respect to the surface plane. The Li and O peaks were unchanged but the Ag peak size decreased greatly, indicating that the Li₂O was present as a film covering the Ag.

3.4.3 ISS

Atomic scattering cross sections are in fact larger than indicated schematically in Figure 3.6, which means that a primary ion scattered from an atom in the second atomic layer cannot easily escape without being scattered again by a surface atom. This and the fact that any ion penetrating beneath the surface has a very high probability of being neutralized imply that ISS is almost entirely specific to the outermost atomic layer. However, the situation is not always clear-cut. Figure 3.15 shows two possible atomic configurations of the outermost layer. In Figure 3.15A, ISS spectral features will be present for both elements A and B, regardless of incidence angle or collection angle. On the other hand, in Figure 3.15B features will be present for both A and B only if near-normal incidence and collection angles are used. For any other angles, there will appear a peak only for element A.
3.5 COMPOSITIONAL INFORMATION

Since quantification is the subject of Chapter 8, it will not be dealt with here in any detail. In any case, UPS does not provide direct compositional information even though the shapes of features in a UPS spectrum do depend upon composition. XPS and AES can provide good compositional information, as pointed out in Chapter 8, but that usually involves making the assumption that the sample is homogeneous. Except for pure metals, relatively few samples have homogeneous near-surface regions, and the matrix effect (i.e., the spatial distribution of elements in the near-surface region of a homogeneous sample) can have a very large effect on peak intensities [26]. Therefore, any quantification based on the assumption of homogeneity must be viewed with great caution. XPS and AES equipment manufacturers make the homogeneous assumption when programming their software, without providing detailed information, which means that the compositions calculated using the software may be quite far from reality. However, as also described in Chapter 8, study of the shape of the inelastic background under spectra can provide useful information about elemental distributions in subsurface layers in inhomogeneous samples, so the situation is not as difficult as it might seem.

Deriving compositional information from ISS spectra is also challenging for two reasons. The first is that accurate cross-sections are not available for elements as functions of the type of scattering ion and its energy, and the cross sections increase significantly as elemental mass increases [27], so that heavy elements give rise to larger relative peaks than do light elements. The second difficulty involves the neutralization probability, that is, the percentage of ions colliding with an element, that is neutralized, which is very high, ~99%. Thus, small variations from one element to another in this probability can have large effects on quantification. Studies of neutralization using a combination of ISS and the measurement of the scattering of neutrals would be useful, but have not been performed, so the usual assumption is that the neutralization probability is the same for all elements.

Since absolute quantification of XPS, AES, and ISS is not easy, another approach is to use relative quantification, that is, to compare spectra from related surfaces. This could take the form of preparing a number of samples in which just one parameter was varied systematically, and then collecting and comparing spectra. Even small differences in the spectra would then be significant and interpretable. A similar approach would be to subject a sample to various treatments in UHV, and again collect and compare spectra. The treatments could be oxidation, reduction, ion sputtering, annealing, etc., and the sample might oscillate between two distinct states as a result of these treatments. In a study of TiO$_2$(001) [28], sequential reduction, oxidation, and sputtering was applied, with analysis after each treatment by XPS, AES, and ISS, and it was found that the chemical state at the surface changed systematically and reproducibly with the various treatments, in a cyclical manner. The study demonstrated that very small changes in features or lineshapes in spectra can be significant.

A useful way of reporting comparative XPS, AES, and ISS data is by way of peak-area ratios (in the case of AES, in the undifferentiated $N(E)$ vs. $E$ spectra). Such ratios contain both compositional and matrix effects, of course, but the use of ratios tends to minimize those effects, and the resultant relative compositions are more accurate than those based on the assumption of homogeneity.
3.6 ELEMENTAL SENSITIVITY

The question often arises as to what are the elemental sensitivities in XPS, AES, and ISS. The answer is complex because the elemental sensitivity depends upon the technique, the element, the nature of the sample, including compositional and matrix effects, the instrument used, and the parameters used for data collection. Each of these is discussed below.

The three techniques XPS, AES, and ISS have different information depths, dependent in the first two on experimental conditions. ISS collects information from the outermost surface layer only, while in AES the information depth is governed by the incident and collection angles, and the primary beam energy; in XPS, it is determined by the incident photon energy and the collection angle. Thus, the observed sensitivity of a technique to any one element will depend on the spatial distribution of that element. If an element is not located in the outermost couple of layers, but is distributed in the immediate subsurface layers, then it will not appear in ISS spectra, but may yield large XPS and AES features. Again, an element spread uniformly over a surface will give rise to a larger signal for all three techniques compared to the same amount of that element present as clusters [26]. In a multielement sample, there may be overlapping peaks, which would affect sensitivity, since less prominent, but well-separated, peaks might have to be used.

The relationship between elemental sensitivity and the nature of the physical process is also different in each of the techniques. It is simplest for ISS, in that the scattering cross section increases monotonically with mass. In AES, the Auger electron yield per K-electron vacancy is higher than the x-ray yield for lighter elements, but becomes lower for heavier elements [6]. Relative sensitivity factors are provided by equipment suppliers for XPS and AES since the factors will depend on the analyzers used, and can vary by factors of 30–100. Thus, some elements are easier to detect than others. Using both AES and XPS can be advantageous because a given element may have a large sensitivity factor in one technique and a small one in the other. Carbon is an example, having a relatively high sensitivity factor in AES but a low one in XPS. Thus, a C-contaminated surface may appear to be relatively clean when using XPS but not when using AES.

Hydrogen is an element that is virtually impossible to detect with these methods. This is unfortunate because surface hydrogen is often present and can determine the chemical behavior of a surface. Surface hydrogen has been observed directly using ISS [29,30] but only at extremely small scattering angles that are not accessible with most ISS systems. Hydrogen has no core-level electrons so it cannot be observed directly with either XPS or AES, but it can sometimes be observed indirectly by XPS because of its presence as part of a surface group. For example, hydroxyl groups on oxide surfaces yield O 1s peaks at higher BEs than the oxide O 1s peaks. If it is necessary to establish that hydrogen, or an H-containing molecule, is definitely present, then either one of the SIMS family of techniques, or electron stimulated desorption (ESD), must be used.

All the various instruments available for XPS and AES produce different signal intensities for a given element for reasons such as differences in sample area analyzed, in electron optics and analyzer transmission function, and in type of electron detection. These topics are discussed in detail later in this chapter. The data collection parameters used can also have a great influence on elemental detectability. Elemental detectability can always be improved via the data collection parameters; for example, a small peak can be amplified by making multiple (N) scans over the energy range around the peak for a long time. The number of counts increases with N, but the background noise increases with $\sqrt{N}$. Using a lower energy resolution setting also increases the signal strength, but at the cost of poorer spectral resolution.

3.7 CHEMICAL-STATE INFORMATION

Of these techniques, XPS offers the best ability to provide chemical-state information. In this context, chemical state is often taken to mean that of an element in one or other of its known various valence states. What XPS actually measures is the influence on the BE of a given orbital of the
electronic structure surrounding an element, whether the element is in a well-defined valence state or not. This is a more general definition of chemical state that is appropriate to the interpretation of XPS data. For example, on a completely oxidized surface, the metallic constituent may indeed be in one well-defined valence state. However, bombardment with energetic inert-gas ions will remove selectively oxygen atoms and ions, leaving an oxygen-depleted surface (i.e., a sub-valent oxide, see Chapter 10). The metallic element may then be reduced to a range of intermediate valence states, which is usually reflected in the XPS spectra [31].

Following their discovery in 1954 [32] that photoemission spectra could be used for elemental identification, Siegbahn et al. went on to demonstrate [33] that spectral shifts could be used to provide chemical-state information. Their classical example [34] is that of ethyl trifluoroacetate, whose C 1s spectrum is shown in Figure 3.16. Each of the four carbon atoms in this molecule has a different chemical environment, resulting in four different C 1s BEs, as seen in Figure 3.16. In most cases, however, BE shifts are not as obvious as in Figure 3.16 and may be difficult to detect.

This point is illustrated by the high-resolution spectra recorded from Kapton (a polyimide polymer used for coating spacecraft in orbit at altitudes of 200–700 km) [35]. The structure of Kapton is shown in Figure 3.17; it can be seen that the C atoms are in six different chemical positions and the O atoms in two. Survey spectra taken before and after exposure to atomic oxygen (AO) and to air give the compositions (calculated on the basis of a homogeneous distribution) shown in Table 3.1.

