A STUDY OF THE SILVER X-RAY SOURCE FOR PHOTOELECTRON SPECTROSCOPY

by

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ABSTRACT

A novel x-ray anode for electron spectroscopy is investigated for application in the surface analysis field, monochromatic Ag Lα (hν=2984.3eV), its energy being capable of exciting 1s electrons up to chlorine in the periodic table.

Resolution available with this source is satisfactory, with a limitation of approximately 1.5eV. An increase in sensitivity is achieved for those peaks in the range 1500–3000eV, whilst there is no serious reduction within the conventional XPS energy range. The agreement between experimental sensitivity factors and theoretical cross-section values is good, allowing the transmission function for the VG ESCA3 MkII spectrometer to be confirmed constant from 0–3000eV.

A comprehensive investigation of the LEG51 electron flood gun preceded its successful application for the charge neutralisation of insulating materials. This allowed the application of this source to such materials as chlorides, pertinent to the breakdown in passivity on stainless steels, and silicon compounds, involving thermal oxides on silicon of interest to the microchip industry, zeolites for catalysis in the petrochemical industry and siloxane copolymers for the ophthalmic industry. The ability to excite the 1s orbital, together with the 2p and KLL Auger lines, affords calculation of Auger parameters and extra-atomic relaxation energies for the accurate description of the chemical environment of a particular chemical species.
A method for internal energy referencing is investigated, involving the vacuum-deposition of Au, Cu and Pt metals. This allows the measurement of photoelectron binding energies to an accuracy of ±0.1-0.2eV for insulating materials, when referenced to the vacuum level.
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Chapter 1. Introduction and Literature Survey

1.1 Surface Analytical Techniques

The technique of surface analysis is relatively new in scientific terms but has developed rapidly, particularly since the early 1970's. X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), secondary ion mass spectrometry (SIMS) and ion scattering spectroscopy (ISS) are the more common techniques, particularly XPS and AES which are also sufficiently compatible to be available in the same commercial spectrometer.

The possibility of surface analysis on a commercial level has been present since 1967 when the first commercial instruments were introduced, following improvements in the levels of ultra high vacuum (UHV) attainable. The underlying principles, however, stem from the identification of the photoelectric effect by Hertz at the end of the last century, and the historical developments have been given in detail by Jenkin et al \(^\text{(1)}\). The credit for the development of XPS in its modern form is due primarily to Professor Kai Siegbahn and co-workers, from whose work in the late 1950's followed the ability to distinguish metal from metal oxide states \(^\text{(2)}\). This led to the adoption by his group of the title ESCA (electron spectroscopy for chemical analysis) for this technique.
The applicability of XPS (i.e. ESCA) to both research and industrial problems in the world today is very wide (see Figure 1.1). Though the cost of instruments can be prohibitive to an individual researcher, analytical time can be easily obtained on a hire basis since regional centres for surface analysis are being established for the benefit of research and industry alike.

1.2 The theory of XPS

The process of photoionisation is:

\[ M + h\nu \rightarrow M^+ (\ell) + e^- \quad \ldots.. \quad 1.1 \]

The events on an atomic level to produce this effect are shown in Figure 1.2(a) for silicon, depicting the creation of an orbital vacancy. De-excitation of the excited species can occur by x-ray fluorescence or
emission of an "Auger" electron, as shown in (b) and (c). The incident x-ray beam can interact with an electron in the K-shell to cause its ejection as a 1s photoelectron, providing that the exciting x-rays possess sufficient energy to cause such a process. A K-shell vacancy thereby results, representing an excited state, which is relievable by the dropping of an electron from an outer level to the vacated inner level leading to the direct emission of a characteristic x-ray (x-ray fluorescence). Alternatively, another electron (e.g. L₂) can fill the K shell vacancy, with the excess energy being expended by the ejection of a further electron (e.g. L₃). The electron produced by this process is an example of de-excitation by Auger electron emission and would be designated a KL₂L₃ electron.
Thus the XPS technique involves bombardment of a surface with soft x-rays so that photoionisation results. The photoelectrons produced escape from the outermost layers of atoms and are then separated into an energy spectrum and detected. The process involves the use of a vacuum environment which is necessary to retain the surface to be examined in an unaltered state throughout the analysis period, which is often long.

Photoelectrons emitted under soft x-ray excitation originate from a definite core level. Thus their kinetic energy is well defined and can be used to determine the binding energy of the electron, which Carlson\(^{(3)}\) described as the difference in energy between the initial and final states of the photoexcited species. Thus:

\[
E_{KE} = h\nu - E_{BE} - E_{r} - w \tag{1.2}
\]

where:

- \(E_{KE}\) = the kinetic energy of the photoelectron,
- \(E_{BE}\) = the binding energy of the photoelectron,
- \(h\nu\) = the photon source (in this case x-ray) energy,
- \(E_{r}\) = the recoil energy, which is dependent upon the atomic mass of an element. This can normally be ignored since it is smaller than uncertainties concerning the natural linewidth of the exciting radiation, and
- \(w\) = the spectrometer work function.
XPS normally involves the use of Mg Kα (hv = 1253.6eV) and Al Kα (hv = 1486.6eV) sources to attain photoelectron information. These two anode materials have become popular due to their ease of construction, narrow linewidth and acceptable x-ray intensity. They excite core levels of all elements, and are frequently constructed together in the form of a twin anode.

Whilst the exciting radiation can withdraw core level electrons of particular binding energies, the intensity of a peak induced will relate to the photoelectric cross-section for the individual orbital concerned. Figure 1.3(a) demonstrates the sensitivity available, i.e. the photoelectric cross-section, when using Al Kα radiation, these values being calculated by Scofield\(^\text{(4)}\). The greatest sensitivity is found for peaks whose binding energies are closest to the energy of the exciting x-rays themselves. Hence the energy of the Al Kα x-ray is sufficient to excite the 1s core levels of elements up to magnesium in the periodic table, producing good sensitivity in this range. However for elements whose 1s level cannot be excited, such as aluminium, the 2p core level is the most intense available, which can be seen to be far less satisfactory.

To overcome this sensitivity problem for elements beyond magnesium in the periodic table it is possible to utilise a higher energy x-ray source. Figure 1.3(b) shows the sensitivity available with Ag La radiation (hv = 2984.3eV), these photoelectric cross-section values being calculated by Yarzhemsky et al\(^\text{(5)}\). Ag La exhibits a wider range of 1s core level accessibility and avoids the necessity for use of less sensitive photoelectron lines for elements aluminium through to chlorine in the periodic table. Figure 1.3(b) also shows no great penalty in 2p
Figure 1.3 Variation of photoelectron cross-section with atomic number sensitivity for this source, when comparing cross-section values relative to the F 1s core level.

However, the prime reason for the restricted use of such x-ray sources is their poor resolution in comparison to that available with Al Kα, primarily due to the presence of intense x-ray satellites. Factors influenced by poor resolution include the following:

a) the measured position of a photoelectron peak on an energy spectrum, which is characteristic of a particular element,

b) the shape of a photoelectron peak, which determines any chemical state information that may be available,

c) the intensity of the peak, since this determines the sensitivity available for that particular element, and

d) the separation of different peaks in the energy spectrum, since such measurements can be useful for the determination of chemical state effects when such information from one peak is unavailable.
For accurate measurement of a photoelectron peak position the resolution available must be good. Components contributing to the resolution include those due to:

a) the width of the photoelectron peak, $W_{PE}$
b) the linewidth of the core level itself, $W_C$
c) the linewidth of the exciting radiation, $W_X$
d) the width component due to the spectrometer analyser, $W_{Sp}$, and
e) the width component due to electrostatic charging, $W_{El}$.

Similarly, components contributing to the width of an Auger peak include those due to:

a) the width of the Auger peak, $W_A$
b) the linewidths of the core levels involved in the Auger process, ($W_{C1}$, $W_{C2}$, and $W_{C1C2}$), since band-to-core transitions often occur,
c) the width component due to the spectrometer analyser, $W_{Sp}$, and
d) the width component due to electrostatic charging, $W_{El}$.

The contributions due to the individual core levels are difficult to measure, and are normally beyond the control of the operator.

$W_{El}$ is important when analysing insulating samples using XPS, and methods for its counteraction will be discussed in greater detail in Chapter 4. For $W_X$ in the case of polychromatic sources such as Al Kα, the unresolved x-ray line components must also be considered, since these increase the effective linewidth causing loss in resolution. The $\alpha_1$ and $\alpha_2$ components for Al Kα are evident in Figure 1.4, the x-ray spectrum for Al foil. The linewidth of Mg Kα (full peak width at half
maximum height, FWHM = 0.8eV) is slightly preferable to that for Al Kα (FWHM = 1.0eV) for high resolution studies, and this comes about because the \( \alpha_1 \) and \( \alpha_2 \) components are more closely spaced. The importance of x-ray linewidths and methods for their reduction are discussed later in this chapter.

Figure 1.4 The x-ray spectrum for Al Ka radiation

The component \( W_{Sp} \) involves the width contribution due to the spectrometer itself, and is within the control of the operator. The process for the separation of the photoelectrons excited into an energy spectrum for the ESCA3 MkII spectrometer is achieved through the use of a hemispherical sector analyser using grid pre-retardation, as shown in Figure 5(a). This double retardation enables only the photoelectrons of the correct energy to pass through the analyser. The initial preretardation increases the resolution of the spectrometer at the expense of intensity.

Thus both pass energy and slit width dimensions affect the analyser resolution (\( \Delta E \)), since:

\[
\Delta E = \frac{W E_p}{200} \tag{1.3}
\]
Reducing the value of $W$ or $E_p$ will improve resolution providing that sufficient electrons are present to avoid a decrease in sensitivity, though for the ESCA3 the utilisation of slit widths below 4mm separation can lead to electron dispersion and a consequential decrease in signal-to-noise level obtainable.

The normal mode for use in XPS work is known as fixed analyser transmission (FAT), or constant analyser energy (CAE), in which $\Delta E$ is held constant at all times. This involves electronic ramping of the potential of the grid mesh, with respect to which voltages for both hemispheres and slit plate are kept constant.
Having energy analysed the photoelectrons it remains for those left to be detected. This is achieved by the use of a channel electron multiplier, or channeltron, which is shown in Figure 1.5(b).

Figure 1.6 shows the experimental configuration of the spectrometer used for this study: a VG ESCA3 MkII spectrometer possessing a standard twin Mg/Al anode x-ray source and the unique monochromatic Ag Lα source. With monochromatic sources, an electron flood gun is necessary for the neutralisation of insulating materials. The analyser itself is contained within a vessel of u-metal to protect the photoelectrons from the Earth's magnetic field or fields originating from other external sources. Amplification of the pulses produced by individual electrons (the channeltron has a gain of about $10^6$) allows production of an XPS spectrum, which can in the simplest case be via an X-Y plotter connected to the spectrometer and ratemeter control units, as shown in Figure 1.5(c). The accuracy of this method, however, is insufficient when one considers that quantitative analyses are often acquired over lengthy periods. Hence the majority of spectrometers in use today are interfaced to a computing facility, which invariably controls acquisition, offers data storage, and data handling, on completion or even during the process of an experiment.

Electron spectrometer manufacturers can offer a dedicated computing system with the instrument, and home-grown facilities can be extended further by use of main frame computers. Computerisation present in the Surface Analysis Laboratory at the University of Surrey includes the Apple VGS1000 data system supplied by VG Scientific Ltd. and the VG 3040 data system based on a DEC PDP8e micro computer, both of which have been used to control the VG ESCA3 MkII spectrometer, and are connected to the
Figure 1.6 The VG ESCA 3 Mk II photoelectron spectrometer
university main-frame PRIME system. Though different, these facilities offer similar services, such as background subtraction, peak deconvolution, curve synthesis and satellite subtraction.

1.3 XPS Energy Determination

Photoelectron peak positions are often reported in terms of the apparent electron binding energy \( E_{BE} \), since this value is then independent of excitation source. What is actually being measured however is the kinetic energy, as shown in Figure 1.7, since binding energies are merely derived from the subtraction of the experimentally measured kinetic energy of an electron from the photon source energy.

![Figure 1.7 Kinetic energy spectrum for copper](image)

From equation 1.2 it appears that kinetic energy and binding energy values are interconvertible. However this description is only applicable to free atoms in space, and is insufficient for situations where atoms are physically adjacent to one another such as in chemical compounds, since their adjacent electron orbitals will interact on the process of photoemission. Thus a more flexible description is required.
The kinetic energy values for Auger electrons and photoelectrons produced from core transitions in solids are influenced by the chemical environment of the excited atom\(^{(2,6)}\). There are two influencing factors for such shifts, often known as chemical shifts:

a) Changes occur in the electrostatic potential arising from the surrounding field of neighbouring atoms or ions. This contribution is caused by the difference between the self-consistent one-electron potentials in the free atom from that present in the compound in which the atom is incorporated, and appears on the initial state of the core electron. Hence it is often termed core-level shift, and

b) Due to the presence of core holes following photoemission, rearrangement or "relaxation" of the electron distributions within the chemical environment of the excited atom occurs. The electrostatic forces associated with core holes tend to polarise the surrounding electron cloud, this causing the redistribution of individual electrons. Thus the core holes are effectively screened by the formation of a larger density of electrons around them. Such redistribution produces a relaxation shift which appears to change the core level with respect to its position in the ground state. In reality it arises since the energy of the final state is lower.

Following work by Hartree\(^{(7)}\) on the self consistent field (SCF) approach, theoretical determinations of binding energies on an atomic level have been developed in recent years. An accurate binding energy value can be obtained from the difference between the energy of an ion and that of the atom. This assumes that the electron orbitals remain frozen on ejection, from which Koopman's Theorem\(^{(8)}\) would be valid:

\[ E_{BE}^{(j)} = E_{ion}^{(N-1)} - E_{atom}^{(N)} \quad \ldots \quad 1.4 \]
However, the binding energy of an electronic hole state \((j)\) is expressed by Koopman as:

\[
E_{BE}(j) = -\varepsilon(j)
\] 

where \(\varepsilon(j)\) is the eigenvalue derived for the one electron Schrodinger equation for an orbital \(j\) of an \(N\) electron atom. Since in reality some relaxation of the orbitals will occur following photoemission to leave the binding energy of the electron smaller in value than that predicted, the difference that exists between \(E_{BE}(j)_1\) and \(E_{BE}(j)_2\) is due to a polarisation potential induced by other orbital relaxations on atomic field conditions changing to those of ionic.

Thus:

\[
E_{BE}(j) = -\varepsilon(j) - R^\alpha(j)
\] 

where \(R^\alpha(j)\) is known as the "relaxation" energy.

Since the inner atomic shells are closer to the nucleus and thus their behaviour more influenced by it, it follows that the majority of contributions to \(R^\alpha(j)\) must come from the outer atomic shells, since these are less affected by the nucleus and thus more responsive to change with respect to the chemical environment of the atom.

Values for \(R^\alpha(j)\) can be calculated directly from methods such as Shirley's equivalent core approximation\(^{(9)}\). The relaxation energy \(R^\alpha(j)\) contains two components: \(R^{\text{ea}}(j)\), which is the extra atomic relaxation energy associated with the chemical environment, and \(R^{\text{ia}}(j)\).
which is the intra atomic component, the latter being more atom-like and less variable with changes in chemical environment. Thus:

\[ R^a(j) = R^{ia}(j) + R^{ea}(j) - E^{corr}(j) \quad \ldots \ldots \quad 1.7 \]

where:

\[ E^{corr} \] is a factor due to the change in electron correlation associated with the process of ionisation.

Hence relaxation occurs due to the contraction of electrons from outer atomic shells, and even from surrounding atoms, towards the core hole produced, to directly effect the photoelectron energy on emission.

Combining the two equations gives:

\[ E_{BE}(j) = - \zeta(j) - R^{ia}(j) - R^{ea}(j) + E^{corr}(j) \quad \ldots \ldots \quad 1.8 \]

The binding energy of an electron is dependent on the chemical environment that surrounds it, and the XPS technique is capable of elemental valence state determination, which is not usually the case for AES. The value \( R^{ea}(j) \) for solids is due to screening of the core hole by surrounding electrons. Since the photoemission process takes only \( 10^{-17} \) of a second to occur, in this time the surrounding electrons will not change position (i.e. the lattice will not be able to relax), such that each of the values in equation 1.8 may change with environment to produce a chemical shift:

\[ \Delta E_{BE}(j) = - \Delta \zeta(j) - \Delta R^{ia}(j) - \Delta R^{ea}(j) + \Delta^2 E^{corr}(j) \quad \ldots \ldots \quad 1.9 \]
Since e(j) and R^{ia}(j) both depend on the valence band electrons q linearly, and since also the value of E^{corr} is likely to remain unaltered, the chemical shift becomes:

\[ \Delta E_{BE} (j) = K Aq - \Delta R^{ea} (j) \] ...... 1.10

If KAq is known or can be calculated, the level of extra atomic relaxation energy can be determined. Attempts have been made to deduce the atomic changes which correlate with chemical shifts including those of: Hoogewijs et al^10^ using the Friedel model, Siegbahn et al^11^ using the simple ionic model, and calculations using Pauling electronegativity principles^12^.