![Figure 3.16 C 1s XPS spectrum recorded from ethyl trifluoroacetate, whose molecular structure is shown at the top. The four C atoms are each in a different chemical environment, giving rise to peaks at four different BEs. (From Siegbahn, K., Nordling, C., Fahlman, A., Nordberg, R., Hamrin, K., Hedman, J., Johansson, G., Bergman, T., Karlson, S., Lindgren, I., and Lindberg, B., Electron Spectroscopy for Chemical Analysis—Atomic, Molecular and Solid-State Structure Studies by Means of Electron Spectroscopy, Almquist & Wiksells, Stockholm, 1967.)](image-url)
The as-received Kapton surface had a composition close to the theoretical, while on AO treatment, the O 1s peak intensity decreased significantly compared to that of the C 1s. However, the high-resolution C 1s, O 1s, and N 1s spectra in Figure 3.18 provide much more information. In the as-received state (a), the C 1s spectrum contains one large and rather broad peak, corresponding to unresolved peaks due to the C atoms labeled 1–5 in Figure 3.17, and a smaller peak at higher BE that can be attributed to the C atom in position 6, bonded to carbonyl. With increasing AO exposure, the smaller peak diminished, thought to be a result of surface reaction to form CO₂, which desorbed. At the same time, the peak in the O 1s spectrum due to carbonyl also decreased, but to a greater extent than the C(6) peak, so that the O/C compositional ratio also decreased. If this interpretation is correct, then the N 1s spectrum should also have altered, since all the N atoms in Kapton are bonded to carbonyl groups, and indeed that is what was found, as can be seen from the N 1s spectrum. With AO exposure, the predominant N 1s peak diminished as a new one formed at a lower BE and increased in intensity.

In some previous studies on Kapton [36,37], it was found that the surface oxygen content increased with AO exposure, contrary to the above observations. In those studies, the samples were exposed to air after the AO exposure and before taking XPS data. After the 24 h AO exposure, the sample described above was exposed to air for 3h and then analyzed again, whereupon the O content was found to have nearly doubled. This demonstrates that it is important to carry out such experiments in situ in order to understand the processes occurring during AO exposure, since air exposure alters the results.
In some cases, air exposure between treatment and XPS analysis does not affect the results, but this should always be tested and never assumed. An example is shown in Figure 3.19 [38]. In this study, Pd metal, anhydrous PdO, and hydrous PdO powders were given various treatments in a catalytic reactor operating at 1 atm, exposed to air, and then analyzed. The spectrum shown in (a) was taken from Pd metal powder that had been reduced in hydrogen in the reactor, and consisted of only the metallic Pd 3d features, indicating that the reduction was complete, and that air exposure at room temperature did not result in oxidation of Pd. Spectrum (b) was recorded after exposing the reduced Pd metal powder to methane oxidation conditions in the reactor, transferring the sample in air to the XPS system, and then collecting XPS data. Features due to both Pd metal and PdO were clearly present, which is interesting because the reaction mixture consisted of methane, which is a reducing species, and oxygen, an oxidizing species. This spectrum thus indicates that a layer of PdO had formed over the Pd metal, showing that PdO was the catalytically active species under the conditions.

The spectra shown in (c) and (d) were from fresh anhydrous PdO before and after reduction, respectively, in hydrogen in the reactor. The treatment converted the near-surface PdO back to metallic Pd, but there was peak broadening on the high-BE side due to the presence of subsurface PdO. A similar treatment on hydrous PdO gave similar results, as shown in (e) and (f). A mild sputter treatment with Ar ions also reduced hydrous PdO to Pd metal as shown in (g).

In order to understand the behavior of a complicated system, the different elemental spectra from all the elements involved should be compared, and consistency attained. Analysis of the spectrum from just one element may give a partial explanation, but a more complete explanation can be found only by analysis of all of the relevant peaks. This also provides a check on the consistency of the analysis, since if it is found that changes in all the spectra are not self-consistent, then the interpretation must be rethought. For example, consider the thermal decomposition of silver carbonate (Ag₂CO₃) as studied by XPS [9]. A fresh silver carbonate powder sample was analyzed before and
FIGURE 3.19 High-resolution Pd 3d XPS peaks from (a) and (b) Pd powder after hydrogen and methane/oxygen oxidation, respectively, (c) and (d) anhydrous PdO before and after reduction, respectively, (e) and (f) hydrous PdO before and after reduction, respectively, and (g) PdO after ion sputtering. The specimens were exposed to air between each treatment. (From Hoflund, G.B. and Hagelin-Weaver, H.A.E., to be published.)

after annealing at 350°C and then at 500°C (survey spectra shown in Figure 3.8). The resultant Ag 3d spectra are shown in Figure 3.20A, in which the peaks recorded from the fresh sample exhibited a single peak at a BE characteristic of either Ag$_2$CO$_3$ or AgO. Although the sample was nominally Ag$_2$CO$_3$, the presence of AgO could not be eliminated. After annealing at 350°C, another single peak was present with a BE characteristic of Ag$_2$O, suggesting that Ag$_2$CO$_3$ decomposes by losing a CO$_2$ molecule to form Ag$_2$O. Annealing at 500°C resulted in another single Ag 3d peak at the BE characteristic of Ag metal, due to desorption of O$_2$.

Now consider the corresponding O 1s and C 1s spectra shown in Figure 3.20B and C, respectively. Again, the spectra labeled (a) in these figures were obtained from fresh Ag$_2$CO$_3$. The predominant O 1s peak was due to either Ag$_2$CO$_3$ or AgHCO$_3$. The presence of a significant shoulder due to hydroxyl groups or possibly water suggests the presence of bicarbonate. No O 1s features due to Ag$_2$O or AgO were present, which indicates that these species were absent and the Ag was present as Ag$_2$CO$_3$. The corresponding C 1s spectrum exhibits two well-defined and well-separated peaks due to carbonate/bicarbonate species and adsorbed hydrocarbons, respectively, the latter being present on all air-exposed surfaces. Annealing at 350°C produced the spectra shown in (b). A C 1s peak was not positively identifiable in the survey spectrum, and the O 1s peak was reduced by a factor of about 3 as the Ag$_2$CO$_3$ was converted to Ag$_2$O, consistent with the O 1s spectrum (b) in Figure 3.20B, which exhibits a well-defined Ag$_2$O feature as well as a feature due either to hydroxyl groups or to adsorbed water. The spectrum in the C 1s region was essentially noise. After annealing at 500°C, the O 1s peak in the survey spectrum decreased greatly, while the
high-resolution O 1s spectrum indicated that the low level of oxygen remaining was present as hydroxyl groups/water, subsurface dissolved oxygen, and Ag$_2$CO$_3$/AgHCO$_3$. The C 1s feature was consistent in that a small amount of Ag$_2$CO$_3$/AgHCO$_3$ was present as well as some hydrocarbons. This group of spectra demonstrates that the chemical behavior of the system was much more complex than that indicated by the Ag 3d spectra on their own.

In principle, chemical-state information can also be derived using AES, by observing changes in peak shapes and positions, but the complexity of the Auger process means that interpretation is usually too difficult. No chemical-state database has yet been formulated for AES. There are, however, special cases where AES can provide useful chemical-state information.

### 3.8 SPECTRAL RESOLUTION

It can be seen in the above examples that peaks recorded at high resolution often overlap. Ideally, peaks would be very narrow and well separated. In practice, they are broadened by three factors: (1) the full width at half-maximum (FWHM) of the x-ray line, $\Delta E_x$, (2) the width of the analyzer energy window, $\Delta E_A$, and (3) the natural line width of the orbital in the atom, $\Delta E_2$. The overall energy resolution ($\Delta E$ in units of eV) is given by

$$\Delta E = \left( \Delta E_x^2 + \Delta E_A^2 + \Delta E_2^2 \right)^{1/2}$$

(3.9)

$\Delta E_2$ cannot be altered, while the analyzer energy window width can be set so that it does not limit resolution. Thus, it is the x-ray line-width that usually limits the overall energy resolution in XPS, which is the critical factor in the unambiguous extraction of chemical-state information. Mg K$_\alpha$ x-rays have a natural line-width of 0.70 eV, while line widths from other possible anode metals can be as broad as several electron volts (Table 3.2). Reduction in x-ray line-width, and hence improvement in resolution, can be achieved by the use of a monochromator. For example, the Mg and Al K$_\alpha$ widths can be reduced to about 0.35 eV. Monochromatization also removes the x-ray satellite lines and most of the Bremsstrahlung background, leading to cleaner spectra. The disadvantage of a monochromator is that the incident x-ray flux is reduced significantly (by as much as a factor of 40), thereby reducing the photoemission signal strength. Improvements in signal detectability, for example, multichannel detection, are beginning to overcome this problem. When a spectrum contains...
several closely spaced and overlapping peaks whose separation and identification is essential for the analysis, then it is worth compromising on the loss in signal strength caused by using a monochromator.

According to Equation 3.1, only core levels with BEs less than the energy of the x-ray line can be ionized, which, with the conventional Mg and Al sources, can occasionally be a limitation. Photoelectrons from levels with higher BEs can of course be excited by x-rays of higher energy. One source that has been found useful for that application is Ti, whose $K_{\alpha}$ line energy is at $\sim 4510$ eV.

However, the line width is 2.0 eV, so that the energy resolution, and hence the ability to acquire chemical-state information, is much reduced. The situation is not helped by the fact that chemical shifts in core levels at higher BEs are usually small.

The cross-section for photoemission of an electron in a core or molecular level is dependent on the photon energy. An important consequence of this statement relates to the VB electrons that have large cross-sections for photoemission by UV light but very small ones for photoemission by x-rays. One good choice of anode for XPS VB photoemission is therefore Zr, for which the $M_{\alpha}$ line has a photon energy of 151.4 eV and a line width of $\sim 0.77$ eV. With Zr $M_{\alpha}$ radiation the VB cross-sections are large, the spectral resolution is not significantly limited by the photon line-width, and electrons in core levels with BEs between 20 and 145 eV can also be excited. The latter are not accessible with most UV sources and are useful because they are quite sensitive to chemical state, even if a compositional analysis cannot be made.

Curve-fitting techniques to separate the contributions of the various species are widely used, and manufacturers usually supply programs for them, but, caution should be exercised when using them.

### TABLE 3.2

<table>
<thead>
<tr>
<th>Source*</th>
<th>Energy (eV)</th>
<th>Line Width (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr $M_{\alpha}$</td>
<td>151.4</td>
<td>0.77</td>
</tr>
<tr>
<td>Mg $K_{\alpha}$</td>
<td>1253.6</td>
<td>0.70</td>
</tr>
<tr>
<td>Al $K_{\alpha}$</td>
<td>1486.7</td>
<td>0.85</td>
</tr>
<tr>
<td>Mono-Al $K_{\alpha}$</td>
<td>1486.7</td>
<td>0.26</td>
</tr>
<tr>
<td>Mono-Si $K_{\alpha}$</td>
<td>1739.9</td>
<td>0.35</td>
</tr>
<tr>
<td>Zr $L_{\alpha}$</td>
<td>2042.4</td>
<td>1.7</td>
</tr>
<tr>
<td>Au $M_{\alpha}$</td>
<td>2122.9</td>
<td></td>
</tr>
<tr>
<td>Ag $L_{\alpha}$</td>
<td>2984.3</td>
<td>1.3</td>
</tr>
<tr>
<td>Mono-Ti $K_{\alpha}$</td>
<td>4510.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Mono-Cr $K_{\alpha}$</td>
<td>5946.7</td>
<td>2.0</td>
</tr>
<tr>
<td>Mono-Cu $K_{\alpha}$</td>
<td>8047.8</td>
<td>2.4</td>
</tr>
</tbody>
</table>


* "Mono" refers to use of a monochromator.
It is all too easy to allow a program free rein to produce a fit involving many component peaks, some of which may have no chemical or physical meaning. If possible, it is better to have available a set of peak shapes and positions of all the species that may be present, and then to add these together in the appropriate proportions to obtain an envelope that is the best fit to the experimental one. The use of an x-ray monochromator for recording both the experimental envelope and the spectra of the standards yields the best results.

3.9 DEPTH PROFILING

Most samples encountered are layered, either naturally or intentionally, or are otherwise spatially inhomogeneous, over depths greater than the information depths available with these techniques. The layer structure or the inhomogeneity can in principle be uncovered by depth profiling using inert-gas ion sputtering [45]. Surface analysis performed after each sputtering dose then provides some sort of elemental depth profile. However, there are several processes that may distort the compositional profiles so obtained, and in addition there is the problem of ion-beam damage leading to chemical reduction of some species. Nevertheless, under carefully controlled conditions it can prove useful. Analysis of buried information is discussed in Chapter 10.

3.10 MODULAR INSTRUMENTATION

The four techniques described here generally share a similar instrumental platform and have a functional modularity, but of course the actual components used for a module vary with the technique. In this section, upgrades to existing modules, as well as new modules that have been introduced in the last 10 years, are discussed. In the following sections, the modules for each of the techniques are discussed individually, concentrating on the commercially available instruments and their figures of merit, and also on emerging developments in the types of samples analyzed and the conditions under which they can be analyzed.

3.10.1 EXCITATION SOURCES

The primary excitation sources are a flux of vacuum ultraviolet (VUV) light for UPS, of x-rays for XPS, of electrons for AES, and of ions for ISS. Ideally, all the particles making up any one flux are identical, that is, the photon and the electron fluxes would be mono-energetic, and the ion flux would consist of ions of a single mass, energy, and charge.

3.10.1.1 UV Sources

In conventional UPS, UV photons are produced using an inert gas, usually He but occasionally Ne, in a plasma-discharge lamp. If He is being used, then, according to the pressure of He in the discharge capillary, either the HeI line at 21.21 eV or the HeII at 40.82 eV can be selected. Control of the gas pressure in the discharge zone is crucial, particularly when trying to maximize the HeII or NeII line intensity, and it is normal to leave a lamp operating for a long time continuously once it has started, to save time. A system of differential pumping in the source housing ensures that UHV can be maintained in the experimental chamber. The line-widths of the resonant lines are narrow (∼20 meV), so that, unlike the x-ray sources for XPS, there is negligible contribution to instrumental broadening from the UV source. The most important application of UPS is in the angle-resolved mode, in which the angular orientation of the specimen, as well as that of the analyzers, can be changed, so that all emission angles are covered.

As discussed in Section 3.3.2, UPS can also be performed using radiation from a synchrotron, and indeed much additional and valuable information can be gathered by so doing. For a full description of the design of, and techniques available with, synchrotrons, see Chapter 7.
3.10.1.2 X-Ray Sources

X-rays are generated by accelerating electrons emitted from a heated filament onto a metal anode with an applied voltage of 10–15 keV. The x-ray spectrum so generated consists of a continuous radiation band (Bremsstrahlung) on which discrete lines characteristic of the anode material are superimposed. For a standard x-ray source using a dual Mg/Al anode source, a thin aluminum foil is interposed between the anode and the sample, to reduce the Bremsstrahlung background, to prevent stray electrons from hitting the sample, and to maintain the UHV in the system. Since the imaginary component of the atom scattering coefficient decreases monotonically with increasing energy both before and after an absorption edge, the thin aluminum foil functions as an imperfect high-energy cutoff filter. Without monochromatization, seven different Mg or Al K-emission lines are produced: the unresolved K\(_{\alpha1,2}\) and the K\(_{\beta3,4}\), K\(_{\gamma3}\), K\(_{\delta6}\), and K\(_{\pi}\) lines [10]. Of these, the K\(_{\alpha1,2}\) lines are the most intense. Thus, an XPS spectrum will contain peaks excited not only by K\(_{\alpha1,2}\) but by the other five emission lines as well. The peaks excited by the minor emission lines are called satellites. The K\(_{\alpha3}\) and K\(_{\alpha4}\) source satellites are of sufficient intensity (3%–8% of the principal lines) for many vendors to provide a software algorithm that allows them to be stripped from the observed spectra.

For complete removal of satellite lines, and nearly all the Bremsstrahlung radiation, coupled with a valuable improvement in line width, an x-ray monochromator should be used. It so happens that, for Al x-rays, diffraction from the (1010) plane of a quartz crystal at a Bragg angle of 78.5° selects the larger component of the K\(_{\alpha}\) doublet, and rejects all other wavelengths. If then the x-ray source anode is placed at a particular point on a focussing sphere (often of diameter 0.5 m), the quartz crystal at another, and the sample at a third, x-rays will be dispersed by the crystal and refocussed on the sample. In this way, the line width of the Al K\(_{\alpha}\) radiation is reduced from 0.85 to 0.35 eV. Another advantage of a monochromator is that the hot anode is removed from the near vicinity of the sample, thereby eliminating any possible degradation of the sample by heating. However, a disadvantage is that the x-ray intensity is reduced by a factor of up to 40. In principle, it is also possible to use Ag L\(_{\alpha}\), Ti K\(_{\alpha}\), and Cr K\(_{\beta1}\) radiations in monochromators, since their photon line-energies are multiples of Al K\(_{\alpha}\) which means that a quartz crystal could again be used for dispersion.