1.4 Auger Transitions

Peaks due to Auger transitions are a common feature of XPS spectra, although they are often less well defined than photoelectron peaks, due to the more complex selection rules applicable. However, the Auger process jkl can yield electrons of well defined kinetic energy, \( E_{KE}(jkl) \), this value being dependent on \( E_{BE}(j), E_{BE}(k) \) and \( E_{BE}(l) \). Auger peaks so produced are becoming of increasing importance in chemical analysis applications, since their energies contain relaxation components that are complementary to those of photoelectron peaks in the same spectrum.
The photoionisation process (equation 1.1) produces a core hole which precedes the Auger process jkl, as shown in Figure 1.2:

\[ M^+ (j) \rightarrow M^+ (k) M^+ (1) + e^- \quad \ldots \quad 1.11 \]

Following the work of Kowalczyk\(^{(13)}\) on the Auger process, it was found that three independent stages could be ascribed to this event:

1) Initial ionisation

\[ M + h\nu \rightarrow M^+ (j) + e^- : E_{BE} \quad \ldots \quad 1.12 \]

2) and 3) Final state creation

\[ M \rightarrow M^+ (k) + e^- : E_{BE} (k) \quad \ldots \quad 1.13 \]

\[ M^+ (1) \rightarrow M^+ (k) M^+ (l) + e^- : E_{BE} (kl) \quad 1.14 \]

Since the kinetic energy of the Auger electron is dependent on the individual core level binding energies for levels \( j, k \) and \( l \), it can be determined directly:

\[ E_{KE} (jkl) = E_{BE} (j) - E_{BE} (k) - E_{BE} (kl) \quad \ldots \quad 1.15 \]
However, the component $E_{BE}^{(kl)}$, being the photoionized 1-shell containing a k-shell core hole, cannot be evaluated directly from the original atom M. Attempts to solve this problem first involved an equivalent core approximation, whereby binding energy values from the next element in the periodic table were used to compensate for the (kl) hole-hole interaction\(^{(14)}\), but this gave poor agreement with experiment. Improvements were gained by the involvement of valence band electron polarisation effects with the final state vacancy\(^{(15)}\), but this method has been superceded by semi-empirical methods. However, it has been used in the compilation of more elaborate models\(^{(9,16)}\), including the formation of a Born-Haber cycle\(^{(17)}\).

The more popular semi-empirical method for Auger energy calculations is summarised thus:

$$E_{KE}^{(jk1)} = E_{BE}^{(j)} - E_{BE}^{(1)} - F(kl : f)$$

$$+ R^{ia} (kl) + R^{ea} (kl) \quad \ldots \ldots \ 1.16$$

where :

$F(kl:f) = \text{the coupling energy of the two holes in the final state.}$

Since the $R^{ea}$ component involves a flow of electrons towards the k hole on its formation, the l hole formation environment is thus made more negative, causing the $E_{BE}^{(kl)}$ value to be lowered. $R^{ea}$ values are large for metals, since the conduction band electrons screen the k hole by being drawn down from the conduction band.
Total relaxation energies for photoemission and Auger emission are given by:

\[
R_T (j) = R_{ia} (j) + R_{ea} (j) \quad \ldots \ldots 1.17
\]

\[
R_T (kl) = R_{ia} (kl) + R_{ea} (kl) \quad \ldots \ldots 1.18
\]

these involving the simple addition of the intra atomic and extra atomic components. The relaxation energy is supplied mostly to the emitted electron, whilst the atomic nuclei remain "fixed" to their relative positions. The extra atomic components \(R_{ea}(j)\) and \(R_{ea}(kl)\) are governed by:

1) the magnitude of the central positive charge formed on emission, and
2) the degree of neutralisation of the positive charge, via screening charges originating from the valence or conduction bands.

The difference in chemical shifts following the two processes is attributable more to the effect of polarisation of electron clouds than any other.\(^{(18)}\).

1.5 The Auger Parameter

The Auger parameter was first defined\(^{(19)}\) to be:

\[
\zeta = F (kl : f) - R_{ia} (kl) - R_{ea} (kl) \quad \ldots \ldots 1.19
\]
and described the difference in energy between 1 electron emission with and without k hole presence. Whilst suitable for comparisons with theoretical models, the presence of $R^{ia}$ and $R^{ea}$ terms made experimental comparisons difficult, since the $R^{ea}$ component is the only one sensitive to the chemical environment.

Whilst accurate Auger and photoelectron peak positions can be measured experimentally, they are affected nonetheless by changes in the reference energy level, which can occur due to changes in work function or specimen charging. Thus the reliability of individual peak position measurements cannot be guaranteed at any one time.

However, the comparison of Auger and photoelectron chemical shifts can overcome this problem. Work by Kowalczyk et al.\textsuperscript{(13)} studying sodium in a variety of compounds found good correlation between differential shifts and theoretical values. Following this, Wagner\textsuperscript{(20)} developed a complete treatise on the chemical information obtainable using the Auger parameter. The definition was, in this case, given by the equation:

$$\alpha = E_{KE}(jkl) - E_{KE}(i)$$

$$= E_{KE}(jkl) + E_{BE}(i) - \nu$$ \hspace{1cm} \ldots \ldots 1.20$$

Subsequently, this was modified by Gaarestroon and Winograd\textsuperscript{(21)} to produce a Modified Auger Parameter, being:

$$\alpha' = \alpha + \nu$$

$$= E_{KE}(jkl) + E_{BE}(i)$$ \hspace{1cm} \ldots \ldots 1.21$$
This value was more constant and less confusing than the original Auger parameter since it was independent of photon energy and thus always positive.

Wagner's definition of the difference in the Auger energy was:

\[
\Delta E(jk1) = \Delta \zeta(j) - 2\Delta \zeta(k) + \Delta R^{ea}(k1) - \Delta R^{ea}(j)
\]

\[
= -\Delta \zeta(k) + 3\Delta R^{ea}(j)
\] .... 1.22

Combining equations 1.21 and 1.22 gives:

\[
\Delta \alpha = \Delta E_{KE}(jk1) - \Delta E_{KE}(i)
\]

\[
= -\Delta \zeta(k) + 3\Delta R^{ea}(j) + \Delta \zeta(i) - \Delta R^{ea}(i)
\] .... 1.23

this assuming that \(\Delta e(i) = \Delta e(j) = \Delta e(k)\), and \(i = j = k = 1\)

Thus:

\[
\Delta \alpha = 2\Delta R^{ea}(j)
\] .... 1.24

From equation 1.24 it can be seen that the chemical shifts in the Auger parameter are due to the effects of extra atomic relaxation only.
The findings of Kowalczyk et al\textsuperscript{(13)} were comparable:

\[
\Delta E (jkl) - \Delta E (i) = \Delta R_{ea} (k1) \quad \ldots \ldots 1.25
\]

though their result is not compatible absolutely with that of Wagner, since classical theory suggests that:

\[
\Delta R_{ea} (k1) = 4 \Delta R_{ea} (j) \quad \ldots \ldots 1.26
\]

The Auger parameter can be used to determine values of $R_{ea}$. The work of Kowalczyk et al was repeated by Fiermans et al\textsuperscript{(22)} for zinc compounds and substantiated somewhat, leading to the conclusions that for zinc chalcogenides $R_{ea}$ decreases with compound ionicity, whilst for zinc halides $R_{ea}$ was found to decrease with halide electronegativity.

There are two separate components contributing to chemical shifts: a core-type photoelectron component and an Auger electron line component. Both can occur at the same time\textsuperscript{(23)} making experimental isolation difficult. It is through this difficulty that the concepts of Auger parameter and extra-atomic relaxation energy measurements have been introduced, with some success.

Chemical shifts calculated from the photoelectron and Auger lines present in an XPS spectrum can be absolute values, providing that data is available for the free atoms concerned. Unfortunately, this is rarely the case, leading to the necessity for lengthy calculations. Thus a method was required for the extraction of absolute relaxation energy values from Auger parameter chemical changes, which led to the work of
Bechstedt and co-workers\(^{(24,25)}\), whose methods have been adopted in this study, and others\(^{(20,13)}\).

The method outlined by Bechstedt was of particular application to silicon compounds. This involved a VG ESCA3 electron spectrometer with polychromatic Ag L\(\alpha\) and Al K\(\alpha\) radiations to measure \(\Delta R_D^{ea}\) from experimental Auger parameters, static dielectric constants and plasmon energies of solids, for silicon core levels in a range of compounds. Calculated relaxation shifts \(\Delta R_D^{ea}(1s)\) and \(\Delta R_D^{ea}(2p)\) were in reasonable agreement with experimental values, and gave a good description of the extra-atomic polarisation effect for a deep level. Their results are discussed further in Chapter 4.

1.6 Chemical State Plots

A useful application of the Auger parameter has involved the so-called "fingerprinting" method developed by Wagner\(^{(26)}\). In such chemical state plots tripartite axes are used for plotting Auger peak kinetic energy value, photoelectron peak binding energy value and their product the Auger parameter (+ photon energy) value. From this a unique diagonal line on the plot can describe the chemical state of a particular element in a compound. Figure 1.8 shows one such plot for silicon, this involving the 2p and LMM Auger lines. Due to variation in static charging and experimental accuracy, rectangular blocks rather than definable points were decreed more appropriate. Values greater than the line \(A_{\text{const}}\) indicate \(R^{ea}(j)\) to be decreased while \(R^{ea}(kl)\) increases making \(A\) larger. For values on the line:

\[
\Delta E_{KE}(jk) = \Delta E_{KE}(i) = -\Delta E_{BE}(i) \quad \ldots \ldots 1.27
\]
That is:

\[
\Delta E_{BE} (j) - \Delta E_{BE} (k) - \Delta E_{BE} (i) + \Delta R^{ea} (kl) = - \Delta E_{BE} (i) \quad \ldots \ldots 1.28
\]

and if \( i = k \) or \( i = 1 \), and

\[
\Delta E_{BE} (j) - \Delta E_{BE} (k) = \Delta h\nu (jk) \quad \ldots \ldots 1.29
\]

\[
\Delta h\nu (jk) + \Delta R^{ea} (kl) = 0 \quad \ldots \ldots 1.30
\]

Thus for \( \Delta R^{ea} \) to be zero, \( \Delta h\nu (jk) \) will need to be zero, which necessitates that there is no energy difference between the photons emitted from \( jk \) transitions for an element in different chemical states.

Although there has been some discussion, it has been clearly shown by White and Gibbs\(^{(27)}\) that x-ray energies do shift with changes in chemical state. Thus \( h\nu (jk) \) and \( \Delta R^{ea} (kl) \) will not be zero, and lines representing \( A_{const} \) will not exhibit constant values for \( \Delta R^{ea} (jk) \). The fact that x-ray energies do shift is very important, since this facilitates useful studies of element chemical behaviour within wide ranging compounds. For example, it has been shown\(^{(28)}\) that the Al Ka peak shifts with Al coordination number and Al-O distance, and also that Si Ka peak shifts can predict the degree of polymerisation of \( \text{SiO}_2 \) tetrahedra\(^{(29)}\).
Figure 1.8 Chemical state plot for silicon

Thus the Auger parameter has increased in popularity and use to become a definitive experimental measurement, since its value is both sensitive to chemical state and insensitive to specimen charging, assuming the latter to be uniform across the energy spectrum. It can give a fingerprint of the given states since it uses the Auger peak excited by the Bremsstrahlung radiation together with the binding energies of the level from which the Auger electron is ejected. However, as shown by Bechstedt et al. the "chemical" shift on the final hole level is not necessarily the same as that on the initial hole level; they differ by the extent to which chemical shifts occur on the x-ray lines. To be correct, the chemical state plot should include the binding energy of the initial core hole and for this a higher energy x-ray source is required.
1.7 Higher Energy Sources for XPS

Although XPS has been virtually standardised to the use of MgKα and Al Kα x-ray sources, these "conventional" sources can only bring forth strong ejection of Auger lines from half the elements in the periodic table\(^{(30)}\). To combat these inherent restrictions, an electron beam can be used to cause deeper core level ionisation, but this possibility has several problems:

1) extensive charging can occur,
2) radiation damage can occur, and
3) cross-section values for deeper core level ionisations using electrons are relatively small, giving poorer signal-to-background ratios when compared with that for x-radiation.

The use of such higher energy x-ray sources allows deeper core level lines to be excited, which can give more information on the chemical composition of the surface. Furthermore, the extra Auger lines consequently available are of even more interest. High energy XPS (sometimes termed HEX) was one of three topics outlined by Siegbahn in 1982 (Pittsburgh Conference, USA) for the future growth of XPS, liquid state XPS and x-ray photoelectron diffraction (XPD) being the others.

Thus a variety of attempts have been made to find a high energy x-ray source to complement Mg Kα and Al Kα, and the choice of anode materials investigated has been wide, as shown in Table 1.1. The most common problem encountered in this search has been the invariable broad natural linewidths possessed by promising cases, in comparison to conventional sources, restricting their resolution and rendering them far
<table>
<thead>
<tr>
<th>X-RAY</th>
<th>PHOTON ENERGY (eV)</th>
<th>LINENWIDTH (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si Ka</td>
<td>1739.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Zr La</td>
<td>2042.4</td>
<td>1.6</td>
</tr>
<tr>
<td>Au Mo</td>
<td>2122.9</td>
<td>2.15</td>
</tr>
<tr>
<td>Mo La</td>
<td>2293.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Ag La</td>
<td>2984.3</td>
<td>2.6</td>
</tr>
<tr>
<td>Ti Kα</td>
<td>4510.9</td>
<td>2.0</td>
</tr>
<tr>
<td>Cr Kα</td>
<td>5417</td>
<td>2.1</td>
</tr>
<tr>
<td>Cu Kα</td>
<td>8055</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 1.1 List of high energy XPS anode materials

less suitable for XPS. This is demonstrated in Figure 1.9. Only a small number of these anodes have been developed successfully, usually to overcome a specific problem unresolvable with conventional XPS. The most noteworthy case is that of Si Kα.

Figure 1.9 The natural linewidths of various X-ray anode materials
The more commonly studied anode materials are discussed below.

1.71 Si Kα X-rays

The silicon Kα x-ray source (hv=1739.4 eV) was first developed for the specific analysis of aluminium compounds, particularly for aluminium in the presence of copper, such as in passive layers on aluminium brass and aluminium bronze alloys\(^{(31)}\). Its use avoided peak overlap problems which were experienced using conventional XPS. A less severe problem was also encountered on analysing 2p photoelectrons of arsenic and selenium, where due to low kinetic energy values on excitation by Al Kα x-rays, the photoelectron peaks were lost in the secondary electron cascade background.

This photon source energy enabled the Al 1s photoelectron to be excited, but also offered further chemical information by examination of the equally strong KLL Auger peak observed. Possession of a not unreasonable linewidth for general XPS use led to the compilation of peak sensitivity factors for subshells from 45 elements\(^{(29)}\), which showed good agreement with theoretical cross-section values. The source proved to be a reliable and useful one for XPS, being able to withstand reasonable power loadings, with its main applications being for the studies of aluminium and bromine.

28
1.72 Zr Lα X-rays

The origin of the zirconium Lα x-ray source (hν=2042.4eV) was similar to that for Si Kα, being developed by Castle and co-workers\(^{(32)}\). Indeed, the need for Zr Lα followed work with Si Kα in that, whilst the latter possessed energy sufficient to excite the Al 1s photoelectron, it could not excite the Si 1s photoelectron (binding energy 1840eV), which was thought useful for the measurement of Auger parameters\(^{(33)}\) in aluminosilicate materials. Using Si Kα for such studies, a shortage of reference lines existed for silicon since, though the chemical shift of the 2p lines for both Al and Si oxides was good, it was difficult to detect small shifts resulting from structural features in complex compounds. The use of Zr Lα x-rays allowed the study of Si 1s, KLL and LMM Auger lines, although the latter were very low in sensitivity, and represented the lowest useful energy in the L series. It fitted in well with the Mg, Al and Si Kα series of energies and was more amenable for use as an anode material than the next in the K series, phosphorus.

The manufacture of the Zr Lα source was found to be easy, and a useful feature was that due to the high oxide solubility in the bulk at higher temperatures a metal surface was always present on the anode during operation\(^{(33)}\). However, the natural linewidth of 1.6eV reduced resolution and a further problem involved the presence of an intense Lα2 satellite peak whose intensity is 30% of that for the Lα1 primary peak. Monochromatisation is possible using a conventional α-quartz crystal, but it is not efficient due to reflection condition and absorption problems. Thus spectra produced by unmonochromatic Zr Lα radiation possess the characteristic increasing background level with
increasing binding energy, as shown in Figure 1.10, resulting in the subsequent loss of resolution at high binding energy values. Though a photoelectron peak may be present, its intensity will be weak enough to render it inseparable from the high background level.

Figure 1.10  Zr La survey scan of muscovite mica

1.73 Au Mα X-rays

Gold anodes have been prepared by electroplating onto copper^{(34)}, but the spectral resolution available using Au Mα is disappointing, and poorer than that obtainable with Zr Lα. The slightly greater photon energy (hν=2122.9eV) allows excitation of some deeper L, M, N, and O shell orbitals, but x-ray intensities are similar in efficiency to those for Zr Lα, leading to similar peak intensities. There is also a possibility of anode contamination occurrence, such that the advantages of using this source are limited, it being more desirable to use a radiation that generates intense Auger lines from all the elements, such as Ag Lα.
1.74 Ti Kα, Cr Kα and Cu Kα X-rays

The use of these anode materials for high energy XPS work involves a substantial rise in the incident photon source energy, since Ti Kα possesses the lowest energy at 4510.9eV. On utilising such high energies substantial changes begin to occur in the interactions between photons and the sample, and it has been suggested(35) that this problem begins to exist on passing 3000eV.

Ti Kα, with a polychromatic linewidth of 2.0eV, is not suitable for accurate chemical state analysis using core level peaks since the 6.0eV separation of the α₁ and α₂ components restricts identification(36), due to the Kα₂ satellite being very strong. The x-ray induced Auger lines are of interest, the KLL series being extended to scandium for Ti Kα (likewise to titanium for Cr Kα and to cobalt for Cu Kα). Nevertheless, adequately intense LMM Auger series are excited from elements from scandium through to cobalt using conventional XPS sources. New x-ray lines are excited later in the periodic table, but an x-ray energy between 1 and 3KV can excite stronger lines from other Auger series for each case. Hence the value of these Kα lines is difficult to fully substantiate.

From the work of Fellner-Feldegg et al(37) there is an optimum x-ray intensity when:

\[ E_p = 8 E_x \] ....... 1.31
where:

\[ E_p = \text{the bombarding electron energy and} \]
\[ E_x = \text{the binding energy value for the deepest core level involved in x-ray production.} \]

Hence when using a similar primary beam energy, higher energy x-rays will not be as strongly excited as those of a lower energy. Indeed, what makes the higher Ka series even less attractive for high energy XPS applications is that if the primary beam energy is limited to a maximum value, \( X \), there occurs a drop in the production of x-rays with atomic number.

<table>
<thead>
<tr>
<th>Element</th>
<th>At No.</th>
<th>Energy ( h\nu (\text{ev}) )</th>
<th>Conductivity W/Cm °C (T = 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>47</td>
<td>2584.3</td>
<td>4.29</td>
</tr>
<tr>
<td>Au</td>
<td>79</td>
<td>2122.9</td>
<td>3.18</td>
</tr>
<tr>
<td>Al</td>
<td>13</td>
<td>1486.6</td>
<td>2.37</td>
</tr>
<tr>
<td>Mg</td>
<td>12</td>
<td>1253.6</td>
<td>1.56</td>
</tr>
<tr>
<td>Si</td>
<td>14</td>
<td>1739.4</td>
<td>1.49</td>
</tr>
<tr>
<td>Zr</td>
<td>40</td>
<td>2042.4</td>
<td>0.23</td>
</tr>
<tr>
<td>Ti</td>
<td>22</td>
<td>4510.9</td>
<td>0.22</td>
</tr>
</tbody>
</table>

Table 1.2 Thermal conductivity values

Another important factor when considering the use of high energy XPS sources is that their energies can become damaging to specimens for analysis due to high Bremsstrahlung radiation presence. This is particularly the case for Ti Ka x-rays, where a 40KV power supply is required, and for Cr Ka and Cu Ka x-rays where a 70KV level applies. Chromium and copper can withstand such loadings, due to their conduction properties, but the poor conductivity (Table 1.2) and relatively low melting point for titanium restrict the level for Ti Ka use.
There is another problem concerning the use of Ti, Cr and Cu Kα x-rays since, due to their high energies, electrons from low energy subshells (and thus possessing very high kinetic energy values) will consequently suffer greater transmission losses, in comparison with softer (i.e. lower energy) x-rays exciting similar orbitals (as shown in Figure 1.3). This follows from the rule outlined by Helmer and Weichert (38) for high kinetic energies:

\[ T = C \frac{1}{E_{KE}} \] ~ 1.32

where:

- \( T \) = the analyser transmission function and
- \( E_{KE} \) = the kinetic energy value.

Generally, photoelectron and Auger peak intensities depend on cross-section subshell values for different incident x-ray beams, which are largest for subshells of binding energy value closest to, but less than, the beam energy. Table 1.3 lists the peaks of greatest cross-sections for a variety of x-ray sources.

<table>
<thead>
<tr>
<th>X-ray</th>
<th>Photon Energy</th>
<th>Highest Cross-sections</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1s  2p  3d</td>
</tr>
<tr>
<td>SiKα</td>
<td>1739.4</td>
<td>Al  Br  Hf</td>
</tr>
<tr>
<td>ZrLα</td>
<td>2042.4</td>
<td>Si  Sr  Ir</td>
</tr>
<tr>
<td>AuKα</td>
<td>2122.9</td>
<td>Si  Y  Ir</td>
</tr>
<tr>
<td>MoLα</td>
<td>2293.2</td>
<td>P   Zr  Au</td>
</tr>
<tr>
<td>AgLα</td>
<td>2904.3</td>
<td>Cl  Ru  At</td>
</tr>
<tr>
<td>TiKα</td>
<td>4510.9</td>
<td>Sc  Te  Th</td>
</tr>
<tr>
<td>CrKα</td>
<td>5417.0</td>
<td>Ti  Ba  Th</td>
</tr>
<tr>
<td>CuKα</td>
<td>8055.0</td>
<td>Co  Dy  Th</td>
</tr>
</tbody>
</table>

Table 1.3 Highest cross-sections available for high energy XPS sources
Using different x-ray sources, Wagner\textsuperscript{(34)} has calculated photoelectron peak intensities and shown that Ti K\textsubscript{\alpha} offers no advantage over Ag L\textsubscript{\alpha}, Au M\textsubscript{\alpha} and Al K\textsubscript{\alpha} x-rays in this respect.

1.75 Mo L\textsubscript{\alpha}, Rh L\textsubscript{\alpha} and Ag L\textsubscript{\alpha} X-rays

The possibility for use of molybdenum, rhodium and silver L\textsubscript{\alpha} x-rays as high energy XPS sources (together with Zr L\textsubscript{\alpha} and Ti K\textsubscript{\alpha}) has been outlined by Keski-Rahkonen and Krause\textsuperscript{(33)}. A major benefit involves the increased accessibility to second row element K shells, this being important due to low excitations of L and M shells for low atomic number elements. With strong K shell excitation, strong Auger peaks are necessarily available, this being the case for most elements in the periodic table (e.g. using Ag L\textsubscript{\alpha}). The L lines of elements yttrium to tin, however, are relatively broad and weak and also require monochromatisation for investigations to progress.

<table>
<thead>
<tr>
<th>X-ray Transition</th>
<th>Energy hv(eV)</th>
<th>( \lambda^* (\text{\AA}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>L\textsubscript{\alpha} L\textsubscript{III} M\textsubscript{\textit{\gamma}}</td>
<td>2904.34</td>
<td>4.15443</td>
</tr>
<tr>
<td>L\textsubscript{\alpha} L\textsubscript{III} M\textsubscript{IV}</td>
<td>2978.21</td>
<td>4.16294</td>
</tr>
<tr>
<td>L\textsubscript{\alpha} L\textsubscript{II} M\textsubscript{IV}</td>
<td>3150.94</td>
<td>3.93473</td>
</tr>
<tr>
<td>L\textsubscript{\alpha} L\textsubscript{III} M\textsubscript{\textit{\gamma}}</td>
<td>2633.70</td>
<td>4.7076</td>
</tr>
<tr>
<td>L\textsubscript{\alpha} L\textsubscript{II} M\textsubscript{\textit{\gamma}}</td>
<td>2606.10</td>
<td>4.4183</td>
</tr>
</tbody>
</table>

\( \lambda^* = 1.0000256 \text{\AA} / \lambda^* \)

Table 1.4 The polychromatic nature of Ag L\textsubscript{\alpha}
It can be seen from Figure 1.9 that Ag Lα has particular attractiveness as a possible source for XPS, since it can generate 1s electrons unavailable on use of conventional sources. However, the inherent problem of broad natural linewidth predominates, and the value of 2.6eV (30) would be increased to over 3eV when the width component due to the core line, $W_c$ was added. Hence a method to overcome this problem, such as monochromatisation, became essential prior to development. The polychromatic nature of Ag Lα is shown in Figure 1.11 and in Table 1.4, where the strongest components are listed. Satellite

![Figure 1.11 The x-ray spectrum for Ag Lα radiation](image)

peaks cause major problems for all x-rays of the L-series (Y through to Sn), since the $La_{3,4}$ to $La_{1,2}$ ratio is approximately 50%.

In order to extend his Auger parameter approach to XPS analysis, Wagner (34) noted that a photon energy of at least 3000eV would be necessary. He concluded that the more flexible anode materials were Ti Kα, Ag Lα and possibly Au Mα due to its high Bremsstrahlung component.
The intensity of flux from several anode materials was determined by Greene and Cosslett\textsuperscript{(40)} using a photon yield per electron formula:

\[ N = A (E_0 - E_x)^{1.63} \]

where:

- \( E_0 \) = the electron beam energy,
- \( E_x \) = the inner shell ionisation energy, and
- \( A \) = a constant, dependent upon the anode material used and on the energy level in question.

Using the values obtained, and also the known fraction of \( \beta \) x-rays, relative fluxes were found as in Table 1.5. These values assume that Al K\( \alpha \) x-rays are attenuated 50\% on passing through a 10\( \mu \)m aluminium window, and the other radiations attenuated minimally on passing through a 25\( \mu \)m beryllium window.

<table>
<thead>
<tr>
<th>X-ray</th>
<th>Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al K( \alpha )</td>
<td>1.00</td>
</tr>
<tr>
<td>Ti K( \alpha )</td>
<td>0.27</td>
</tr>
<tr>
<td>Ag L( \alpha )</td>
<td>0.25</td>
</tr>
<tr>
<td>Au K( \alpha )</td>
<td>1.04</td>
</tr>
</tbody>
</table>

Table 1.5 Relative fluxes for different x-rays

On multiplying these relative fluxes at each energy by cross-section values obtained from Scofield\textsuperscript{(44)} for selected core levels, relative yields were provided, as shown in Table 1.6.
Table 1.6 Relative yields of core level lines

These values were uncorrected for the photoelectron λ value (λ = inelastic mean free path), or for the analyser transmission function. Despite this, trends can be identified for relative peak intensities using the different x-ray sources. The photoemission intensity obtained for Ti Kα is only approximately half that for Ag Lα use, the 6.0eV separation between the α1 and α2 components of the Ti Kα source causing a severe restriction on its use for the achievement of even basic chemical state information. This drop in intensity on increasing photon energy could indicate Ag Lα to be the hardest x-ray suitable for XPS of all elements, if its broad natural linewidth could be reduced by monochromatisation.

1.8 The Use of Monochromators

The application of high energy x-rays has been hindered by the broad natural linewidths they generally possess, which limits resolution. One method that is available to overcome this problem involves monochromatisation. This leads to the removal of x-ray satellites which restrict resolution, an improvement in signal-to-background ratios for spectra and the removal of the Bremsstrahlung component of the radiation.
The dispersion of x-ray energies by crystal diffraction, which is a common method for monochromating, is governed by the Bragg equation:

\[ n \lambda = 2d \sin \theta \]  

where:

- \( n \) = the order of diffraction,
- \( \lambda \) = the x-ray wavelength,
- \( d \) = the crystal spacing and
- \( \theta \) = the Bragg angle.

Quartz has proved an efficient material for this purpose, since it possesses advantages in relation to its ability to exist as large perfect crystals that can easily be bent or ground to produce the desired curvature for its surface. It can also be heated to high temperatures without causing damage or distortion, such that it can remain present for spectrometer bake-out periods. Early experiments involved the use of a cylindrically bent crystal, from which the use of spherically bent crystals developed, which can improve resolution without losses in sensitivity. The latter possess a better x-ray collection efficiency, although they are more difficult to prepare.

The production of a bent crystal causes each wafer to possess a non-uniform distribution of strain and therefore a variation in lattice spacing, which causes considerable aberration where x-rays penetrate (approximately \( 3 \mu m \) below the surface). This effect is reduced in seriousness, however, by the partial cancellation of the geometrical aberration contribution, due to the lack of crystal surface conformation.
to the Rowland circle (see Figure 1.12). The monochromator resolution is dependent upon the degree of such aberrations, and also on the inherent resolution from the finite number of atomic planes involved in the Bragg diffraction.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Al Kα</th>
<th>Ag La</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy (eV)</td>
<td>1486.6</td>
<td>2984.3</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>8.3393</td>
<td>4.1544</td>
</tr>
<tr>
<td>Order of diffraction, n</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>sin θ</td>
<td>0.97994</td>
<td>0.97635</td>
</tr>
<tr>
<td>Bragg angle θ</td>
<td>78.5</td>
<td>77.5</td>
</tr>
</tbody>
</table>

Table 1.7 Bragg reflection conditions

Conventional monochromator geometry was originally developed for Al Kα, using the Bragg reflection from the 1010 planes of a spherically bent quartz crystal, the conditions for which are listed in Table 1.7(a). Thus a first order reflection involved an angle of 78.5°. Ideally, θ should be as close to 90° as possible, since this minimises geometrical aberrations whilst maximising Bragg diffraction intensity and monochromator dispersion. Following discussions between VG Scientific and the University of Surrey this geometry was investigated for use with Ag La x-rays. It was found that the geometry was usable for the
second order diffraction of the 1010 plane of quartz at an angle of 77.5°, since the wavelength of Ag Lα x-rays is approximately half that for Al Kα x-rays. This is shown in Table 1.7(b). Only minor physical changes were necessary for the introduction of Ag Lα use: the tilting of the crystal by 2° and the adjustment of the anode position by 17.6mm. This produced an x-ray line source of dimensions 6mm x 1mm, which is similar to that obtained for Al Kα use, and linewidth of approximately 1.3eV, which is double that for Al Kα. The reduction in linewidth obtained was thought sufficient to transform Ag Lα into a practical source for XPS, certainly for measurements of chemical shifts in compounds based on the elements aluminium and silicon, since these tend to be significant and thus more easily resolvable. Thus in comparison to Zr Lα radiation, it is the reduction of background intensity following monochromatisation rather than the ultimate resolution obtainable that would favour Ag Lα use. The selection of lines on the monochromatisation of Al Kα and Ag Lα x-rays can be seen in Figures 1.4 and 1.11, from which the Lα1,2 line is both broader (due to the more intense α2 satellite) and less intense in comparison to the Kα1,2 line.

Thus the monochromatisation of Ag Lα x-rays was achieved through the use of a conventional Al Kα monochromator and the replacement of the Al anode with one of Ag, minor readjustment and retuning obtaining the new x-ray line.
Prospects for the use of Ag La radiation

Although interest has been shown in Ag La as a source for higher energy XPS, there are few references available in the literature. Where Ag La x-rays have been used, they are polychromatic and thus restricted in resolution.

Reference has been made to Ag La by Carlson and co-workers\(^{(41)}\), which they used to analyse the KLL Auger spectra for aluminium, silicon and sulphur. There is no evidence of any 1s core level peak determinations, probably due to these peaks being too broad for accurate analysis.

<table>
<thead>
<tr>
<th>X-ray</th>
<th>Energy hv((\text{eV}))</th>
<th>Peak Height</th>
<th>Peak Area</th>
<th>Signal to noise</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgKα</td>
<td>1253.6</td>
<td>44</td>
<td>13</td>
<td>100:1</td>
</tr>
<tr>
<td>AgLa</td>
<td>2984.3</td>
<td>1</td>
<td>1</td>
<td>20:1</td>
</tr>
</tbody>
</table>

Table 1.8 Ne 1s intensity ratios in Mg Kα and Ag La x-radiations

Rh Lα and Ag La x-rays have been used by Keski-Rahkonen and Krause\(^{(39)}\) to study the behaviour of sulphur in the forms of gaseous \(\text{H}_2\text{S}, \text{SO}_2\) and \(\text{SF}_6\). On monitoring the 1s, KLL and 2p positions, a more significant chemical shift was found for the 1s peak, rather than the 2p, which agreed closely with a potential model predicted value. Their energy calculations included intra-atomic and extra-atomic relaxation values, the latter being found to be smaller and only associated with the negative charge flow towards the atom from other
molecular regions. Though gaseous state relaxations were very small in size, it was thought that larger flows of charge could be expected in the solid phase, since these could originate from the surrounding lattice. This was the first study of the KLL Auger series and gas phase 1s core levels for sulphur compounds, and no comparison of signal intensity was made between Ag Lα and conventional XPS sources. However, an indication of the linewidth of polychromatic Ag Lα radiation can be found by using a set of uncorrected intensity ratios of Ne 1s in Mg Kα and Ag Lα as shown in Table 1.3. From this, the large differences between the ratios of height and area confirm the Ag Lα linewidth.