The use of higher energy x-rays for special applications is becoming more common, and many vendors sell sources with anodes other than Mg and Al. Table 3.2 is a tabulation of x-ray sources in current use. They are all commercially available except for monochromated Si K\(_{\alpha}\) [39] and Cu K\(_{\alpha}\) [40,41]. The former uses a quartz crystal at a Bragg angle of 56.85°, but requires special procedures to prepare the Si anode. The latter uses an LiF(220) crystal.

Several different figures of merit can be used to characterize optical sources, and, in principle, similar ones may be used to compare XPS sources. One such figure of merit is the spectral radiance (L\(_{\lambda}\)), defined as the radiance (power per unit area per steradian) per unit wavelength with SI units of W m\(^{-2}\) sr\(^{-1}\) m\(^{-1}\), although the units W m\(^{-2}\) sr\(^{-1}\) nm\(^{-1}\) are usually used [46]. Since h\(\nu\), and not \(\lambda\), is the parameter usually used in XPS, the analogous figure of merit might be L\(_{h\nu}\), with units of W m\(^{-2}\) sr\(^{-1}\) eV\(^{-1}\). This would be a very useful parameter for comparing sources with different anode materials operating at the same source power, but, unfortunately, is not provided by suppliers, so that research workers simply have to make qualitative comparisons based on the source power (in W), as determined by the maximum filament current and the maximum voltage that may be applied to the anode. On output this energy appears mainly as thermal energy, which is usually removed by cycled chilled water. Only about 1% appears as spectral energy. Radiance can be calculated from the source power provided that the area of the source, the solid angle of emission, and the efficiency of conversion of supply power to photon power are known. To determine the spectral radiance, the actual spectral distribution is needed. Several factors determine the spectral distribution of the x-ray source. One is the geometry, as shown in Figure 3.21, for the x-ray photon intensity distributions of three different source geometries [47]. A second is the target material of the source for a fixed geometry and electron power, as shown in Figure 3.22 [47]. In Figure 3.23, it can be seen that the intensities of the


x-ray lines as a function of electron power all increase monotonically, but the slopes depend on the individual material [47]. In order to evaluate experimental differences in photoionization cross-sections for different sources, the measured intensities must be referenced to a standard level recorded using all sources.

One new source that is not yet commercially available, but has great potential, is the table-top synchrotron [48], in which the radius of the electron orbit is a mere 15 cm. Under the operating conditions described in Ref. [48], it has a spectral radiance similar to that of a rotating anode, that is, a factor of about 10 brighter than that of a fixed anode. The spectral radiance can be increased by a judicious choice of target. However, the real potential of a synchrotron lies in its ability to tune the emergent x-rays over an energy range of several keV up to 20 MeV. Furthermore, the spectral distribution function is almost flat over this range, that is, nearly ideal. Many important photoemission studies that cannot be performed with classical x-ray sources can be with synchrotron radiation. The use of radiation from large diameter (tens of meters) synchrotrons also allows chemical imaging at a lateral resolution of around 20 nm using a photoelectron microscope. Unfortunately, there are only about 50 operational synchrotron facilities worldwide, and there is greater demand than time available. Although the table-top synchrotron, at its present level of development, will not achieve 20 nm lateral resolution, it is likely to be reasonably affordable compared to large synchrotrons, thereby allowing greater numbers of research workers to carry out experiments of greater sophistication.

### 3.10.1.3 Electron Sources

Electron sources for AES and SAM consist of an emitter, either thermionic or field emission, a set of electron lenses for beam focus and transport, and an optional electron energy selector for high-energy resolution. Almost all electron guns provided by suppliers come with a four-pole electrostatic deflector, which allows the beam to be moved in any direction perpendicular to the optical axis; the deflection system for scanning Auger microscopy (SAM) is more complex. The beam stability is determined by the power supply. Figures of merit used for these electron sources are radiance, spot size, and energy spread, and a comparison of them for the various sources is shown in Table 3.3. The suppliers normally make this information available.

Field-emission sources have radiances that are similar to those of synchrotron sources; for example, a synchrotron source operated at 3 GeV and 300 mA stored beam current, an x-ray conversion efficiency of 0.01, a solid angle of $2\pi \times 10^{-3}$ sr, and an area of 0.1 mm$^2$, has a radiance of
∼2 × 10^{11} \text{ W mm}^{-2} \text{ sr}^{-1} [50], to be compared to those quoted in Table 3.3 for field emission. The energy spread in field-emission sources rivals those of x-ray sources used for XPS. They are used in the more sophisticated SAM instruments, where lateral resolution in the nanometer range is currently the best achieved in dedicated laboratory instruments. The lifetimes of the various types of filament are determined by the material properties and the operating conditions. On the horizon is a new field-emission cathode, based on an array of carbon nanotubes. It has been demonstrated that a single carbon nanotube with a tip diameter of ∼20 nm has a brightness that is a factor of 10 greater than that of conventional field emitters [51]. Field-emission carbon-nanotube cathodes have been used to make miniature x-ray sources with brightnesses comparable to classical ones [52]. However, the x-ray line-widths are much too large for photoemission.

### 3.10.1.4 Ion Sources

Ion sources for ISS comprise a beam of ions, electrostatic lenses for focus and ion transport, an optional mass filter, and an optional energy filter/selector. They are available with or without deflectors, the latter being used mostly for sputter cleaning. The most commonly used ion is He⁺, but Ne⁺ and Ar⁺ have also been employed; the ions are generated from the gases by electron impact ionization. Alkali metal ions, that is, Li⁺, Na⁺, and K⁺, produced by the surface ionization of directly heated alkali aluminosilicate plugs are also used. Figures of merit for ion sources include the ranges of beam energy, beam current, and spot size, and the spread in the beam energy; beam current and spot size are adjustable independently. Typical operating parameters for a noble-gas ion source for ISS are as follows: beam energy 10 eV–5.0 keV, beam current 1–50 nA, spot size 1–20 mm, and energy spread <5 eV at low current. For an alkali ion source, the corresponding figures would be as follows: beam energy 50 eV–5.0 keV, beam current 1–100 nA, spot size 1–10 mm, and energy spread 0.4 eV (calculated for thermal spread).

The typical energy range for primary ions used in ISS is in fact 1–2 keV, which means that the energy spreads for the sources are acceptable, and an energy selector would be an unnecessary expense. Mass filters, which actually filter according to mass/charge ratio, remove multiply charged ions from the transported beam. When using He, the most commonly used gas, multiply charged ions are not a problem, and so a mass filter is not normally required.

A less common type of ion source used in ISS is the duoplasmatron, a schematic of which is shown in Figure 3.24; it is used when negatively charged primary ions are to be scattered from surfaces. A gas discharge is generated between a cathode and an anode, and the plasma so formed

### Table 3.3

<table>
<thead>
<tr>
<th>Source</th>
<th>Radiance (W mm⁻² sr⁻¹)</th>
<th>Spot Size</th>
<th>Energy Spread ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>2 × 10⁷</td>
<td>30–100 μm</td>
<td>1.0–3.0</td>
</tr>
<tr>
<td>Thoriated W⁺</td>
<td>4 × 10⁸</td>
<td>5–50 μm</td>
<td>1.2</td>
</tr>
<tr>
<td>LaB₆</td>
<td>2 × 10⁸</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Field emission</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cold</td>
<td>2 × 10¹⁰</td>
<td>&lt;5 nm</td>
<td>0.3</td>
</tr>
<tr>
<td>Thermal</td>
<td>2 × 10¹⁰</td>
<td>&lt;5 nm</td>
<td>1.0</td>
</tr>
<tr>
<td>Shottky</td>
<td>2 × 10¹⁰</td>
<td>15–30 nm</td>
<td>0.3–1.0</td>
</tr>
</tbody>
</table>

* Calculated at 1900 K using the Richardson–Dushman equation and the maximum brightness equation [49].
contains positive ions, negative ions, and neutrals. Either positive ions or negative ions can be extracted, but neutrals with velocities parallel to the source axis and moving toward the exit will also enter the next stage. Deflection is therefore used to separate ions from neutrals, followed by a mass filter to select ions with the desired mass/charge ratio. Duoplasmatron sources are bright sources with energy spreads of the order of 15 eV, and spot sizes of 40–300 μm. A duoplasmatron-like ion source that produces a microbeam with a spot size less than 0.1 μm is being developed [54].