<table>
<thead>
<tr>
<th>Li</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Na</th>
<th>Mg</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>1s</td>
<td>0.0838</td>
<td>0.0024</td>
<td>0.0003</td>
<td>0.0082</td>
<td>0.0294</td>
<td>0.0294</td>
<td>0.0294</td>
<td>0.0294</td>
</tr>
<tr>
<td>2s</td>
<td>0.805</td>
<td>0.0375</td>
<td>0.0014</td>
<td>0.0041</td>
<td>0.0197</td>
<td>0.0681</td>
<td>0.0681</td>
<td>0.0681</td>
</tr>
<tr>
<td>2p 1/2</td>
<td>1.73</td>
<td>0.0864</td>
<td>0.0014</td>
<td>0.0041</td>
<td>0.0197</td>
<td>0.0681</td>
<td>0.0681</td>
<td>0.0681</td>
</tr>
<tr>
<td>2p 3/2</td>
<td>3.25</td>
<td>0.166</td>
<td>0.0100</td>
<td>0.0209</td>
<td>0.0410</td>
<td>0.151</td>
<td>0.269</td>
<td>0.448</td>
</tr>
<tr>
<td>3s</td>
<td>5.53</td>
<td>0.283</td>
<td>0.0209</td>
<td>0.0410</td>
<td>0.151</td>
<td>0.269</td>
<td>0.448</td>
<td>0.448</td>
</tr>
<tr>
<td>3p 1/2</td>
<td>8.72</td>
<td>0.444</td>
<td>0.0770</td>
<td>0.137</td>
<td>0.269</td>
<td>0.448</td>
<td>0.448</td>
<td>0.448</td>
</tr>
</tbody>
</table>

Table 1.9 Photoionisation cross-sections for Ag Lα radiation

Theoretical photoionisation cross-sections of atoms from hydrogen to zinc in the periodic table have been calculated by Yarzhemsky and co-workers in the USSR \(^5\) for the Ag Lα line. This was an extension to previous studies under the leadership of Nefedov involving calculations for Mg Kα, Al Kα, Y Mα, Zr Mα, F Kα and Au Mα \(^42,43\). Their results
are summarised in Table 1.9. The comparison of total photoionisation cross-sections available for the F 1s line in these radiations can be seen in Figure 1.13. Thus a substantial decrease occurs on the use of Ag Lα, although in comparison to possible values for Ti Kα (as yet not calculated) through an extrapolation of this line the former is much the more preferable. This again indicates the possibility that Ag Lα is the hardest x-ray suitable for general XPS applications.

![Figure 1.13 Comparison of cross-sections for Mg Kα, Al Kα and Ag Lα x-rays (F 1s)](image)

A comparison of the number of lines excitable using various x-ray sources is shown in Figures 1.14 and 1.15. The major feature of Ag Lα is the ability to excite 1s electrons from aluminium through to chlorine in the periodic table, none of which is well catered for in conventional XPS. Following the successful monochromatisation of these x-rays, the resolution is sufficient for the attainment of chemical state information.
Figure 1.14 Ag La ls core level capability

Thus the particular attributes of Ag La x-rays (when monochromatic) are:

1) Strong core level peaks are generated for all major elements, particularly from Al through to Cl in the periodic table,
2) Auger peaks are generated from nearly every element, which allows the accurate measurement of Auger parameters,

\[ A^I = E_{BE}(1s) + E_{KE}(KLL) (- h \nu) \]
\[ A^{II} = E_{BE}(2p) + E_{KE}(LMM) (- h \nu) \]

3) As well as improved sensitivity for elements whose major peaks occur in the 1500–3000eV binding energy range, there is no serious reduction in sensitivity in the conventional XPS energy range, which can be a shortcoming for high energy sources.

4) Monochromatisation gives improvements in signal-to-background ratio, reduced beam induced damage and removal of Bremsstrahlung and interfering satellites.

5) Although its linewidth is broader than conventional Al and Mg Ka x-rays, it is nonetheless narrower than any other source above 2000eV, making it highly suitable for accurate chemical state analysis.

6) Its energy of 2984.3eV is thought to be very close to the upper limit for "useful XPS" of 3000eV.

7) Silver possesses the highest thermal conductivity of any material at room temperature, and thus has the ability to withstand greater power loadings. Static silver coatings alloyed to a copper anode should be able to operate continuously at over 1.5KW, this partially compensating for the loss in count rate suffered on monochromating.
Considering the above characteristics of monochromatic Ag Lα as a high energy source for XPS a study was thus undertaken to develop its use as a complementary source to the conventional Mg Kα and Al Kα polychromatic x-rays used in the surface analysis field.

Following the initial investigation into the resolution available with monochromatic Ag Lα x-rays, it is intended to confirm these limitations and accurately determine the optimum conditions for good signal intensities. Furthermore, for the successful use of this x-ray source the spectrometer energy scale requires calibration up to 3000eV, which is beyond the range of spectrometer design.

For the quantitative application of this x-ray source, it is also intended to determine experimental sensitivity factors available on its use. This would enable meaningful comparisons to be made with data from conventional x-ray sources.

Due to the higher energy of the Ag Lα source, photoelectrons are excited from a greater depth within a sample. The wide range of electron kinetic energies available makes it worthwhile to determine λ, the inelastic mean free path, for these electrons (and from it the analysis depth involved) on the use of this source.

Having gained the ability to analyse samples using monochromatic Ag Lα x-rays in both a qualitative and quantitative manner, its possible application to the solving of materials science/engineering problems will be investigated, with particular reference to the availability of 1s core level electrons available for Al, Si, P, S and Cl, each of which are unavailable using conventional x-ray sources.
Chapter 2. Resolution, Optimisation and Calibration

2.1 Reference Materials

The standard reference materials for the calibration of commercial spectrometers are silver and gold. The latter was used for this study, consisting of a 3000Å layer of gold evaporated onto a silicon substrate material.

In the previous chapter it was stated that the resolution available for a photoelectron peak is reduced by width contributions from the analysis peak itself, the linewidth of the x-radiation used and components due to the spectrometer analyser and electrostatic charging respectively. Since gold is a conducting material, the effects of \( E_{El} \) will be minimal, whilst for a particular analyser setting the effects of \( W_{Sp} \) will be invariant. Since \( W_{P} \) is difficult to measure, the successful utilisation of monochromatic Ag La x-rays will depend primarily on the component \( W_{X} \).

The entrance to analyser slit width was set to a 4mm width (it's maximum setting), and was held constant throughout the monitoring of resolution. The experimental conditions were as follows:

- Number of channels : 100
- Channel width : 0.2eV
- Total time in each channel : >2 mins
- Analyser Energy : 2-200eV
- Analyser slit widths : 4mm
- Electron take-off angle : 45°
X-ray anode settings : 14KV, 40mA = 560W
Spectrometer vacuum : $10^{-9}$ mbar
Electron flood gun settings : not used

Full width at half maximum height (FWHM) measurements of resolution were taken for the Au 4f7/2 and Au 3d5/2 peaks, these possessing binding energy positions of 74 and 2206eV respectively.

Figure 2.1 Variation of resolution with analyser energy for Ag Lα x-rays (monochromatic)

The results for the Au 4f7/2 line are shown in Figure 2.1. The FWHM value of 8.2eV for a 200eV analyser energy is unsatisfactory since a maximum of 2.0eV is generally considered to be acceptable for the retrieval of accurate chemical state information using XPS. The use of a 50eV analyser energy permits the attainment of such information, since the FWHM is reduced to a value of around 1.9eV. Beyond this point (i.e. on the application of 20, 10 and 5eV analyser energies) the resolution improves less significantly, although a limit of approximately 1.3eV is
achieved on the use of a 5eV analyser energy.

The use of an analyser energy of 20eV for the analysis of the deposited gold layer produced the survey spectrum as shown in Figure 2.2. To obtain this 20 scans (1000 secs/scan) were made, with 4mm entrance slits. The cross section available for the Au 3d doublet is excellent, whilst the MNN Augers are also strong. The use of a 10eV analyser energy enables the separation of the Au 4f doublet into its 7/2 and 5/2 components. It is evident from this study that the conventional peaks used for calibration, such as the Au 4f7/2, possess low signal intensities in monochromatic Ag Lα radiation. However, the cross section available for the Au 3d5/2, for example, is a factor of at least ten times better, and it is for peaks of this energy that the use of the Ag Lα source becomes advantageous.

As a further test of this x-ray source, a survey scan was acquired for freshly cleaved mica, which is an insulating planar sample that is generally considered difficult to analyse accurately. In this instance the electron flood gun was necessary for charge neutralisation, the settings being 0V accelerating potential and 0.2mA emission current, which were recommended for use by the instrument manufacturers. The failure to obtain a spectrum from an insulating material without the use of an electron flood gun demonstrates that the effect of stray incident electrons within the instrument is negligible. The spectrum obtained can be seen in Figure 2.3, and demonstrates the ability to measure the Auger parameters for both silicon and aluminium, since the 1s and KLL Auger regions display good sensitivity.
Figure 2.2 Survey scan for gold in monochromatic Ag La radiation

Figure 2.3 Survey scan for mica in monochromatic Ag La radiation
Thus the larger chemical shifts for silicon and aluminium compounds can be measured using an analyser energy of 50 or 20eV. For the measurement of less substantial shifts a lower value would be necessary, and this would lengthen acquisition times.

2.2 Comparing Monochromatic Ag Lα Capability

A comparison between the resolution of monochromatic Ag Lα with that for other XPS anode materials is shown in Figure 2.4. The values for monochromatic Ag Lα are comparable with those of Si Kα (a high energy source previously investigated in this laboratory(28)) and, more importantly, with those for conventional Al Kα and Mg Kα x-rays. Indeed, a limit is achieved that is only slightly inferior to that for Al Kα, which is encouraging. Of course, Al Kα can be monochromated itself to further improve its resolution and produce a linewidth of ≈ 0.6eV, about half that available for Ag Lα.

However, on the reduction of analyser energy to obtain good Ag Lα resolution, it necessarily follows that fewer photoelectrons will be able to traverse the hemispherical sector analyser and be counted. Figure 2.5 summarises the intensity problem, though reference needs to be made to Figure 2.1 to obtain the relevant FWHM values. Thus an analyser energy of 200eV, for example, gives a count rate of 520 counts/second for the Au 4f7/2 peak. This figure does not include plotted points for the intensities obtained when using analyser energies of 5eV or 2eV, since the values obtained are so low as to render them unusable for normal work.
Figure 2.4 Resolution comparisons for different x-ray lines
Figure 2.5 Variation of count rate with resolution for Ag Lα x-rays (monochromatic)

Figure 2.6 shows a comparison of count rates obtainable for the Au 4f7/2 line, on the use of a 50eV analyser energy, using the quartet of sources referred to in Figure 2.4. No clearer indication can be given of the lengthier acquisition periods necessary when using monochromatic Ag Lα radiation.

2.3 Counting Statistics Following Monochromatisation

The severe decrease in signal intensities on the optimisation of resolution necessitates a compromise between these two parameters. This involved the use of a 50eV analyser energy, together with a 4mm analyser entrance slit width, for the acquisition of narrow scan spectra. These values produce a resolution (FWHM 1.9eV) suitable for chemical state determination for elements such as aluminium and silicon, as noted in Chapter 1, and also acceptable counting statistics (= 60 counts/second),
these values being for the Au 4f7/2 line.

2.3.1 The optimisation of signal intensities

To obtain full optimisation of signal intensity when using monochromatic Ag La x-rays, one vital function involves the optimisation of the α-quartz crystal reflection conditions, through tilting in x, y and θ directions and also via the optimum placement of the Ag anode itself, variable through the use of a z shift.

In comparison to recent instrumentation, the ESCA3 MkII spectrometer possesses no transfer lens, a 4 inch rather than a 6 inch analyser and single channeltron detection rather than multichannel detection. These differences result in a considerable reduction of signal intensity, which highlights the importance of signal optimisation.

The diffraction conditions using α-quartz for the monochromatisation of Al Ka x-rays are efficient. In comparison, those for Ag La x-rays are reasonable, but count rates are nonetheless a factor of $10^4$ down, partly due to the reduced transmission function of the analyser at higher energies. Also, a well collimated system should produce a sharp peak due to the diffraction of the x-rays, whilst the use of α-quartz does tend to produce a smaller, less sharp (i.e. broader) peak. At present the popularity of α-quartz crystal use for monochromators remains unchallenged, though in the future it is likely that another material possessing better reflection conditions will be developed and introduced to improve counting statistics further. This could be a man-made rather than a natural material.
For the positioning of the x-ray beam a phosphor screen was used. Signal intensities were recorded using an argon ion-cleaned copper specimen (the Cu 2p\(\frac{3}{2}\) peak being generally used) which was moved into position following "optimisation" of the x-ray conditions.

![Figure 2.6 Count rate comparisons for different x-ray lines](image)

The result for the original conditions, as received on spectrometer installation, can be seen in Figure 2.7, with the "sharpest" peak producing a maximum of 37 counts. This occurred for the Ag anode (i.e. the z shift) at a setting of 7.05cm from its base position, \(\theta\) being set to 10°. On experimentation, it was found that this situation could be improved through the movement of the anode to a position 6.95cm from its base position. This is shown in Figure 2.8 and, though a greater count rate is induced, a sharp peak is not produced as would be expected and desired. Following further investigations involving the Ag anode position variation and crystal rotation, the 7.05 position is the only one capable of producing a sharp peak in intensity for the Cu 2p\(\frac{3}{2}\) line,
the others giving higher count rates but very uneven performance on rotation. This behaviour introduced doubts concerning the uniformity of the α-quartz crystal itself.

Examples of the spectra obtainable with the monochromator diffraction conditions set to their original or "old" configuration can be seen in Figures 2.9 and 2.10. The survey scan for copper shown in Figure 2.10 (17 scans at 100eV analyser energy) is fairly noisy, above which the Cu 3p peak is only just distinguishable. The Cu 2p3/2 narrow scan shown in Figure 2.9 (10 scans at 50eV analyser energy) possesses a peak maximum of approximately 180 counts.

By use of a different rotary drive monochromator set-up a "new" monochromator position could be predicted from variation of the parameters, to hopefully produce better quality data and/or shorter acquisition times. The same α-quartz crystal was used, with only its
support housing being changed. The highest recordable count rate for
this configuration was obtained with the anode at a position 6.9 cm from
its base position, and measured over 190 counts. However, as shown in
Figure 2.11, this condition did not produce a sharp single peak. In
fact, the clearest single peaks were obtained at an anode position of
6.85 cm, and produced two separate sharp peaks, 180 degrees apart, as
shown in Figure 2.12.

![Graph 1: Cu 2p3/2 line](image1)

Figure 2.9 Cu 2p3/2 line:
original or "old" configuration

![Graph 2: Survey scan of copper](image2)

Figure 2.10 Survey scan of copper:
original or "old" configuration

The spectra obtainable with this "new" position are shown in Figures
2.13 and 2.14. These are directly comparable with the previous spectra
shown in Figures 2.9 and 2.10. The survey scan is less noisy, with the
positions of the Cu 3p and Cu 3s photoelectron peaks being
distinguishable from the background. Similarly, the Cu 2p3/2 narrow scan
is better resolved and reaches an intensity maximum of over 650 counts
after 10 scans. The acquisition conditions for these spectra were similar to those used previously.

Figure 2.11 Cu 2p3/2 signal intensity: maximised (new configuration)

Figure 2.12 Cu 2p3/2 signal intensity: optimised peak symmetry (new configuration)

Following this experiment the original monochromator crystal housing was returned to the spectrometer. The performance was then compared between the "old" position, as had been measured originally, and the "new" position, as predicted from the second configuration used. The original settings, which for completeness were x = 6.875 and y = 2.95 crystal settings, produced a plot as shown in Figure 2.15a, where an anode position of 6.95/7.05 produces a count rate of around 240 for the Cu 2p3/2 peak. In comparison, on adjustment to the proposed settings (x = 6.67 and y = 2.34), a plot was produced as shown in Figure 2.15b, where the peak is more specular, appears at an anode position of 7.0 and produces a count rate of 420 for the Cu 2p3/2 peak.
Thus a notable increase in counting statistics could be produced on optimisation of the reflection conditions for the α-quartz crystal. In the context of the count rates available for the monochromatic Ag Lα source, this increase is substantial. Thus it is recommended for all spectroscopists utilising a crystal monochromator to carefully maximise the reflection conditions on installation of a system and on subsequent routine calibration procedures.

One problem highlighted by this study involved the failure to produce sharp peaks when rotating the α-quartz crystal in many of its positions, as shown in Figures 2.7 and 2.8. This indicated that a level
of assymmetry was present within the crystal, which might explain why optimisation in this case was difficult to obtain. Thus the increases in count rate obtained were not due to "new" diffraction conditions being induced from the α-quartz crystal, but merely due to "better" conditions being found. With no assymmetry present in a crystal, conditions should be more straightforward for the optimisation procedure.

2.4 Spectrometer Calibration

The electron spectrometers manufactured today are designed for the use of conventional x-ray anode materials. Thus the energy scale is calibrated up to 1500eV, over which confidence in results can be expected. When the Ag Lα x-ray source is employed on such instrumentation, it cannot be assumed that this accurate calibration will apply up to a value of 3000eV. Thus a calibration procedure needs to be applied in this instance. Since this source is of particular use for the analysis of aluminosilicate materials the use of aluminium foil and silicon wafer samples as reference materials was appropriate. The samples were mounted onto a specimen holder using double-sided adhesive tape. During analysis with XPS, they were charge-neutralised by the electron flood gun at a setting of 0V acceleration potential and 0.2mA emission current, as used previously for mica.

Narrow scan spectra were acquired using conditions similar to those described for the studies of gold. The Al 2p and KLL Auger and the Si 2p and KLL Auger lines were acquired in Mg Kα (the Augers being excited through the Bremsstrahlung radiation) as well as in monochromatic Ag Lα radiation (the Augers being directly excited), for which the 1s regions were also acquired. The individual peak positions are shown in Table
2.1, whilst the Auger parameter data is shown in Table 2.2.