3.10.2 ENERGY ANALYZERS

An energy analyzer consists of an energy dispersing element, entrance and exit slits, and (optionally) entrance and exit lenses. Many commercial instruments use an entrance lens, but only a few an exit lens. In XPS, μXPS, iXPS, AES, and SAM, energy dispersion is achieved by deflection in an electrostatic field. The three types of electrostatic energy analyzer commonly in use are the CMA, the double-pass CMA (DPCMA), and the concentric hemispherical analyzer (CHA). An electrostatic energy analyzer is also the commonly used method of energy dispersion in ISS, but time-of-flight (TOF) analyzers are also used, in which the primary ion-beam is pulsed, and the time taken for a scattered ion to reach a detector, at a known distance from the surface, is measured. In the DPCMA, better energy resolution is achieved by placing two CMAs in series. A schematic of a CMA is shown in Figure 3.25. The analyzer consists of a pair of coaxial cylinders with entrance and exit apertures at the front and back ends, respectively, of the inner cylinder. To reach the detector, a particle must travel along a trajectory that takes it from the entrance aperture, through the space between the two cylinders, through the exit aperture, and into the detector. An ideal CMA has a circular entrance aperture of zero width. The position of the entrance slit relative to the sample position, S in Figure 3.25, determines the entrance angle, α. In the figure, α is the angle between the cylinder axis and the central trajectory shown beginning at S. The distance L from S to the focal point on the axis, F in Figure 3.25, depends on α. To discriminate charged particles on the basis of their energies, an electric field is set up between the two cylinders. The inner cylinder is usually grounded, and for the analysis of electrons a negative potential, −V, is used to generate an electrical field between the two cylinders. Only those electrons with energy E satisfying the condition

\[ E = K_e V \left[ \ln \left( \frac{R_2}{R_1} \right) \right]^{-1} \]  \hspace{1cm} (3.10)
are focused at \( F \), where
\[ K_o \] is a constant
\( e \) is the elementary charge
\( V \) is the magnitude of the applied potential
\( R_1 \) is the radius of the inner cylinder
\( R_2 \) is the radius of the outer cylinder \[ 55 \]

The same equation applies for univalent positive ions (charge = \( Ze \), with \( Z = 1 \)), but a positive potential, \(+V\), is applied to the outer cylinder. For \( \alpha = 42^\circ 18.5' \), the analyzer becomes a second-order focussing device, since the first-order spherical aberrations vanish, and then \( K_o = 1.3099 \). In practice, the entrance aperture has a finite width, which allows electrons with entrance angles of \( \alpha - \Delta\alpha \) to \( \alpha + \Delta\alpha \) to enter into the space between the two cylinders. For small values of \( \Delta\alpha \) on either side of \( \alpha = 42^\circ 18.5' \), electrons of energy \( E \) will be brought to the same focal point, therefore all CMAs are constructed using this particular acceptance angle. However, an unavoidable consequence of a finite width entrance slit is that electrons with energies slightly smaller and slightly larger than \( E \) will also be brought to focus very close to \( F \). This leads to an uncertainty in the value of \( \Delta E \) for any given applied deflecting voltage. Notice that all the electron trajectories cross in a small region of space within the inner cylinder just before they reach the detector. This crossing region is called the circle of least confusion, and is shown magnified below the analyzer in Figure 3.25.

If there is no ring slit at the circle of least confusion, the relative energy resolution is given by

\[
\frac{\Delta E}{E} = \frac{C_s (\Delta\alpha)^3}{D_E + C_C (\Delta\alpha)} \tag{3.11}
\]
where
\[ D_E \] is the specific linear energy dispersion
\[ C_S \] is the spherical aberration coefficient
\[ C_C \] is the chromatic aberration coefficient
\[ \Delta \alpha \] is the in-plane half-angle of acceptance into the analyzer (in radians)

If a ring slit of width \( W \) is placed at the circle of least confusion, the relative energy resolution is then given by

\[
\frac{\Delta E}{E} = \frac{0.9W}{R_i} + \frac{1}{4} \left[ \frac{C_S (\Delta \alpha)^3}{D_E + C_C (\Delta \alpha)} \right]
\]

where \( R_i \) is the radius of the inner cylinder. An appropriate choice of \( W \) for any given set of concentric cylinders will result in improved resolution, but at the expense of a reduction in transmission. The ring slit is not normally adjustable by the user, which represents a consideration that must be addressed at the time of purchase. Although the energy resolution of a CMA is adequate for classical AES and ISS, it is not adequate for XPS or for lineshape analysis in AES. In order to obtain better energy resolution, the DPCMA was developed, and an example is shown in Figure 3.26A. Two hemispherical, retarding grids are placed in front of the sample. The nearer hemispherical grid is at the same potential as the sample, usually ground. When used as an electron energy analyzer, a negative potential, \(-V_1\), is applied to the second hemispherical grid in order to decelerate the electrons to a selected pass energy \( E_p \). The same potential is applied to the inner cylinder. A potential \(-V_2\), such that \( V_2 > V_1 \), is applied to the outer cylinder, the difference \( V_2 - V_1 \) determining the pass energy. A spectrum is recorded by ramping the potential on the inner cylinder while maintaining the potential difference between the outer and inner cylinders. The analyzer in Figure 3.26A has four individually selectable entrance/exit slits in the inner cylinder, and two apertures that lie in planes perpendicular to the cylinder axis, one at the midpoint and one at the end of the inner cylinder. During the first pass, electrons are focused into a region that is smaller than the entrance region. This becomes a source for the second pass CMA, which overall has the effect of reducing \( \Delta \alpha \).

Because the pass energy is fixed, so is \( \Delta E \) throughout the spectrum. The improvement in energy resolution comes with a loss in analyzer transmission.

A CHA consists of two concentric hemispheres, of radii \( R_i \) for the inner and \( R_o \) for the outer. The trajectory along which a charged particle moves from the entrance to the exit slits of the analyzer lies on a hemispherical surface with radius \( R_o \), between the two hemispheres. \( R_o \) is equal to \( \frac{1}{2}(R_1 + R_2) \).

An electron of energy \( E \) can move from the entrance slit to the exit slit if the condition

\[
E = \left( \frac{R_1 R_2}{R_2^2 - R_1^2} \right) e(V_2 - V_1)
\]

is satisfied, where \(-V_1\) and \(-V_2\) are the potentials applied to the inner and outer hemispheres, respectively, with \( V_2 > V_1 \) (i.e., the inner hemisphere is more positive than the outer hemisphere) [55]. A spectrum is recorded by scanning the applied potential difference across the concentric hemispheres. For a CHA used without a transport lens, the relative energy resolution is given by the recursive relationship

\[
\frac{\Delta E}{E} = \frac{W_1 + W_2}{2} \left[ \frac{C_S (\Delta \alpha)^3}{D_E + C_C (\Delta \alpha)} \right] + \frac{C_S (\Delta \alpha)^3}{D_E + C_C (\Delta \alpha) + C_E \left( \frac{\Delta E}{E} \right)}
\]

where
\( W_1 \) and \( W_2 \) are the entrance and exit slit widths, respectively
\( C_E \) is the nonlinear energy dispersion coefficient

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The entrance and exit slit widths are adjustable by the user, from outside the instrument, by means of feedthroughs, although with some instruments they are not independently adjustable, in which case $W_1 = W_2$. As with the CMA, there will be a trade-off between transmission and resolution, but at least the user can control this trade-off. For any given set of parameters, the relative energy resolution is constant, so that the absolute energy resolution will increase with increasing $E$. In order to obtain a constant absolute resolution, a transport lens placed between the sample and the analyzer input slit is used to decelerate or accelerate electrons to a selected pass energy, in the range 5–100 eV. The potential difference across the concentric hemispheres is therefore fixed, and spectra are recorded by scanning the transport lens.

Even though the DPCMA is competitive with the CHA-transport lens system with respect to energy resolution, the latter combination is superior with respect to the versatility of sample positioning, the ability to add additional components near the sample position, and the potential of achieving further improvements by increasing the number of elements in the transport lens. For these reasons, the demise of the DPCMA had been anticipated. However, if the claims made by STAIB Instruments for the so-called super-CMA and double-pass super-CMA, which they introduced in 2004 [57], are true, there may be a revival in the use of the CMA-type analyzer. These
analyzers are shown in Figure 3.27A and B, respectively. The super-CMA differs from the standard CMA in that it does not have an entrance slit machined in the front end of the inner cylinder, but instead, electrons from the sample are introduced directly into the front space between the two cylinders, after being retarded by high-precision retarding field optics. This method of introducing the electrons into the analyzer allows for a much larger working distance between the sample and the analyzer than in the standard CMA. The retarding field optics serve the same function as the hemispherical grids used in a standard DPCMA. For the double-pass super-CMA, a CMA optical system and an aperture are placed between the sample and a super-CMA. The additional optics consist of a small CMA, which also has no slits machined in the inner cylinder. Instead, electrons enter the front space between the two cylinders directly, and exit from the space between the two cylinders at the far end. Then they enter a separate, cylindrical aperture, from which they enter the second stage super-CMA. It is claimed that these analyzers retain all the advantages of the classical CMA and DPCMA, but overcome the disadvantages of short working distance, need of fine control on sample positioning, and a small acceptance area on the sample.