![Monochromator positions: a) old and b) proposed](image)

**Figure 2.15** Monochromator positions: a) old and b) proposed

<table>
<thead>
<tr>
<th>Radiation</th>
<th>Region</th>
<th>$\text{Al}^0$</th>
<th>$\text{Al}^{3+}$</th>
<th>$\Delta A$</th>
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<td>Ag La</td>
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<td>72.5</td>
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<td></td>
<td>1s</td>
<td>1556.7</td>
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<td>2.6</td>
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</table>

**Table 2.1** Peak positions: Al foil

<table>
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<th>$A^I$</th>
<th>$A^I$</th>
<th>$A^I$</th>
<th>$\Delta A^I$</th>
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</thead>
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<td>$\text{Al}^{3+}$</td>
<td>$\Delta A^I$</td>
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<td>4.7</td>
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<tr>
<td>Ag La (2p + KLL)</td>
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<td>4.4</td>
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<tr>
<td>Ag La (1s + KLL)</td>
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<td>1s - 2p separation</td>
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<td>0.0</td>
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**Table 2.2** Auger parameter data: Al foil

The linearity of the spectrometer energy scale up to 3000eV appears to be satisfactory from these results. Subtracting the Auger parameter ($A^{II}$) value for Al 2p+KLL Auger in monochromatic Ag La radiation from that for Mg Ka radiation should produce the difference in energy of photon sources used, i.e.
This appears to be confirmed well.

Furthermore, the separation between the Al \( A_1^{II}(2p+KLL) \) and the Al \( A_1^{I}(1s+KLL) \) values using monochromatic Ag La should be equal to the energy of the Al K\( \alpha \) x-ray (i.e. \( 1s - 2p \)). This is confirmed in Table 2.2 since, although the values are not identical, they are acceptable when one considers the limits of chemical shifts on the x-rays themselves.

2.5 Conclusions

1) The novel monochromatic Ag La x-ray anode possesses resolution that compares satisfactorily with those of other x-ray sources, its limit being approximately 1.3eV for the Au 4f7/2 peak. Since chemical state information is obtainable with values of below 2.0eV, this source becomes useful for practical XPS.

2) On obtaining reasonable resolution a corresponding decrease in signal intensity is recorded, particularly when analyser energies of less than 50eV are used.

3) Due to the low count rates experienced by this monochromatic source, the accurate positioning of samples and monochromator reflection conditions is important, since acquisition times can be reduced and quality of data improved.
4) The energy scale for the ESCA3 MkII spectrometer has been calibrated up to 3000eV by use of silicon wafer and aluminium foil samples respectively. These provide standards across the range of materials most usefully made available by the development of this source.

5) The quality of spectra obtainable using monochromatic Ag Lα is good. On the removal of the Bremsstrahlung component, background intensities are low. This allows the accurate measurement of less intense photoelectron and Auger peaks, which are easily obscured on the use of polychromatic x-ray sources.

The resolution available for the monochromatic Ag Lα x-ray source makes it suitable for qualitative XPS analysis. However, for quantitative analyses, experimental sensitivity factors need to be determined for these x-rays.
3.1 Material Selection

Standard materials were selected on the basis conducted previously in this laboratory\(^{(27)}\), and needed to be stable with respect to the following:

1) The conditions of an ultra-high vacuum can be severe,
2) Bombardment with x-radiation can cause heating, decomposition, changes in chemical state and related effects,
3) Bombardment under low energy electron beams, for the charge neutralisation necessary for insulators using this x-ray source, can cause similar effects to (2), as well as electron stimulated desorption and related effects.

Fluorides, being the most widely-stable materials across the periodic table, were selected in their simplest form wherever possible, with the use of secondary elements as standards being avoided if possible. A protocol was developed for which the complete selection process, in order of desirability, was:

1) The choice of a simple fluorine compound of an element, \( X_m F_n \), if stable under the conditions outlined above, e.g. \( NaF \) for the determination of the sensitivity factors for sodium,
2) Failing the above, with no simple fluoride of the element proving suitable for use, a secondary standard needed to be chosen. Thus a simple compound of sodium \( (Na_n X_m) \) was selected where stable, e.g.
NaCl for the determination of the sensitivity factors for chlorine,

3) Failing the above, with no simple compounds of fluorine or sodium being suitable for use, a more complex compound based on one or other of these elements \((\text{Na}_n \text{X}_m \text{F}_o)\) or \((\text{Na}_n \text{X}_m \text{O}_o)\), was selected where stable, e.g. \(\text{Na}_2(\text{SO}_4)\) or \(\text{K}_2\text{SiF}_6\) for the determination of the sensitivity factors for sulphur and/or oxygen and silicon respectively.

4) Failing the above, with no compounds of fluorine or sodium proving stable enough for use, a compound based on aluminium, potassium or oxygen would be selected where stable, e.g. \(\text{Al}_2\text{O}_3\), \(\text{KNO}_3\) or \(\text{ZnO}\) for the determination of sensitivity factors for oxygen, nitrogen and zinc respectively.

All compounds used for standardisation were the purest commercially available, obtained from Koch-Light Laboratories Ltd., Colnbrook, Bucks., U.K., Fisons Scientific Apparatus, Loughborough, Leics., U.K. and BDH Chemicals Ltd, Parkstone, Poole, Dorset, U.K. Each compound, together with its origin and purity, is listed in Table 3.1.

3.2 Sample Preparation

With the exception of the PTFE sample used for determination of a sensitivity factor for carbon, which was run in the normal manner for planar samples, all samples involved the use of powders, for which handling can be a problem. Many of the fluorides are air-sensitive and hydrate very quickly, which can lead to decreased sensitivity and inaccurate results. This can also cause degradation of the spectrometer vacuum or possibly instigate maintenance problems. For efficiency of results and lower acquisition times it is desirable to use fine rather than coarse particles, as demonstrated in Figure 3.1, since the latter
<table>
<thead>
<tr>
<th>Compound</th>
<th>Source</th>
<th>Purity (%)</th>
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</tr>
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<td>NaF₄B</td>
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<tr>
<td>(C₂F₆)ₙ</td>
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<td>KNO₃</td>
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<td>P</td>
</tr>
<tr>
<td>ZnO</td>
<td>Fisons</td>
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</tr>
</tbody>
</table>

Abbreviations:  
*T* = Technical grade  
P = Pure grade

Table 3.1 Standard materials: origins and purities

can lead to increased x-ray and photoelectron losses, due to shading effects and electron scattering on photoemission.

Thus experimental procedures were designed to handle individual materials on their merits, according to their degree of reactivity. Three methods of sample mounting were investigated, having ground the
powders into a fine state using a glass pestle and mortar. These were:

a) directly mounting powder onto double-sided adhesive tape using a "standard" specimen holder constructed of stainless steel. This gave a flat surface to incoming x-rays and outgoing photoelectrons. However, the quality of spectra produced using this method was lowered by a persistent contamination problem, carbon and oxygen being constituent members of the tape material itself, whilst the similar presence of silicon was not helpful for the $K_2SiF_6$ sample. Also, for particularly difficult samples to handle, the possibility of heating or baking in-situ, to effect desorption of surface contaminants, was not possible. Consequently, this technique was only adopted for samples known to be reliably stable,

b) impressing into indium (or gold) foil. This technique has been popular elsewhere\cite{44,27}, since such foils are malleable and able to grip fine powders. Indium proved the more commercially viable option, and a
reliable supplier was found within the U.K. (Mining and Chemical Products Limited, Alperton, Wembley, Middlesex). The material was supplied in ingot form, which was subsequently rolled to 0.5mm thickness sheets. Assuming the powder to be analysed was in a sufficiently fine form, this method proved ideal, the conductive nature of this substrate material allowing the possibility of baking samples in-situ. An adjustment in specimen holder design involved the use of a recessed holder that allowed indium sheets of dimensions 3cm x 1cm to be wrapped around set positions prior to the imbedding of the powder, which had previously been dried in an oven at 120° C, without the need for double-sided tape. The surface produced using this method was particularly good, with the compaction of powder onto the foil producing a cake of more than one unit thickness,

c) sample pelletisation under pressure. Having dried the sample over a more lengthy period (6-8 weeks at 120° C) the material was compacted using a vacuum hydraulic press, as used for the preparation of KBr discs in infra-red spectroscopy, to produce a pellet. The pellet has an advantage in that it possesses a good surface for XPS, being nominally flat, this reducing x-ray and photoelectron shading effects more noticeably than mountings of a more conventional manner (such as (a) and (b) above). However, the characteristics of the material being pressed are relevant since if it is not completely dry, or immediately hydrolyses on exposure to air, the water content remaining is subsequently impressed into the structure of the pellet on pressurisation. Since the pellet is very dense outgassing problems when it is placed within the spectrometer can continue for considerable lengths of time. This is a major drawback for this method. Further problems can arise with contamination, since the hydraulic press chamber is in intimate contact with the powder under severe conditions. Where this method was utilised, to ensure that a
fresh surface was made available, the pellet was scraped immediately prior to entrance into the spectrometer under flow of argon gas.

Thus the usual experimental procedure for XPS sample preparation was as follows, this involving over 80% of samples analysed:

1) cut indium foil master (3cm x 1cm),
2) grind powder (previously dried in an oven at 120°C) in pestle and mortar,
3) place foil onto recess area of specimen holder, before wrapping and crimping to fix firmly,
4) place ground powder onto indium foil,
5) impress powder into foil by either:
a) use of a metallurgical press with aluminium foil wrap to reduce contamination, or
b) use of a glass pestle, gently rolled across the surface.

A continuous, flat coverage of powder on the indium is most desirable, the substrate material being undetectable with XPS.

3.3 Experimental Procedures

Most of the samples were to some extent reactive in air so that repetition was often necessary before reproducibility of results was obtained. Several of the metal fluorides, such as NaF, TiF$_3$ and VF$_3$ were problematical, as indeed was ZnF$_2$, which was subsequently passed over as a standard and replaced by the use of ZnO.
Experimental procedure often lowered contamination levels significantly, due to:

1) rendering the powdered sample to as fine a state as possible prior to drying,
2) adopting extended drying times to remove any moisture present,
3) speedy sample mounting onto indium foil under flow of argon gas,
4) immediate placement into spectrometer, prior to evacuation to at least $10^{-8}$ mbar,
5) heating of specimen holder to 100°C for 24 hours,
6) baking out, if necessary, of samples in-situ at 100°C for 48 hours,
7) maintenance of good spectrometer vacuum throughout acquisition periods, for the attainment of good quality spectra, and
8) accurate specimen positioning under the monochromatic x-ray beam, for reduction in total counting times.

When analysing such sensitive materials, it is desirable to obtain results in as short a time as possible, to ensure confidence that the sample has not changed during the elapsed analysis time. Unfortunately, the use of monochromatic Ag Kα x-rays for this purpose is far from ideal, due to the very low count rates experienced which lead to these times being long. However, in an effort to combat this problem rigorous selection was made of both acceptable and unacceptable data, this policy resulting in some standards being analysed several times before results could be considered reliable. One common problem encountered was that samples were not sufficiently dry. Other samples showed a tendency to grow carbonate layers during acquisition. Fortunately, the peak shift (chemical shift) between fluoride and carbonate is sufficient to allow peak separation through deconvolution, though it was normal practice to
Particularly difficult samples to handle were LiF and NaF$_4$B, both of which needed lengthy acquisition periods (up to 300 narrow scans at 100 seconds/scan) due to the low photoelectric cross-sections of the Li 1s and B 1s core orbitals in monochromatic Ag L$_\alpha$ x-rays, the photon energy being 2984eV and their binding energies being 55eV and 188eV respectively. NaF$_4$B invariably tended to produce its carbonate which was removed by deconvolution. However, before such techniques can be applied spectral signal/noise ratios must be good. The times thus involved enhance the possibility of specimen change during the time of analysis. Lithium fluoride was found to be problematical even when comprehensively dried, so that in-situ baking was always a necessary precaution.

3.4 Survey Scan Spectra

Survey scans for standard samples (see Figure 3.2) were acquired on a regular basis, primarily to monitor relative proportions of contamination present but also to control any unexpected spectral features, if and when they occurred. Ideally, it would be more acceptable to acquire a survey scan for each standard used, but counting statistics for the monochromatic x-ray source deemed this impractical, since one wants to acquire spectra under as similar conditions as possible, particularly with regard to spectrometer vacuum, x-ray filament age and condition, and flood gun filament age and condition. The acquisition conditions for survey scans were:
Number of channels : 3000
Channel width : 1eV
Total time in each channel : >5 secs
Analyser energy : 100eV
Analyser slit width : 4mm
Electron take-off angle : 45°
X-ray source settings : 14KV, 40mA = 560W
Spectrometer vacuum : 10^-9 mbar
Electron flood gun settings : 0V, 0.2mA

3.5 Narrow Scan Spectra

Whilst a survey scan gives an overview of elements present in a sample, this view is generally only a qualitative one. For quantitative data, one must acquire narrow scan spectra, since these involve higher resolution and thus give more accurate results.

The conditions used for the attainment of narrow scan spectra in this study were :

Number of channels : 100
Channel width : 0.2eV
Total time in each channel : >6 mins
Analyser energy : 50eV
Analyser slit widths : 4mm
Electron take-off angle : 45°
X-ray anode settings : 14KV, 40mA = 560W
Spectrometer vacuum : 10^-9 mbar
Electron flood gun settings : 0V, 0.2mA
Both peak height\(^{(45-47)}\) and peak area\(^{(45,48,49)}\) measurements were recorded for the major peaks of the spectrum, as well as those for the O 1s, C 1s, In 3d5/2 and In MNN Auger lines. The indium Auger peak was selected since, should any undesirable reaction occur between the standard material and the substrate into which it was impressed, any
changes in chemical state instigated would be clearly evident. This was always monitored, problems only occurring if samples were not sufficiently dry.

Data handling of these spectra, examples of which are shown in Figures 3.3 and 3.4, involved the removal of s-shaped background signals (50), this procedure being much less dependent on selected window position and being more accurate than the removal of a linear background.

Figure 3.3 Na 1s narrow scan for sodium fluoride standard

Figure 3.4 F 1s narrow scan for sodium fluoride standard
Spectra were generally terminated on a signal-to-noise specification rather than on a time basis, with a ratio of 40:1 being deemed acceptable. Some photoelectron peaks of poor cross section did not reach this value, and were counted for longer times, within reason, during which no noticeable growth in contamination level occurred. It was on these occasions that the thermal conductivity properties of silver (see Table 1.2) proved a distinct advantage, since other anodes might have experienced overheating problems, particularly over the periods required for LiF and NaF$_4$B confirmatory runs.

Peak height and area values obtained are dependent on a number of factors including:

a) the atomic concentration of the element in the compound,

b) the relative differential cross section for each individual orbital, and

c) the escape depth of the electrons.

The escape depth can vary greatly from orbital to orbital using high energy sources, since electrons can possess kinetic energies of between 10s and 1000s of electronvolts. An electron of high kinetic energy will possess a large escape depth value, since it will be able to withstand more inelastic collisions than an electron of lower kinetic energy.

Experimental sensitivity factors were calculated using the equations

\[
S_{\text{height}} (X_{ab}) = \frac{N_{X} \cdot I_{\text{height}} (X_{ab})}{N_{X} \cdot I_{\text{height}} (R_{cd})} \cdot \frac{S_{\text{height}} (R_{cd})}{S_{\text{height}} (R_{cd})} \quad \ldots \ldots 3.1
\]

\[
S_{\text{area}} (X_{ab}) = \frac{N_{X} \cdot I_{\text{area}} (X_{ab})}{N_{X} \cdot I_{\text{area}} (R_{cd})} \cdot \frac{S_{\text{area}} (R_{cd})}{S_{\text{area}} (R_{cd})} \quad \ldots \ldots 3.2
\]
where:

\[ S = \text{the sensitivity factors}, \]
\[ I = \text{the measured peak intensities of unknown orbital } a,b \text{ of element } X \text{ and reference orbital } c,d \text{ of element } R, \]
\[ N_X = \text{the surface atomic concentration of } X, \text{ and} \]
\[ N_R = \text{the surface atomic concentration of } R. \]

Table 3.2  Sensitivity factors relative to F 1s in Ag La radiation  
(Periods 2 and 3)

The results for monochromatic Ag La radiation are shown in Tables 3.2 and 3.3, and plotted in Figures 3.5 and 3.6. Among these values are some 1s and 2p orbitals reported for the first time. Of particular
interest is the 1s series from Si through P and S to Cl in the periodic table. The points plotted in the figures are the experimental results obtained, whereas the lines drawn are through the calculated photoionisation cross-section values for Ag La from Yarzhemski and co-workers(5) which were shown in Chapter 1 (Table 1.9). The agreement can be seen to be reasonably good.

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<th>Z</th>
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<td>0.40</td>
</tr>
</tbody>
</table>

Table 3.3 Sensitivity factors relative to F 1s in Ag La radiation (Period 4)

The subshell peak intensities increase in an exponential manner with atomic number. The breaks present in these curves, such as at Z = 21 in the 2p plot, when a decrease in intensity occurs are due to the possibility of distinguishing between the separate spin states (e.g.
2p\(^1/2\) and 2p\(^3/2\) in the 2p atomic orbital). The possibility of spin orbit splitting\(^{(5)}\) and separation of different components is dependent upon analyser energy used.

The in-situ sample baking procedure, when employed, did not change the chemical state of the element(s) being analysed. Hydrocarbon contamination was found to be extremely low on most samples, being generally 2-3% of the F 1s signal intensity. The oxygen signal, being monitored as an indication of sample hydrolysis, was kept below 5% of the F 1s intensity. Due to the importance of accuracy in this work, samples failing to satisfy these conditions were rejected, and subsequently re-analysed. Very occasionally it proved necessary to etch slightly the surface with argon ions, from the AG2 ion gun connected to the spectrometer analyser chamber. The usual conditions for this practice were 3KV energy and 1.5KV focus voltage, for a period of 5-15 seconds. This effected the removal of adsorbed species at the specimen surface, following which no changes in chemical state were detected. Due to the methods of sample preparation employed, coverage of the indium foil substrate was good, the indium signal being generally below 1% of that for the F 1s region.

3.6 Determination of the Instrument Transmission Function

Having obtained empirical sensitivity factor values for a range of elements across the periodic table and being in possession of theoretical cross section values calculated by Yarzhemski and co-workers, it is possible to determine the transmission function for the ESCA3 MkII spectrometer across the 3000eV energy spectrum when monochromatic Ag L\(\alpha\) radiation is used.
Figure 3.5 Sensitivity factors for 1s orbitals in monochromatic Ag Kα radiation
Figure 3.6 Sensitivity factors for 2p orbitals in monochromatic Ag Ia radiation
Following the approach of Seah (51), the current of photoelectrons $I_A$ of kinetic energy $E_A$ from an element $A$ is:

$$I_A = \sigma_A \int_\gamma=0 \int_\phi=0 \int L_A(\gamma)$$

$$X \int_{y=-\infty}^{\infty} \int_{x=-\infty}^{\infty} J_0(xy) T(xy\gamma E_A)$$

$$X \int_{z=0}^{\infty} N_A(xyz)$$

$$X \exp \left[ -\frac{Z}{\lambda_M(E_A) \cos \theta} \right] dx dy d\phi d\gamma \quad \ldots \ldots \quad 3.3$$

where:

$\sigma_A$ = the cross section for emission of a photoelectron from the relevant shell per atom,

$D(E_A)$ = the detection efficiency for each electron transmitted by the electron spectrometer,

$\gamma, \phi, x, y$ and $z$ = the angles as shown in Figure 3.7,

$L_A(\gamma)$ = the angular asymmetry of photoemission intensity,

$J_0(xy)$ = the characteristic x-ray line flux intensity at a point $(x,y)$ on the sample being analysed,

$T(xy\gamma E_A)$ = the analyser transmission,

$N_A(xyz)$ = the atom density of $A$ at $(x,y,z)$,

$\lambda_M(E_A)$ = the photoelectron inelastic mean free path in the matrix $M$,

and

$\theta$ = the angle of emission of the photoelectron with respect to the sample.
normal.

Figure 3.7 Geometry of the XPS analysis configuration

A comparison of two peaks from the same energy spectrum allows a simplification of the above equation. Hence, for a binary compound AB, where both surface roughness and spectrometer detector terms cancel:

\[
\frac{I_A}{I_B} = \frac{\sigma_A^X L_A(\gamma) G(E_A) N_A \lambda_{AB}(E_A)}{\sigma_B^X L_B(\gamma) G(E_B) N_B \lambda_{AB}(E_B)} \quad \ldots \quad 3.4
\]

where:
\( \sigma, L, N, \lambda = \) as above,

\( G = \) the instrumental acceptance functions.

Also, since:

\[
\frac{S_A}{S_B} = \frac{I_A}{I} - \frac{N_B}{N_A}
\]

...... 3.5

where:

\( S_A \) is the experimental sensitivity factor for element A, and

\( S_B \) is the experimental sensitivity factor for element B,

it thus follows that:

\[
\frac{S_A \sigma_B^X L_B(y)}{S_B \sigma_A^X L_A(y)} = \frac{G(E_A)}{G(E_B)} \frac{\lambda_{AB}(E_A)}{\lambda_{AB}(E_B)}
\]

...... 3.6

The aforementioned methodology allowed Seah to evaluate reference sets of data for differing experimental conditions covering a wide range of electron spectrometer types.

Hence a plot can be drawn to demonstrate the energy dependence of the product \( G^\lambda \), with the matrix dependent terms separated out. It is also possible to interpret the separation of intrinsic (LHS) and extrinsic (RHS) terms from the intensity equation (equation 3.4).
Using the data available in this case a plot for $G\lambda$ versus kinetic energy can be drawn as shown in Figure 3.8. It can be seen that the product appears to be constant (and thus energy independent) up to a value of 3000eV, with the discrepancy between the sensitivity factor and cross section values being very small (typically <10%). The inelastic mean free path value, $\lambda$, has previously been shown to obey an approximate square root dependence with kinetic energy over normal and extended XPS ranges. This implies that the transmission function varies as $E^{-0.5}$, at least over ranges typically up to 1500eV. This present data suggests that a similar dependence applies up to 3000eV.

Previous workers using the ESCA3 MkII spectrometer have reported a similar dependence. In particular, Castle and West stated an energy dependence as follows (for the high energy Si Kα x-ray source):

$$G\lambda = \text{constant}\ (\pm 0.15, \ E_{KE} = 0 - 1500eV) \quad \ldots \ldots \ 3.7$$

This range of constancy up to 1500eV was supported by the work of Hall et al, using a Hewlett-Packard spectrometer, who found $G\lambda$ to be constant over the range 900 - 1500eV.

However, above a kinetic energy value of 1500eV Castle and West found a markedly different energy dependence for $G\lambda$, this being:

$$G\lambda = 4.35E_{KE}^{-5.52}\ (\pm 0.20, \ E_{KE} = 1500 - 1800eV) \quad \ldots \ldots \ 3.8$$
This variation in energy dependence is shown in Figure 3.9.

This present study appears to contradict this finding, in that a range of constancy is found beyond 1500eV with no apparent non-linear dependence.
Figure 3.9 Variation of the instrument transmission function with electron energy (Si Ka radiation)

The instrument transmission $G$ is the product of the area analysed by the bombarding x-rays and the transmission function $T$. Since for the ESCA3 MkII instrument pre-retardation is used (38,54,55), it is expected that $G$ would vary inversely with kinetic energy from the electron optics brightness law (56):

$$\frac{B}{U} = \text{constant}$$

where:
B = the photometric brightness of the sample per unit solid angle per unit area, and
U = the potential of the electron.

The theory for pre-retardation in XPS was developed by Helmer and Weichert\(^{(38)}\), who concluded from their work that:

\[ G = kE^{-1} \] \[ \ldots \ldots . \text{3.10} \]

However, this law will only be correct if the apertures and slits between the sample and the detector are always filled with photoelectrons originating from the sample. The acceptance angles\(^{(51)}\) in this case are:

- radially : \( \pm 6^\circ \)
- tangentially : \( \pm 70^\circ \)

In the tangential direction the entrance slit is large. Thus below a certain level of retardation the electrons will not be able to fill the acceptance angle in that direction, allowing the transmission function G to become independent of electron energy.

This change occurs at approximately 200 to 600 eV below the energy of the x-ray photon being used, as found by Castle and West\(^{(28)}\). However, this "transition point" is dependent on:

a) the analyser pass energy,

b) the entrance and exit slit separations, and
c) the sample area irradiated by x-rays.
For the monochromatic Ag Lα line source, the electron optics are different from conventional sources. Although the maximum acceptance angles are similar to those for Mg Kα and Al Kα (and, indeed, Si Kα), the angles are determined by the irradiated sample area. The monochromatisation gives a line source (6mm x 1mm) and hence the angles are much smaller, which prevents the slits being filled with photoelectrons. This significant difference probably accounts for the Gλ value being constant for retardations up to 3000eV. It is noteworthy that the high kinetic energy deviation remains a real artifact, in accord with the work of Seah(51), Jorgensen and Berthou(46), Nefedov(42,43), Vulli and Starke(57) and Castle and West(28), despite it not being repeated with this set-up. This sharp deviation is not an instrumental problem, since it appears to occur for all spectrometer types and makes. Changes in x-ray energy seem to cause a shift in the "transition point" only, this remaining 200 to 0eV below the photon energy value.

A possible source of the problem is the use of Hartree-Slater wave functions for the calculation of theoretical cross sections, in which the inclusion of a systematic error is possible. This was pointed out by Reilman et al(58), who outlined the valence band and near valence subshells as possibly being problematical. However, the scale of any errors incurred and the range over which they exist is uncertain, and as such remains a problem to be understood in the future.
3.7 Inelastic Mean Free Paths

In an attempt to improve the quantitative interpretation of data obtained using monochromatic Ag Lα x-rays, experiments were conducted to calculate the inelastic mean free paths ($\lambda$), and through this the electron escape depths (often taken as $3\lambda$), of electrons excited by this radiation.

Freshly cleaved mica was used as the substrate material, onto which consecutive layers (1 to 10) of calcium stearate were deposited to give varying thicknesses of overlayer. The results produced were disappointing and of poor reproducibility since signal intensities for peaks varied with both time and spectrometer conditions.

This brought into question the stability of such organic layers for the duration of XPS analysis within a UHV system. Previously Langmuir-Blodgett (LB) layers have been thought to be UHV compatible, though reservations have been noted in the literature\(^{59}\). These experiments subjected the layers to more lengthy exposures than usual under such conditions. The samples needed to withstand bombardment from x-rays, even if monochromatic, and flood gun electrons for periods of up to 12 hours. It has been noted\(^{60}\) that x-ray degradation does occur to such layers, and this was chiefly attributed to the use of the conventional x-rays themselves, following which a time-dependent problem was solved by extrapolation back to zero time. This study suggested that electron bombardment might also be a significant factor, together with UHV and x-ray induced damage.
Thus use was made of the inelastic mean free paths obtained by Clark et al\textsuperscript{(36)}, in which the high energy Ti K\textalpha source was utilised to attain \( \lambda \) values over a 600 to 4430eV range with gold substrates and in-situ deposition of poly(paraxylylene) films. The results of their work are summarised in Figure 3.10, showing an approximate square root dependence for \( \lambda \) with energy. This allowed the relationship \( \lambda \propto KE^{(-0.5)} \) to be applied for the determination of the instrument transmission function outlined in the previous section.

![Diagram](image-url)

*Figure 3.10 Variation of \( \lambda \) with \( KE^{1/2} \) for Mg K\textalpha and Ti K\textalpha x-rays*
3.8 Conclusions

1) The sensitivity available with the monochromatic Ag L\alpha source is good, particularly in the range 1500-3000V. Access is gained to new core level orbitals, particularly in the 1s series aluminium to chlorine in the periodic table, whilst there is no corresponding serious decrease in sensitivity for lighter elements. This could indicate monochromatic Ag L\alpha to be the highest x-ray source useful for general XPS applications.

2) The experimental determination of sensitivity factors for monochromatic Ag L\alpha x-rays has produced results in good agreement with theoretical photoelectric cross-section data produced in the literature.

3) The determination of the instrument transmission function for the ESCA 3 MkII spectrometer up to 3000eV has shown this parameter to remain constant with kinetic energy, which is a satisfactory result. This finding contradicts with transmission functions calculated for other polychromatic sources by other workers for high kinetic energies. However, the monochromatisation of Ag L\alpha x-rays does change the area of sample illuminated by the incident x-rays, which affects the degree of photoelectron filling of the apertures between the sample and the detector. This important difference could account for the constancy in transmission function found.

4) The results obtained from these experiments enable a level of confidence to be used on the application of this novel x-ray source for the solving of materials problems, since data can be compared both qualitatively and quantitatively with that for conventional x-ray sources.
One such example involves the possible role played by chloride ions in the breakdown of passivity to permit corrosion of stainless steels. A study was thus undertaken involving monochromatic Ag Lα for the development of a greater understanding of the behaviour of chlorine.
Chapter 4. A Study of the Surface Chemistry of Chlorides

4.1 A Study of Chlorides

The use of the Auger parameter can be applied to chlorine using the monochromatic Ag La source. Chlorine is an element of great interest, though relatively little is known about it in relation to its surface chemistry or microchemistry behaviour. It has become of importance to corrosion scientists in recent years due to its apparent ability to penetrate passive layers on steels, rendering them active and thus able to corrode\(^{(61)}\), with possible catastrophic failures. Suggestions have been proposed as to how chloride ions can instigate this process but only a little experimental progress has been made. The hydroxychloride ion is thought to be involved, with subsequent hydrogen embrittlement.

The XPS measurement of 1s photoelectron peak positions together with those for the 2p and KLL (and LMM) Auger lines permits calculation of Auger parameters and extra-atomic relaxation energies for individual core levels. These might help to elucidate the situation of chlorine in the lattice of the passive layer. Also, the Cl 1s possesses a binding energy of 2823eV, whilst that for the 2p is 200eV, and this large energy separation is a most severe test of the energy calibration of the spectrometer and a good test of the applicability of the Auger parameter for high energy XPS studies.
4.11 Previous chloride studies

The study of the chemistry of chlorine is not a new one, and XPS has proved useful in this field. It was found long ago by Thomas (62) that the C 1s energy in halogenated methanes varied linearly with substituent electronegativities. The importance of final state effects (i.e. relaxation) in determining core ionisation energies and basicities subsequently emerged (63,64), with particular reference to gas phase acidities as determined both theoretically (65) and experimentally (66).

Electronegativity was defined by Pauling (12) as the power of an atom in a molecule to attract electrons to itself. However, this has remained difficult to quantify. Two separate contributions exist: one from the competition for electrons between individual atoms, and the other from the ability of atoms to accept charge. The former dominates the electronegativity of fluorine, for example, since it attracts electrons strongly but is only slightly polarisable, being a small, compact atom. Chlorine, on the other hand, is influenced by both factors, since it attracts electrons weakly but is also a bigger atom, making it more polarisable.

Aitken and co-workers (67) deduced that two chemical sources contribute to electronegativity:

a) a substituent can affect the ground state charge distribution (attraction or repulsion of electrons), and
b) a substituent can cause delocalisation of charge to affect the acceptance of charge by a molecule.
Their study of core level and Auger lines showed that relaxation effects increase in the order:

\[ H = F < CH_3 < Cl < Br \]

which agreed with simple theory and chemical experience. These relaxation energy values were found to decrease with distance between substituent and charge-changing site.

Together with those in the gas phase, some studies of chloride compounds have been conducted in the solid phase, involving crystalline\(^{(68-71)}\) and frozen in solution\(^{(72,73)}\) metal halides. Work carried out by Kuroda et al\(^{(73)}\) led to the conclusion that the separation between the Na 1s and Na KLL peaks differed for crystal and quick frozen aqueous solutions, while the Na 1s-anion core electron peak separation was unaffected. This was interpreted in terms of extra-atomic relaxation, since relaxation is influenced by the polarisability of the surrounding ions (for ionic crystals), particularly the nearest-neighbour ions.

Following Basalo and Pearson\(^{(74)}\) an estimation of the magnitude of the polarisation energy can be made:

\[
E_p = -\frac{nAq}{r^2} + \frac{nB\mu^2}{2r^3} + \frac{nU\mu^2}{2\alpha r^4} - \frac{nG\mu^2}{r^8}
\]

\[ \ldots \ldots 4.1 \]
where:

\[ \begin{align*} 
n &= \text{the number of nearest-neighbour ions}, 
q &= \text{the central ion charge change following hole creation}, 
\alpha &= \text{the polarisability of the nearest neighbour ion}, 
r &= \text{the central ion to nearest neighbour ion separation}, 
\mu &= \text{the induced dipole created} = \frac{\alpha \Delta q (1 + ba/r^3)}{r^2}, 
b &= \text{a constant depending on the arrangement of the neighbouring ions, being 1.15 when } n = 4, \text{ and 2.37 when } n = 6, \text{ and} 
B &= \text{a constant chosen such that } \frac{dE_p}{dv} = 0. 
\end{align*} \]

This allowed Kuroda to deduce the correlation between change in polarisation energy of nearest neighbour ions and change in Auger parameter for a series of sodium halides, using Tessman's values for polarisabilities and water molecule-ion distances quoted by Maeda and Ohtaki.

The optical behaviour of a crystal is related to the dielectric properties of the bonds within that crystal, which influence the velocity of electromagnetic radiation. The dielectric constant of a crystal has two components, namely:

1) ionic polarisation, and 2) electronic polarisation.
The electronic polarisation is known to be the only component effective at visible frequencies, and is given by:

\[ K = n^2 \] ....... 4.2

where:

\( K \) = the electronic dielectric constant, and
\( n \) = the refractive index.

Tessman\(^\text{[75]}\) noted that since the electronic component is due to the electronic polarisation of the ions within the crystal, it should be possible to determine the electronic polarisability for individual ions. This was found to be so using the Lorentz expression:

\[ \frac{n^2 - 1}{n^2 + 2} - \frac{3V_m}{4\pi} = \alpha_m \] ....... 4.3

where:

\( \alpha_m \) = the electronic polarisability of molecules within a crystal,
\( V_m \) = the molar volume of the crystal divided by the number of molecules there contained, and
\( n \) = the refractive index.