The super-CMA shares the following features with CHA analyzers [57]:

- Simultaneous analogue and pulse counting modes
- Constant energy resolution or constant resolving power modes
- Electronically controlled energy resolution, from <100 meV up to 6 eV

The development of new types of energy analyzer and the improvement of older ones are still active areas of research, and some of these developments and improvements may appear on the market in the next 10 years. Just as miniaturization has been important in other fields, so is it also important in
surface analysis. Miniaturization of the CMA and the DPCMA has been achieved by Grzelakowski et al. [58], who have designed a CMA that fits onto a 70 mm diameter flange. It was constructed by mounting a miniature electron gun equipped with a cerium hexaboride filament coaxially inside the analyzer, and placing a channeltron detector at the image position (Figure 3.28). Using the FWHM of the elastic peak in a spectrum recorded from contaminated W(100), the developers calculated a relative energy resolution of 0.9%, indicating that there was no significant loss in resolution on miniaturization. An AES spectrum from contaminated W(100) in the analogue detection mode is shown in Figure 3.29, illustrating that spectra of high quality may be obtained with small devices. A miniature

FIGURE 3.28 Miniature CMA with coaxial electron gun and channeltron, mounted on a 70 mm flange: S, sample; O, outer CMA cylinder; I, inner CMA cylinder; and F, fringing field correction rings. (From Grzelakowski, K., Man, K.L., and Altman, M.S., Rev. Sci. Instrum., 72, 3362, 2001. With permission.)

FIGURE 3.29 AES spectrum from contaminated W(100) using a miniature CMA. (From Grzelakowski, K., Man, K.L., and Altman, M.S., Rev. Sci. Instrum., 72, 3362, 2001. With permission.)
DPCMA has also been developed for recording photoemission spectra from gas-phase molecular beams, or from molecular cluster beams under conditions of higher density [59].

Another new type of energy analyzer based on cylindrical electrodes is the TCMA (tri-CMA), which consists of three coaxial cylindrical electrodes, as shown in Figure 3.30 [60]. It has a theoretical relative energy resolution of 0.03% at $\alpha = 33^\circ 55'$ and is being developed for the purpose of AES lineshape analysis, in order to provide chemical-state information. A high-resolution carbon KLL spectrum obtained by it from a carbon-contaminated Si(111) surface is shown in Figure 3.31, exhibiting characteristic satellite lines.

Almost all commercial instruments that employ a CHA as the energy analyzer also use a transport lens between the sample and the analyzer entrance. Such a lens is used not only to focus an area of the sample surface onto the entrance slit of the CHA, but also to retard the electrons or ions so as to control the absolute energy resolution $\Delta E$.

![TCMA diagram]


![Carbon KLL Auger spectrum]

**FIGURE 3.31** Carbon KLL Auger spectrum in both $N(E)$ and $dN(E)/dE$ modes from contaminated Si(111) using a TCMA. (From Kościelniak, P., Kaszczyszyn, S., and Szuber, J., *Vacuum*, 63, 361, 2001. With permission.)
The most commonly used transport lenses are multielement and electrostatic, employing four or five elements, although a magnetic immersion lens can also be used (e.g., the axis instrument). With a four-element lens, the magnification of the image, and the energies of the electrons forming it, in the entrance plane of the analyzer, may be kept constant as the energies of the electrons emitted from the sample are increased or decreased. If the electron energies in the sample image in the entrance plane of the analyzer are constant and independent of the applied, scanned, accelerating, or decelerating voltages, then the position of the image in the detector plane will also be fixed. With a five-element lens, the capability of making the size of the output angle at lens element 5 the same size as the input angle at lens element 1 is also available.

When a transport lens is operated in the magnification mode, its magnification \( M \) and the slit width into the analyzer determine the acceptance area, which defines the lateral resolution for \( \mu \)XPS. Thus, \( M \) is an important figure of merit for the analyzer. The acceptance area is the analyzer entrance slit width divided by \( M \). The smallest available slit width and the largest value for \( M \) will therefore determine the theoretical minimum lateral resolution for the instrument. In the magnification mode, the acceptance angle into the analyzer is usually controlled by a further aperture, called the iris, located inside the lens at the first diffraction plane. The function of the iris can probably best be illustrated by some graphics taken from the trade literature. The multi-element lens used in the particular instrument being discussed may be operated in any one of three magnification modes, that is, \( M = 10, 5, \) or 2. In Figure 3.32, the trajectories are shown for two different sets of 1000 eV electrons being transported through a lens with \( M = 10 \). In each case, the electrons have been retarded to a final energy of 100 eV. The first set of trajectories start on the lens axis at angles of \( 0^\circ, \pm 1^\circ, \) and \( \pm 2^\circ \) relative to the axis, while the second set of trajectories start at the same angles, but 0.5 mm off the lens axis. At the first diffraction plane, the two sets of parallel trajectories focus at different positions. The iris aperture is located at this plane. Using the largest area entrance slit (7 × 20 mm\(^2\)) and \( M = 10 \), the acceptance area is 0.7 × 2 mm\(^2\). When the intensities of the Ag and Cu XPS peaks from a sample consisting of a silver foil covered with a 10 mm diameter copper aperture were plotted as a function of iris diameter, the result shown in Figure 3.33 was obtained. The iris aperture was varied continuously up to 50 mm (wide open). Both Cu and Ag were observed until the iris aperture had decreased to 25 mm, because the acceptance angle decreased at constant acceptance area. For an aperture of 25 mm

![Figure 3.32](Image)

**FIGURE 3.32 (See color insert following page 396.)** Trajectories of 1000 eV electrons through a transport lens set at \( M = 10 \) with retardation of the electrons to a final energy of 100 eV. Black lines indicate trajectories from a point on axis at angles of \( 0^\circ, \pm 1^\circ, \) and \( \pm 2^\circ \) to the axis, and blue lines the same from a point 0.5 mm off axis. (From SPECS literature: www.specs.com. With permission.)
diameter, the acceptance angle would have been about \( \pm 8^\circ \). Thus, the lens settings may affect the energy resolution through their effect on \( \Delta \alpha \). The explanation for the results illustrated in Figure 3.33A can be established by examining the distribution of intensity as a function of position. The distribution is cylindrically symmetric, and is Gaussian at small distances from the center, but has a very wide low intensity tail. The iris aperture’s function is to truncate the tail, as illustrated in Figure 3.33B.

The transmission of an energy analyzer is an important parameter, because the sensitivity of a technique for any given element will depend on it. Dubé and Roy [62] have developed a generalized approach for calculating the transmission function, but the equation derived by them depends critically on the initial and boundary conditions. Procedures for measuring this function have been
published in the literature [63], so it may be found empirically for some instruments. A more useful figure of merit is called the étendue, the product of transmission and slit area. The user should measure this function for the conditions appropriate to a specific application, particularly in cases where stringent quantification measurements are to be made.

As has been mentioned at the beginning of this section, a TOF analyzer is sometimes used in ISS instruments. In a TOF analyzer, bunches of charged particles with different energies enter a flight path that has a fixed length to a particle detector. The particles are discriminated on the basis of their velocities, that is, the time taken to traverse the flight path, which depends on their masses and energies. In conventional ISS, all the incident particles have ideally the same mass, charge, and energy. Through collisions with a sample surface, the energy of a particle is reduced, and usually the charge also. Thus, the collision process converts a mono-energetic particle beam to a multiple-energetic beam, and the TOF analyzer measures the energy distribution of the latter. A TOF analyzer can analyze positive, negative, and neutral beams, although in ISS the scattered beam is always positive. It may also provide higher energy resolution ($\Delta E$) than an electrostatic energy analyzer [64]. An excellent review of TOF analyzers, as well as electrostatic analyzers, for ISS, may be found in a recent text by Rabalais [65].

The electrostatic analyzers discussed above may all be used for simultaneous rather than single energy detection since they disperse a band of energies at the image position in the analyzer exit plane. If the exit slit is removed, then the whole energy band is available for detection. However, the range of energies is small. For example, a CHA operated in the fixed analyzer transmission (FAT) mode will disperse a range of energies given by the interval $\pm 0.1E_p$, where $E_p$ is the pass energy, imaged in the analyzer detector plane. For $E_p = 100$ eV, this results in a band of width 20 eV, which is often the width used to record a single spectral peak in XPS (e.g., C 1s, O 1s, etc.) in the high-resolution mode. An entire spectrum may be collected over some appropriate time interval using a position-sensitive detector in the exit plane of the analyzer.