Assuming that a relationship between ion electronic polarisability and refractive index exists, a correlation might exist between the value for refractive index and the extra-atomic relaxation energy of an ion. Gallon and co-workers\(^\text{[77]}\) found a reasonable correlation while studying
compounds of zinc. These results were substantiated by West and Castle\textsuperscript{(35)} using Zr L\textalpha radiation, who found a similar correlation for the Auger parameter of silicon in silicates. The Auger parameter was shown to be capable of detecting changes in coordination, water content and degree of ionic bonding, for both crystalline and amorphous solids, which would not be apparent if the Si 1s chemical shift was considered in isolation. This is shown in Figure 4.1.

Following the success of the above work, an attempt was made to find further evidence for the correlation between Auger parameter and refractive index value, using chlorine as the common cation, which might be relatable to its role in the breakdown of passive films.

4.12 Material selection, handling and treatment

The chloride compounds selected for study traversed as wide a range of known refractive index values as possible. Following the fluorides study discussed in Chapter 3, extra precautions were taken to avoid specimen hydrolysis by way of longer drying times, specimen probe heating and in-situ sample baking.

Each chloride, a list of whose purity and source is given in Table 4.1, was ground in a glass pestle and mortar before being placed into a drying oven at 120\textdegree C for at least 48 hours. Samples deemed to be dry following this process were impressed into indium foil previously crimped around the specimen holders as designed and used for the standards work, before entry into the spectrometer. A pumping down period of at least 48 hours was allowed, following which pressures were at least $10^{-9}$ mbar. Samples were heated to 100\textdegree C whilst on the specimen probe for periods of
Figure 4.1 Correlation of Si Auger parameter with refractive index

up to 24 hours. If this proved ineffective, as was sometimes the case, the samples were baked in situ for 48 hours at 100°C.

Narrow scan spectra for the Cl 1s, KLL Auger, 2p and LMM Auger lines were acquired using the following experimental conditions:
Number of channels : 100
Channel width : 0.2eV
Total time in each channel : >6 min
Analyser energy : 50eV
Analyser slit widths : 4mm
Electron take-off angle : 45°
X-ray anode settings : 14KV, 40mA ≡ 560W
Spectrometer vacuum : 10^-9 mbar
Electron flood gun settings : 0V, 0.2mA

Only occasional survey scans were acquired, to elucidate contamination levels. The acquisition of O 1s and C 1s narrow scan spectra allowed constant monitoring of hydrocarbon and hydroxide presence, the latter being more of a problem due to the extremely reactive nature of chlorides in air.

To improve counting statistics and thus lower acquisition times, various methods of sample preparation were attempted, including sample pelletisation, which proved successful for less reactive samples. The advantages and disadvantages of this method have been outlined in Chapter 3 (Section 3.2). This enabled acquisition times to be reduced by up to 50%. To ensure analysis of a fresh surface, the pellets were manually scraped under flow of argon gas immediately prior to placing them into the spectrometer. However, the majority of samples proved too hygroscopic to permit the general use of this technique so that mounting onto indium foil remained the more commonly adopted method. The experimental procedures in this case were similar to those described in Chapter 3.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Source</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>Koch-Light</td>
<td>99.998</td>
</tr>
<tr>
<td>CsCl</td>
<td>Koch-Light</td>
<td>99.9</td>
</tr>
<tr>
<td>BaCl₂</td>
<td>BDH</td>
<td>99.0</td>
</tr>
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<td>CuCl</td>
<td>Koch-Light</td>
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<td>AgCl</td>
<td>BDH</td>
<td>99.0</td>
</tr>
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<td>BDH</td>
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</table>

Table 4.1 Chloride materials: origins and purities

4.13 Results and discussion

Initial experiments involved a study of 17 compounds, the results of which are shown in Table 4.2. The reproducibility of these results was not satisfactory, since compounds often proved difficult to produce in their anhydrous form, despite the drying procedures applied. Even small
amounts of water present can alter the physical properties of a compound, including that of refractive index. Attaining adequate signal-to-noise ratios for accurate peak position measurement for the Cl 2p and Cl LMM lines was particularly difficult, due to their low cross-sections in this radiation. Thus these results should be viewed with caution.

<table>
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<th>Compound</th>
<th>Cl1s</th>
<th>Cl1KL</th>
<th>A'C1</th>
<th>Cl2p</th>
<th>Cl1MM</th>
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<td>201.6</td>
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<td>CaCl2</td>
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<td>201.8</td>
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<td>5208.4</td>
<td>200.4</td>
<td>180.2</td>
<td>380.6</td>
</tr>
</tbody>
</table>

Table 4.2 Peak position and Auger parameter results
Figures 4.2 and 4.3 show plots of the two calculated Auger parameters $A^I(1s+KLL)$ and $A^{II}(2p+LMM)$ versus the reduced refractive index value. The correlation coefficients for these plots are 0.31 and 0.52 respectively, which are not significant at the 5% level. Thus no correlation between Auger parameter and refractive index appears to exist.

However, from a closer examination of the formula used by Kuroda (equation 4.1) it became apparent that $E_p$, the polarisation energy, was dependent primarily on bond length, coordination number and change in charge terms. On differentiating this equation, and eliminating the term $B$, the result is:

$$E_p = -\frac{nu}{r^2} + \frac{nu}{2r^3} + \frac{nu^2}{2\alpha} + \frac{2nu}{9r^2} - \frac{3nu}{18r^3} \quad \ldots \ldots 4.4$$
The magnitudes of these terms are as follows:

\[ q = 3.2 \times 10^{-16} \text{C} \]
\[ r = x \times 10^{-10} \text{m} \]
\[ \mu = y \times 10^{-30} \text{cm} \]
\[ \alpha = z \times 10^{-30} \text{m} \]

The terms \( \mu \) and \( \alpha \) are small enough to be considered insignificant. This allows the expression for \( E_p \) to be well approximated by:

\[
E_p = \frac{-n\Delta q}{r^2} + \frac{2n\Delta q}{9r^2} \quad \ldots \ldots \text{4.5}
\]

Since \( E_p \) is dependent on the nearest neighbour bond length and coordination number, a correlation of Auger parameter with these was thought possible.

Figure 4.4 shows a plot of \( \text{CN}/(r-\text{Cl}) \) versus Auger parameter for the series of chlorides investigated. The values used are taken from Table 4.3. The scatter in the data is again not satisfactory, and thus any trends present are unclear. This was thought to be mainly a product of the specimen hydrolysis problem, since the degree of dryness is probably not similar for all samples. The chlorides of mercury were particularly difficult to prepare, since they often reacted with the indium substrate material to force the use of double-sided adhesive tape for mounting.
<table>
<thead>
<tr>
<th>Compound</th>
<th>CN</th>
<th>R - Cl$^-$ (nm)</th>
<th>Crystal Structure</th>
</tr>
</thead>
<tbody>
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<td>Na Cl</td>
<td>6</td>
<td>0.28</td>
<td>Na Cl</td>
</tr>
<tr>
<td>Cs Cl</td>
<td>8</td>
<td>0.36</td>
<td>Cs Cl</td>
</tr>
<tr>
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<td>0.32</td>
<td>Cubic Fluorite</td>
</tr>
<tr>
<td>Cu Cl</td>
<td>4</td>
<td>0.26</td>
<td>Zn S</td>
</tr>
<tr>
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<td>Hg Cl</td>
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</tr>
<tr>
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<td>0.25</td>
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<td>Cd Cl$_2$</td>
</tr>
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<td>Pb Cl$_2$</td>
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<td>Orthorhombic</td>
</tr>
<tr>
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<td>Na Cl</td>
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<td>Cu Cl$_2$</td>
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<td>Monoclinic</td>
</tr>
<tr>
<td>Ni Cl$_2$</td>
<td>6/3</td>
<td>0.25</td>
<td>Cd Cl$_2$</td>
</tr>
<tr>
<td>Cd Cl$_2$</td>
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<td>Cd Cl$_2$</td>
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<td>Co Cl$_2$</td>
<td>6</td>
<td>0.25</td>
<td>Cd Cl$_2$</td>
</tr>
</tbody>
</table>

Table 4.3 Chloride coordination number and nearest neighbour distance data
Figure 4.4 Correlation of CN/r-Cl with $A^I$

It was considered that this level of correlation, even allowing for experimental scatter, was not altogether surprising since both ionic and covalent chloride data are plotted as one. Thus the different groups were separated, this being straightforward if the compound contained monovalent ions. Following Pauling\(^{(12)}\), the partial ionic character $I_{AB}$ of the bond $AB$ is given by:

$$I_{AB} = 1 - \exp \left( -0.25 \left( X_A - X_B \right)^2 \right) \quad \text{...... 4.6}$$

where:

$X_A$ = the electronegativity of atom A, and

$X_B$ = the electronegativity of atom B

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For compounds of a more complex nature, involving di-valent and tri-valent ions, the acid-base classification developed by Pearson\textsuperscript{(78)} was applied. If the ion associated with a chloride ion is "soft" and polarisable, the compound will display covalent character, whereas if the ion is "hard" and not very polarisable the compound will be ionic.

However, this separation into covalent and ionic species produced little correlation, as shown in Figure 4.5. The reproducibility of the data was not satisfactory.

4.14 Conclusions

1) Despite attempts to bring this series of chloride materials to an equal level of dryness, the poor reproducibility of data involving Auger parameters tends to indicate that this was not achieved, with hydration of some of the chloride materials being a major problem.

2) Whilst the quality of the specimens was less than desirable, it was not felt that this alone explained the results obtained. The experiment involved the use of a high energy monochromatic x-ray source to analyse a series of insulators. To counteract specimen charging an electron flood gun was used. The manufacturer's recommendation of a 0 or 2V applied acceleration potential (at an emission current level of 0.2mA) for the XPS analysis of insulators appeared unsatisfactory in this case and thus worthy of experimental verification.
4.2 Charge Referencing for the XPS Analysis of Insulators

The fact that analysis of non-conducting species differs from that for conducting species has been recognised for some time. Following the photoemission process (equation 1.1), when a photoelectron is ejected...
from an insulating sample there is no electrical contact between the specimen and earth so that no electron flow can be induced to counteract electrically the loss of the photoelectron. Subsequently, a build-up of surface charge develops, $W_{E1}$ (see Chapter 1), that can ultimately affect both measured peak position and peak shape. 

Although charging can be a problem in conventional XPS work, it is made much less serious by the presence of an x-ray window between the source and the specimen. This avoids sample contamination and also provides a source for the removal of surface charge when analysing insulating materials, since on impingement of the polychromatic x-rays with the window, secondary electrons (often less than 8eV energy) are generated, which can be attracted towards any positive charge developing at the sample surface. Thus any peak shifts measurable are often less than one electron volt. This is not serious since an equilibrium steady-state static charge results with photoelectrons generated possessing an energy:

$$E_{KE} = h\nu - E_{BE} - C$$

... 4.7

where C is normally a low, positive number, the "charging" shift.

However, when a monochromatic x-ray source is used, such as high energy Ag Lα, the process of monochromatisation has removed the Bremsstrahlung (background) radiation, causing the x-ray flux to be significantly reduced. This lower flux level cannot excite sufficient electrons on collision with the x-ray window to compensate fully for the build-up of surface charge occurring with time. Thus resulting peak shifts in this case can be very much greater, of the order of hundreds of
electron volts, which prohibits the accurate measurement of peak position. The presence of a positive charge produces a retarding field around the specimen causing photoelectrons to have a kinetic energy value lower than that predicted by equation 4.7, and thus peak shifts are recorded. Furthermore, peak broadening is also more significant, with different sample areas or depths possessing different C values\(^{(82)}\). Following detailed studies a number of techniques have become popular for the counteracting of specimen charging effects. Such methods include the following:

4.21 Referencing to adventitious carbon.

Since carbon is the most common element found in contamination overlayers, it is not unreasonable that reference to it should have developed into a very popular method. Siegbahn et al\(^{(83)}\) first reported such carbonaceous contamination to be present, and attributed it to the pump oils used to obtain UHV conditions necessary for XPS studies, since it became more predominant with specimen exposure to the spectrometer vacuum.

The use of adventitious carbon has been reviewed by Swift\(^{(84)}\), from which it was deduced that though such a reference technique is most convenient it is not altogether satisfactory, since the binding energy value of the C 1s peak can vary from 284.6 to 285.2 eV. This can occur due to its originating from hydrocarbon contamination layers on different substrate materials, for example. It was concluded that reference to C1s was acceptable providing that, on comparison of results with other workers, a universally acceptable reference line was used, such as the Au 4f7/2 at 84.0 eV or the Cu 2p3/2 at 932.7 eV.
The areas of possible doubt concerning the measurement of the C 1s photoelectron peak have been highlighted by Swift, Shuttleworth and Seah (82), who recommended that users determine their own reference position, preferably from a substrate chemically and physically similar to the analysis material, from uniformly thin contamination overlayers (i.e. approximately one monolayer thick).

Many workers have commented on the possible use of carbon as a reference material, and a number of factors have been identified that influence measured C 1s values. These include the following:

a) the chemical state of the carbon in the contamination layer (85),
b) the thickness of the adventitious carbonaceous layer (86),
c) specimen preparation and surface treatment effects (87, 88) and
d) the accuracy of the energy calibration of the spectrometer on which it is determined (89, 90).

The use of specimen surface treatments such as heating and argon ion bombardment make the use of referencing to the C 1s peak experimentally difficult, excepting in very special situations.

The extent of the variation of the C 1s (26, 88, 91-94) with respect to the Au 4f7/2 line can be seen in Table 4.4. However, the use of adventitious carbon as a charge reference technique continues today and can for some instances prove successful, providing the above comments are recognised.
Table 4.4 C 1s reference positions compared with those for gold

4.22 Referencing to a support material peak.

This method involves the use of a key peak in the material to be analysed as a standard, with other peaks measured being referenced to this. For example, the Al 2p peak would be selected from alumina, $\text{Al}_2\text{O}_3$. The standard is effectively part of the system to be analysed and will reflect the static charge state of the system (providing this value is uniform across the sample surface). Clark and co-workers have used this method as a basis for studies of chemical shifts in polymer systems.

However, despite some practical uses, the application of an internal standard as a reference tends to oversimplify the problem, since a value of the molecular formula of the sample needs to be known beforehand and the binding energy of the chemical group employed must be known to remain invariant with environment.
4.23 Referencing to a mixture containing a standard material.

Of further interest has been the possibility of physically preparing sufficiently intimate mixtures of a material with a powder containing a component of known binding energy. This can enable static charge energy referencing to be carried out for insulators, examples of successful applications including powdered graphite\(^{(88,98,99)}\), which has been the most commonly used, molybdenum trioxide\(^{(100,101)}\), lithium fluoride\(^{(102)}\), triplumbic tetroxide\(^{(103)}\), gold\(^{(101)}\) and potassium salts\(^{(104,105)}\).

A major problem involves the preparation of the mixtures of reference material and sample since, for absolute accuracy of results, mixing must be obtained on nearly an atomic scale. The ability to produce such homogeneous mixtures has been of great concern. Work carried out by Wagner\(^{(106)}\) showed that errors of up to 10eV can be produced when analysing mixtures. The problem areas when interpreting recorded data include:

a) the sizes of particles making up the powder mixture itself, which affects the intimacy of mixture obtainable,
b) the possibility of particle-interface interaction between different components, and
c) the probability of differential charging occurrence for particles originating from separate components.
Furthermore, this method gives no assistance for non-particulate material surfaces such as planar samples.

Though mixing on an atomic scale is beyond scientific achievement, such mixing on a molecular scale is possible through the fusion of a standard with the sample to be analysed. However data obtained will be representative of the fused product rather than the individual compounds.

The work of Conner\textsuperscript{(95)} has shown that condensation of both a volatile standard and the sample can be used to good effect. This constitutes the best mixing system investigated to date. However, the method is limited to the use of stable volatile compounds, so that the use of mixtures as a general method of energy referencing must be viewed with caution.

4.24 The use of charge-independent parameters.

The use of parameters such as the Auger parameter has become popular, as discussed in Chapter 1. Such measurements will be independent of the static charge at the specimen surface, providing that this charge is uniform across the surface. Furthermore, any chemical shifts measured will reflect variations in screening energy\textsuperscript{(20)}. The use of the Auger parameter permits the registration of a characteristic value for each system, based on the use of the principal photoelectron and Auger peaks attainable. This "fingerprinting" method was developed by Wagner\textsuperscript{(26)} and is also described in Chapter 1.
The selection of the lines used for calculation of Auger parameters is critical since, for example, valence-type or CVV Auger lines are made up of broad bands and can vary greatly in line distribution with chemical state. Lines selected by Wagner\(^{(107)}\) have tended to be based on those peaks most commonly accessible when using conventional XPS, such as the photoelectron lines for the 1s up to Na, the 2p up to Zn and so on. The corresponding selection of Auger lines is more complicated, since occasionally broad lines have to be used\(^{(108-110)}\).

Having selected reasonable lines, however, the applicability of the Auger parameter is wide, and has been employed in this work, together with the use of an electron flood gun, as discussed below.