Alternatively, a number (e.g., 3, 5, etc.) of single channeltrons may be positioned near the image point for $E_p$, and the signals from them summed as the analyzer is energy-scanned in the normal fashion. In this case, some energy resolution is sacrificed for a large gain in intensity. The latter allows peaks from elements present at low surface concentrations, peaks with low-ionization cross sections, or both, to be recorded in a reasonable time, particularly for low-intensity x-ray sources such as those that are monochromated. The ability to record an extended range of energies simultaneously also introduces the possibility of carrying out real-time surface analysis.

New analyzers that can be used for simultaneous energy analysis over a large range are under development. One of these is the hyperbolic field analyzer (HFA), shown schematically in Figure 3.34 [66]. With this lensless analyzer, an energy range of $E_{\text{max}}/E_{\text{min}} \approx 34$ (compared to 1.2 for the CHA) may be achieved.

3.10.3 DETECTORS

The workhorse detector for instruments using single-channel detection is still the channeltron. The technology itself is old, but manufacturers continue to develop methods of extending the dynamic range, improving detection efficiency at higher masses, and increasing the lifetime of the device. The three parameters—dynamic range, detection efficiency, and lifetime—along with the transit time, are its figures of merit. The transit time is the elapsed time from the initiation of an event until the termination of the resulting electron avalanche; it determines the temporal resolution of the device, and thus places a limit on the maximum count rate. The characteristic curve of a channeltron consists of a plot of gain versus applied collector voltage, and is supplied by the manufacturer with the device. However, the characteristic applies to incident electrons, and since the detector may also be used to detect ions or even neutrals, it should be determined experimentally on installation of the instrument. The resulting plots then serve as standards for comparison of the instrument performance over time.

Detector efficiency is important because it is a parameter in the mathematical expression for spectral peak intensity. For electrons, it is a nonlinear function of the electron KE, while for ions it depends on both KE and mass. Unfortunately, there is no universal mathematical curve for the detector efficiency as a function of particle energy. Thus, for quantitative analysis, the FAT mode should be used to collect data since the detector efficiency will then be the same for all peak energies. Some suppliers include generic information in their handbooks, which are usually free. For example, Burle's *Channeltron Electron Multiplier Handbook* is an excellent choice [67].

Instruments using multichannel detection employ either multiple channeltron detectors (MCD-$n$, where $n$ is the number of channeltrons), micro-channel plates (MCP), charge coupled device (CCD) detection systems, or delay line detectors (DLD). In the case of the MCD-$n$, the channeltrons are spaced at regular intervals across the detector plane, which corresponds to increments in the energy dispersion, with a reference channeltron centrally positioned. The experimental spectrum is then collected by shifting the spectrum of each channeltron to put it in register with that of the reference channeltron, and then adding the intensities for each energy increment. This is a way of exploiting the multiplex advantage without an increase in the time required to record a spectrum. Theoretically, it is possible to do this without degrading resolution, but in practice, there is always some loss in resolution because the shifts to registry are not perfect; however, the loss in absolute energy resolution does not usually exceed 0.1 eV.

An MCP stack may be used to obtain data for particles at a fixed polar angle, but widely varying azimuthal angles. For example, in ISS with a scattering angle of $-180^\circ$, the azimuthal angle of the scattered primary ion is in the interval $0^\circ$–$360^\circ$. The MCP stack intercepts the scattered ions and generates a signal, which is sent to an amplifier. MCPs used in this configuration are called detection-quality MCPs. Such detectors are useful when TOF analyzers are used. The performance figures of merit for the detection quality MCP are the same as those for a channeltron.

CCD detection systems are used in imaging instruments, and consist of an MCP stack, a phosphor screen, a demagnifying lens, and a digital camera (Figure 3.35). The phosphor is an electron-to-light transducer, and as such, needs to respond very quickly to changes in the electron current impinging on the screen. The demagnifying lens is used to enlarge the image on the phosphor so that it fills the input aperture of the camera. The performance figures of merit for the detection system depend on the individual figures of merit. The resolution of an MCP stack is inversely proportional to its pitch, which is the center-to-center distance between adjacent pores, and the pore size determines the magnitude of the electron avalanche beam leaving the stack. As the beam leaves the stack it diverges, the degree of divergence depending on the distance it has to travel to hit the plate and on the accelerating voltage. By keeping the distance between the MCP stack and the phosphor plate short, and adequately controlling the accelerating voltage, divergence can be minimized. Each avalanche beam creates a tiny light source whose intensity is determined by the number of electrons in the beam. These multiple light sources are focussed onto the CCD, which has its own resolution determined by...
the size of a single pixel in its photodiode array. If the pixel size is smaller than that of the pore size of the MCP stack, then the MCP stack will determine the overall detector spatial resolution, and most CCD detectors are constructed in that way. Ideally, the spatial resolution of the detector should be selected so that it is negligible compared to that of the multichannel dispersion analyzer.

Another figure of merit is the temporal resolution, which is the time between successive images and is the reciprocal of the frame rate, the parameter specified by the vendor. A further figure of merit is the number of camera bits. This refers to the number of bits in the analog-to-digital converter that determines the number of intensity levels in the digitized image. For example, a 12-bit camera would provide $2^{12} = 4096$ intensity levels. Cameras with 12, 14, or 16 bits are available.

The latest innovation in detectors is the DLD. A standard DLD consists of an MCP stack and two mutually perpendicular delay-line windings at the exit from the stack. Its operation can be described with reference to Figure 3.36. The perpendicular line shows a single event being detected by an MCP stack. Below the stack a winding path delay-line for the $x$-direction is shown. The avalanche electron generated by the event hits the winding and produces an electrical pulse that propagates to the two end stations, from which two signals register. By measuring the difference in signal arrival time between the stations, the event’s $x$ position can be determined. Similarly, a perpendicular $y$-winding delay-line (not shown) allows the $y$ position to be determined. The summed signal gives the amplified pulse count for the event, and hence a parallel image with pulse-counted data is recorded.
3.11 SPECIAL APPLICATIONS OF XPS

3.11.1 HIGH PRESSURE XPS

XPS has proved to be a powerful tool for, amongst many other applications, the characterization of heterogeneous catalysts and of corrosion processes on materials. However, such studies have been carried out almost entirely on before-and-after specimens, in order that the high-vacuum requirements of the traditional instruments can be maintained. In such cases, it is the surface/vacuum interface that is actually studied. It has always been the goal of research workers to be able to study surface reactions under conditions that more closely represent the native reaction environments. For example, in order to characterize a catalyst–gas interface or a material–liquid interface, instrumentation that allows the sample to be immersed in a gas or a liquid, but does not degrade spectrometer performance, is needed. Now, two relatively high-pressure XPS instruments are commercially available. Both are based on differential pumping; a four-stage arrangement is shown in Figure 3.37 [69]. An alternative high-pressure monochromatic XPS/EELS (electron energy loss spectroscopy) system has three-stage differential pumping, and is equipped with a high-pressure cell [70].

The vacua maintainable in the various differentially pumped stages are determined by the pumping speeds of the pumps used at each stage, and are functions of the nature, and the equilibrium pressure, \( p_0 \), of the particular gas used in the high-pressure cell in the sample chamber. The upper limit for \( p_0 \) in the cell is 1020 Pa, so to maintain a pressure of no more than about \( 10^{-5} \) Pa at the analyzer requires a pressure reduction factor of \( \sim 10^8 \). The pressure in each stage may be expressed in terms of \( p_0 \) by the function \( p_i = C_i(p_0) \cdot p_0 \), where \( i \) indexes the individual stage, and \( C \) is the reduction factor. The three-stage instrument uses turbomolecular pumps with the following pumping speeds: \( TP_1 = 330–680 \) L/s, \( TP_2 = 105–180 \) L/s, and \( TP_3 = 105–180 \) L/s. The results of tests relating the reduction factors to the pressure in the reaction cell are shown in Figure 3.38. For \( p_0 \) in the range 100–1020 Pa, the factors \( C_i(p_0) \) are constant, with respective values \( C_1 = 6.4 \times 10^{-4} \), \( C_2 = 3.0 \times 10^{-6} \), and \( C_3 = 2.1 \times 10^{-8} \) for the first, second, and third differential pumping stages. Thus, at the highest working pressure in the cell of 1020 Pa, the pressure at the analyzer could be maintained at \( \sim 2 \times 10^{-5} \) Pa, adequate for analysis. Since the goal of investigators using high-pressure XPS is to work at the highest sample chamber pressure possible, the reduction factors are important parameters characterizing the system. The lower their values, the higher \( p_0 \) can be for a given target value of the analyzer pressure.

In high-pressure XPS, the maximum pressure possible in the sample chamber is determined in part by the mechanical stability of the x-ray source window and the maximum window thickness.

**FIGURE 3.37** Schematic of a high-pressure XPS instrument with multistage differential pumping. TP, turbomolecular pump; Sch, sample chamber; DS, differential pressure chamber; An, analyzer; V, valve. (From Kleimenov, E., PhD thesis, Technical University of Berlin, 2005. With permission.)
that can be tolerated without severely degrading the source intensity at the sample. For example, Kleimenov [69] calculated that a 100 nm thick silicon nitride window could withstand a pressure difference up to $10^3$ Pa. It can be concluded that there will be some lower limits for the above factors, beyond which there will be no further improvement possible for a given source.

The ability to obtain spectra from samples subjected to in-situ high pressures is not without sacrifice. There will be a consequent pressure-dependent loss in source intensity at the sample surface due to the x-ray transmission properties of the introduced gas. In addition, photoelectrons ejected from the sample undergo scattering off the gas molecules so that the reduction in signal depends on both the nature of the gas and its pressure. Since the scattering cross sections of the photoelectrons are energy dependent, the overall transmission function of the spectrometer changes, which affects data analysis. Correction of spectra for charging encountered with semiconductor or insulator samples is more complicated because the surface charging is also influenced by both gas composition and pressure. The highest pressure that has been reported when using a conventional x-ray source is about 100 Pa [70].

### 3.11.2 Automated XPS

In industry, XPS analysis is often carried out in the context of quality control. For the industrial laboratory, a compact instrument with high sample throughput, low downtime, adaptation for special sample dimensions, and minimum operator intervention is required. For example, XPS is widely used for characterizing the surfaces of silicon wafers, which can have diameters of up to 300 mm.

Most of the instruments aimed at the quality control market are based on the CHA. However, one manufacturer has opted for a Dupont-type band-pass filter analyzer, a schematic of which is shown in Figure 3.39. The grid and absorber electrodes on the left of the diagram function as a low-pass reflective filter. The curved grid electrode is biased at $-V$ volts; photoelectrons with energies lower than eV are reflected by the grid, while those with higher energies are absorbed by the absorber electrode. The reflected electrons travel through a field-free region toward the opposite end of the analyzer, where they encounter a high-pass transmission filter. Thus, electrons with a small energy bandwidth with respect to the nominal electron energy are detected. Typically, the bandwidth ($\Delta E$)
The system has a fully automated multi-sample carousel, and both data acquisition and analysis may be performed entirely under computer control.

Some instruments now allow full remote control and service via the Internet, and the only required manual operation is the loading of the sample holder into the transfer system. Additional information on this class of XPS instrumentation may be found in Refs. [22,32,37].

3.11.3 Dedicated XPS

Dedicated here means state-of-the-art instruments that have been optimized for XPS analysis, but that may have other techniques, such as AES, available on them. They include both small-spot and imaging instruments. Within this category, there are instruments, based on a CHA and a combination of electrostatic and magnetic lenses, that have been specifically designed for small-spot analysis, in which the minimum spot size is 30 μm. Of course, traditional, i.e. so-called large area, XPS can also be performed, as can large-area imaging by means of stage mapping. One manufacturer of imaging instruments has based its design on a 127 mm radius CHA, with either an MCD-3 (3 channeltron array) detector or an MCD-5 detector, and with automated multi-sampling as an option. Other manufacturers offer similar designs, with the main difference between them being the size of the CHA.

The so-called NanoESCA probably leads the field in iXPS at the moment, with a claimed lateral resolution of <200 nm when operated at a synchrotron beamline. A more conventional design uses a monochromatic Al Kα source in which a raster-scanned focused electron-beam generates microbeam x-rays with a spot size adjustable from ~9 to 200 μm. Thus, small-spot XPS is available at ≤10 μm, and imaging XPS with a lateral resolution of 9 μm. Another design can perform small-spot and angle-resolved XPS using monochromatic Al Kα radiation and a 110 mm radius CHA, and uses optics that allow angular information and electron energy information to be imaged in parallel on a two-dimensional detector. Ninety-six angular channels may be accessed without having to tilt the sample. It is ideal for the nondestructive depth profiling of very thin films, and a single angular-resolved XPS experiment may be performed very quickly. Yet another instrument, based on a CHA, has a 2-stage, 11-element electrostatic lens, and a detector system consisting of an MCP with a fast fire wire pulse transmission CCD camera. The spatial resolution for imaging XPS is 10 μm, and angle-resolved XPS may also be performed. Additional information on these products may be found in Refs. [68,71–75].
3.11.4 **Multi-Technique Instruments**

These are instruments designed to accommodate several surface analysis techniques in a single-sample analysis chamber and may not be optimized for any of them, although they usually are for XPS. Current-generation models from the major manufacturers represent evolutionary developments along the following lines:

- **Small-spot and imaging XPS.** Depending on the model, available spot size ranges from a few to ~100 μm, while the state-of-the-art in lateral resolution for iXPS is in the low micrometer range.
- **Parallel data acquisition.** Parallel detection is now the rule, rather than the exception, by one or other of the technologies, that is, based on DLD, MCD, or MCP with camera.
- **Monochromatic excitation sources and greater choice of sources.** In addition to the traditional dual-anode Mg K\(_\alpha\)/Al K\(_\alpha\) and monochromatic Al K\(_\alpha\), single anode Ag L\(_\alpha\), Zr L\(_\alpha\), and Au M\(_\alpha\) sources are available.
- **Better integration of multi-technique attachments.** Most instruments can be tailor-made with a great range of optional, additional techniques. These include the following: SAM with a spot size of <100 nm using either Schottky field emission or LaB\(_6\) electron sources; routine SEM with a secondary electron detector; ISS using rasterable, electron-impact-generated noble-gas ion beams; SIMS using a quadrupole mass analyzer; and UPS using a He discharge lamp.

Additional technical information on multi-technique instruments may be found in Refs. [62,69,72–75].

### 3.12 AES Configurations

#### 3.12.1 Dedicated Instruments

Because lineshape analysis can now be used to obtain chemical speciation data in AES, there are fewer dedicated instruments, and they are all research-oriented scanning instruments with electron-beam spot sizes in the low nanometer range. As a rule, the instruments use Schottky field-emission electron guns, while both CMAs and CHAs are on offer. The claimed lateral resolution ranges from 8 to 12 nm for the top-of-the-range models. Detection is based on either MCD or MCP technology. Although these instruments are designed specifically for AES and SAM, they all allow some modules to be attached for other techniques (e.g., XPS, SIMS, EDS, and ISS). Additional information may be found in Refs. [72,75].

#### 3.12.2 Other Instruments

Instruments designed primarily for low-energy electron diffraction, EELS, or scanning probe microscopy often offer AES/SAM as an option. The SAM specifications are then comparable to those found for dedicated AES/SAM instruments.

### 3.13 ISS

#### 3.13.1 Dedicated Instruments

ISS analysis using instruments designed primarily for XPS is limited to the determination of the energy loss spectrum of scattered primary ions. The energy losses are related to the masses of the collision partners, and thus the qualitative and quantitative elemental composition of the top monolayer...
of a solid can be determined, provided that the ion flux is low enough. A new instrument design for ISS/LEIS was introduced by Brongersma in 1985 [76], allowing both energy-resolved and angle-resolved analysis of scattered primary ions. The design has subsequently become commercially available as an ISS low energy ion scattering (LEIS) instrument [77]. It uses an electron-impact noble-gas ion source with an energy range of 0.5–5 keV and a spot size of ≈0.3 mm. The spatial resolution is 10μm, the absolute energy resolution ΔE is 10% of the pass energy, and the mass resolution, M/ΔM, is in the range 10–20. The analyzer consists of a four-element electrostatic zoom lens and a double toroidal electrostatic analyzer, with a scattering angle of 145° and an azimuthal angle that ranges from 0° to 320°. A TOF option may be added, allowing TOF scattering and recoiling spectroscopy analysis to be carried out, but this requires that a second ion gun be used. It is also possible to modify the instrument to perform TOF-CAICISS (coaxial impact collision ISS) [78]. An instrument optimized for CAICISS is under development [79]. Another ISS variation is mass-resolved ion scattering spectrometry. In this technique, the incident ion beam is mono-energetic, but not mass-selected, and the backscattered ions are mass and energy analyzed [80,81]. Just as the commercialization of XPS and AES instruments has led to their tremendous growth and maturation, so the commercialization of dedicated ISS instruments has positioned ISS to mirror the growth and maturation of its related surface spectroscopic techniques.

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