4.25 The use of a low energy electron flood gun.

This is strictly a method of charge compensation rather than a method of charge referencing, since on its successful application the latter is nonetheless required for the attainment of meaningful binding energy values. The electron flood gun (Figure 4.6) was first demonstrated by Huchital and McKeon\(^{(111)}\) and consists of a filament which feeds electrons to a cylindrical cathode assembly, such that both the current (i.e. the number of electrons) and the accelerating potential (i.e. the electron energy) may be controlled. Thus the electron flood gun enables the surface charge to be made uniform, which is important in the study of powders where uneven surface charge (seen as peak broadening) may be eliminated\(^{(112-117)}\).
The electron flood gun is of use in the following XPS applications:

a) For monochromatic XPS work, though its application is not alone sufficient and requires a small correction to be made from the use of a further internal referencing technique, such as the measurement of Auger parameters outlined previously,

b) Where static specimen charging is not homogeneous, since it can minimise or even remove peak broadening problems\(^{(118)}\), and

c) For absolute calibration of an XPS energy spectrum, where the electron flood gun has been suitably calibrated for a particular instrument configuration.

It has been found\(^{(119)}\) that with a calibrated gun the surface potential can be controlled to within \(\pm 0.1\text{eV}\) for smooth specimens, though such accuracy has not been possible for non-planar specimens as often studied by XPS, with the limitation in this case being \(\pm 0.50\text{eV}\).
The electron flood gun conditions used in the initial chlorides study were 0V accelerating potential and 0.2mA emission current, which were the recommended parameters of the instrument manufacturers. Since, for the VG LEG51 model (using a tantalum ribbon filament), the potential can be varied from 0 to 14V energy and from 0 to 1.0mA emission current, there are a number of settings possible. However, work carried out by Hunt et al (119) investigating the design and operation of electron flood guns showed best results to be obtained using low energy electrons (less than 1eV), with respect to the vacuum chamber at earth, from a source close to the specimen. They concluded that optimum operating conditions, such as sample positioning, exist for particular configurations and must be determined by the individual operator. Whilst it is recognised that low energy electrons would normally be used to maximise the neutralisation effect, and restrict electron bombardment induced reactions, electron stimulated desorption and related effects, the use of such electrons in the initial chloride study may have proved inadequate. Since the understanding of the electron flood gun generally, and particularly its use in the ESCA3 MkII spectrometer, was incomplete, a comprehensive study of its effect and use appeared necessary.

4.251 An investigation of silicon compounds

As a first stage in the investigation of the electron flood gun, use was made of data available from the work of Bechstedt et al (24), whose work involved samples of Si<111> single crystal, SiC powder, Si<sub>N</sub><sub>4</sub> films, SiO<sub>2</sub> formed on Si<111> and Na<sub>2</sub>SiF<sub>6</sub> powder, which were analysed with XPS using Ag Lα and Al Kα radiation (both polychromatic). The special significance of their work, amongst others (9, 13, 20, 120, 121), is that the Auger and other parameters can be
used to determine changes in the relaxation energy of individual core levels. Previously this was only possible after considerable numerical effort\(^{(25)}\). The method involved the measurement of an Auger peak energy together with the binding energies of all the core levels involved in the production of that Auger electron, i.e. the Si KLL and the Si 1s and 2p. Thus the silicon core level relative to the Fermi level, \(E_a(i)\), is:

\[
E_v(i) = -\zeta_{HF}^{\text{HF}}(i) - V(i) - R_D(i) \quad \ldots \ldots \ 4.8
\]

where:

\(\zeta_{HF}^{\text{HF}}(i)\) = the atomic orbital energy of the considered core level \(i\) in the Hartree-Fock (HF) approximation,
\(V(i)\) = the potential shift describing the change of the one-electron HF potential of the free atom to that in the condensed phase, and
\(R_D(i)\) = the dynamic (one-hole) relaxation energy shift of the core level \(i\) if one electron is ejected in the XPS process\(^{(9)}\).

The kinetic energy of an Auger electron in a solid emitted in an \((ijk; \ X)\) transition (\(X\) denoting the final spectroscopic term\(^{(122)}\)) can be referred to the Fermi level as:

\[
E((ijk; \ X)) = E(i) - E(j) - E(k) - \phi(jk; \ X) + R_S(jk) \quad \ldots \ldots \ 4.9
\]
where:

\[ R_S(jk) = R_T(jk) - R_D(j) - R_D(k) \quad \ldots \ldots \quad 4.10 \]

in the two-step model developed by Shirley and Kowalczyk et al.

Also, the electron binding energy related to the Fermi level is:

\[ E(i) = E^V(i) - \phi \quad \ldots \ldots \quad 4.11 \]

For the above expressions, the following descriptions are appropriate:

\( \phi \) = the work function,

\( S(jk; X) = \) the interaction of the two holes \( j \) and \( k \) in the final state \( X \) of the Auger process, and

\( R_S(jk) = \) the difference between the total double-hole relaxation energy \( R_T(jk) \) and the two one-hole relaxation energies \( R_D(j) \) and \( R_D(k) \).

The \( R_S \) term has been denoted the "static relaxation energy" by Shirley and the "cross-relaxation energy" by Hoogewijs et al. It describes the additional relaxation energy shift of the total energy associated with the two localised holes in comparison to two isolated ones. Should the two final-state holes possess the same quantum number \( n \) and angular momentum quantum number \( l \), it holds that \( j = k \), giving:

\[ R_T(j) = 4 \ R_D(j) \quad \ldots \ldots \quad 4.12 \]
which can be factorised to :

$$R_S (jj) = 2R_D (j)$$  \hspace{1cm} \ldots \ldots 4.13$$

Thus the static relaxation energy value is nearly twice the dynamic one.

The dynamic relaxation energy, following Kowalczyk et al.(13), can be separated into two parts, as described in Chapter 1:

$$R_D (i) = R_D^a (i) + R_D^{ea} (i)$$  \hspace{1cm} \ldots \ldots 4.14$$

where :

- \(R_D^a (i)\) = the intra-atomic contribution, which is invariant with chemical environment, and
- \(R_D^{ea} (i)\) = the extra-atomic contribution, which involves the redistribution of electrons from neighbouring atoms and of valence and conduction electrons and is thus dependent on the chemical environment.

The term \(S (jk : \chi)\) is atom-like, and thus should remain almost invariant when comparing different compounds of the same element. This allows the chemical changes of the binding and Auger energies between such compounds to be written as :

$$\Delta E (i) = - \Delta V (i) - \Delta R_D^{ea} (i) - \Delta \phi$$  \hspace{1cm} \ldots \ldots 4.15$$
\[
\Delta E(ijk : X) = \Delta E(i) - \Delta E(j) - \Delta E(k) + \Delta R_{ea}^S(jk) \quad \ldots \quad 4.16
\]

If the dependence on the spectroscopic term \(X\) can be neglected, this gives:

\[
\Delta \zeta(ijk) = \Delta E(ijk) - \Delta E(i) - \Delta E(j) + \Delta E(k) \quad \ldots \quad 4.17
\]

\[
\Delta \alpha(ijk) = \Delta E(ijk) + \Delta E(k) \quad \ldots \quad 4.18
\]

for changes in the Auger parameters \(\zeta(ijk)^{(13,120,121)}\) and \(\alpha(ijk)^{(13,20)}\).

Thus, it follows that:

\[
\Delta \zeta(ijk) = \Delta R_{ea}^S(jk) \quad \ldots \quad 4.19
\]

Furthermore, if the small variation of the change of the potential effect \(\Delta V(i)\) with core level \(i\) can be neglected\(^{(20,125)}\):

\[
\Delta \alpha(ijk) = R_{ea}^S(jk) - R_{ea}^D(i) + R_{ea}^D(j) \quad \ldots \quad 4.20
\]

from eqns. 4.17 to 4.19. Thus the chemical shifts of the Auger parameters are governed only by extra-atomic relaxation energies.
If the two holes in the final state of the Auger process are excited at the same core level (since $j = k$), the approximation that

$$R_s(jj) = 2R_D(j) \quad \ldots \ldots 4.21$$

may be used.

In this way, the chemical changes of the dynamic extra-atomic relaxation energies can be immediately related to the measured shifts of Auger parameters:

$$\Delta R_{D}^{ea}(i) = \frac{3}{2} \Delta \zeta(ijj) - \Delta \alpha(ijj) \quad \ldots \ldots 4.22$$

$$\Delta R_{D}^{ea}(j) = \frac{1}{2} \Delta \zeta(ijj) \quad \ldots \ldots 4.23$$

It was the above equations that were used by Bechstedt and co-workers in their study of the range of silicon compounds outlined earlier. The results of their work are shown in Table 4.5.

4.252 The reproducibility of Bechstedt's work

The previously described chloride study was conducted using a flood gun accelerating potential of 0V and an emission current of 0.2mA. As an initial test of how suitable these settings were for use with this monochromatic source, similar compounds to those used by Bechstedt and co-workers were obtained, in an attempt to repeat their work. (The results for polychromatic Ag $L_\alpha$ should be reproducible when using the electron flood gun for the monochromatic Ag $L_\alpha$ source).
Table 4.5 Measured chemical shifts (eV) of Si KLL, 1s and 2p peaks for silicon compounds

Thus the following samples were used:

1) silicon <100> wafer (n-type),
2) silicon carbide (powder), obtained from the Carborundum Company, Old Trafford, Manchester, UK,
3) silicon nitride (powder), obtained from Koch-Light Laboratories, Colnbrook, Bucks., UK,
4) silicon with thermally grown oxide film (~2000Å thick), and
5) potassium fluorosilicate (powder), obtained from Koch-Light Laboratories, Colnbrook, Bucks., UK.
The silicon oxide used by Bechstedt was not clearly specified, so that it was not possible to use an identical sample. Also, the use of $K_2SiF_6$ and Si $<100>$ rather than $Na_2SiF_6$ and Si $<111>$ will lead to slightly different results being obtained, though data should be comparable.

All powdered samples were dried in an oven at 120° C prior to mounting for XPS analysis by imbedding into indium foil. The planar samples (Si and SiO$_2$) were mounted using double-sided adhesive tape.

The conditions for XPS analysis were as follows:

- Number of channels: 100
- Channel width: 0.2eV
- Total time in each channel: >3 min
- Analyser energy: 50eV
- Analyser slit widths: 4mm
- Electron take-off angle: 45°
- X-ray anode settings: 14KV, 40mA = 560W
- Spectrometer vacuum: <10$^{-9}$ mbar
- Electron flood gun conditions: 0V, 0.2mA

The results of the silicon-based material study can be seen in Table 4.6. Clearly, the calculated extra-atomic relaxation energy values differ greatly from those of Bechstedt (Table 4.5), and this is demonstrated in Figure 4.7. The results were reproducible to ±0.4eV, at best, which was not satisfactory.
Table 4.6 Results of silicon chemistry study using OV, 0.2mA flood gun conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>-ΔE(KLL)</th>
<th>ΔE(1s)</th>
<th>ΔE(2p)</th>
<th>-Δα(KLL)</th>
<th>-Δαe(1s)</th>
<th>-ΔRge(2p)</th>
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<tr>
<td>Si</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SiC</td>
<td>5.6</td>
<td>5.0</td>
<td>6.0</td>
<td>-1.4</td>
<td>0.4</td>
<td>-2.5</td>
</tr>
<tr>
<td>Si3N4</td>
<td>9.4</td>
<td>6.8</td>
<td>9.1</td>
<td>-2.0</td>
<td>0.2</td>
<td>-3.2</td>
</tr>
<tr>
<td>SiO2</td>
<td>7.6</td>
<td>3.6</td>
<td>1.8</td>
<td>7.6</td>
<td>5.8</td>
<td>5.6</td>
</tr>
<tr>
<td>K2SiF6</td>
<td>13.6</td>
<td>9.2</td>
<td>10.1</td>
<td>2.6</td>
<td>3.8</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Figure 4.7 Extra-atomic relaxation energies for OV, 0.2mA flood gun conditions
The conclusion from this work was that the electron flood gun setting of 0V and 0.2mA was unable to compensate for the effect of monochromatisation of the x-ray.

4.253 The optimisation of electron flood gun settings

The VG LEG 51 electron flood gun possesses two variables: the electron accelerating potential and the electron emission current, i.e. the energy and number of electrons can be varied. Table 4.7 shows the variation in the Si x-ray energy for silicon and silicon nitride, seen as the Si (1s-2p) peak separation, with increase in accelerating potential for a constant emission current level (0.2mA). The results indicate the advisability of the use of the flood gun at higher accelerating potentials, with the 0V setting demonstrating an unacceptable non-linearity of the spectrometer energy scale.

In addition to the monitoring of peak separations for the removal of charging effects, the Si 1s peak resolution was recorded (since it possesses the greatest cross section of those peaks analysed) to see if any variation in peak shape was evident (due to differential charging) on increasing the accelerating potential. The spectra obtained for $\text{Si}_3\text{N}_4$ are shown in Figure 4.8, from which the use of at least 2V accelerating potential appears to give the best result.

The FWHM values from Figure 4.8 are plotted in Figure 4.9, together with data for silicon <100>, muscovite mica and Na Y zeolite materials. The planar samples, i.e. Si <100> and mica, appear to be neutralised by the use of "0V" electrons, with 10V electrons not noticeably improving resolution. However, the powder samples appear to require higher...
Table 4.7 Variation of x-ray energy with flood gun setting

<table>
<thead>
<tr>
<th>Flood Gun Setting</th>
<th>Kinetic Energy (eV)</th>
<th>Si11s</th>
<th>Si12p</th>
<th>1s - 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>mA</td>
<td>Si11s</td>
<td>Si12p</td>
<td>1s - 2p</td>
</tr>
<tr>
<td>----</td>
<td>----</td>
<td>-------</td>
<td>-------</td>
<td>---------</td>
</tr>
<tr>
<td>0</td>
<td>0.25</td>
<td>1146.2</td>
<td>2884.5</td>
<td>1738.3</td>
</tr>
<tr>
<td>2</td>
<td>0.25</td>
<td>1148.4</td>
<td>2887.8</td>
<td>1739.4</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>1150.2</td>
<td>2890.0</td>
<td>1739.8</td>
</tr>
<tr>
<td>6</td>
<td>0.25</td>
<td>1152.2</td>
<td>2892.0</td>
<td>1739.8</td>
</tr>
<tr>
<td>8</td>
<td>0.25</td>
<td>1154.0</td>
<td>2893.8</td>
<td>1739.8</td>
</tr>
<tr>
<td>10</td>
<td>0.25</td>
<td>1156.0</td>
<td>2895.8</td>
<td>1739.8</td>
</tr>
</tbody>
</table>

potentials, probably due to their discontiguous nature, with the
Si$_{3}$N$_{4}$ sample being charge-managed by the use of a potential of 4V or
more. The Na Y zeolite appears more complex in its behaviour and is
adversely effected by the use of neutralising electrons generally, with
electron stimulated desorption effects being instigated (seen through
variation in spectrometer operating pressure). This may be a reflection
of the high surface area and activity of this material.

To examine the effects experienced by a specimen when the two flood
gun variables are changed, landing current measurements were made using a
Keithley model 600B electrometer and an ion-cleaned copper specimen
holder. Thus the currents induced by the impingement of the flood gun
electrons onto the specimen holder were recorded over the 3000eV analyser
retard potential.
Figure 4.8 Variation of Si 1s position and shape with flood gun accelerating potential

Figure 4.9 Effect of accelerating potential on Si 1s resolution
Figure 4.10 Variation of landing current with flood gun accelerating potential

Figure 4.10 shows the initial landing current plot obtained for a range of accelerating potentials (emission currents being held constant at 0.2mA). The most noticeable feature is the wide variation in landing current experienced by the specimen holder over 3000eV when 0V flood gun electrons are used, again demonstrating its unsuitability. The 2V accelerating potential appears to improve the situation somewhat, but it is not until a value of 6V is used that the desired constancy in landing current (i.e., constancy in effective neutralisation) across the energy spectrum is obtained.
Figure 4.11 Variation of landing current with flood gun emission current

The effect of the other flood gun variable, the emission current, on measured landing currents can be seen in Figure 4.11. This shows the 0.2mA setting used for the earlier chloride study and for the repeat of Bechstedt's study to be only just satisfactory, with a level of at least 0.25mA appearing more suitable.

Figure 4.10 appears to indicate that the lower energy flood gun electrons are somehow not being allowed to reach the specimen, since the measured flux decreases with analyser retard potential. Higher energy electrons (6V and above) do not appear to experience such a problem, and therefore "land" on the specimen. It is possible that the variation in flux measured for the lower energy flood gun accelerating potentials is due to these electrons being impeded in their journey from the filament to the sample.
One explanation for this effect is that there is a field breakthrough occurrence from the analyser retarding grid into the sample area. Lower energy electrons are easily deflected away, whilst those of higher energy are able to reach the sample since they possess sufficient energy to avoid being impeded. Thus when the 0V setting is used, the peak shift applied to the Si 2p peak (=2884KE) will differ from that applied to the Si 1s peak (=1144KE), and the two peaks "float" independently. Such is the seriousness of this problem that even the use of the Auger parameter will be rendered meaningless.

During a subsequent routine maintenance period, when the electron flood gun filament was being changed, it was noticed that its collimator assembly was not completely straight. It was possible that a slight knock on a laboratory bench might have caused it to misalign, presuming it not to be a manufacturing error. Upon rectification of this fault, it was found that the landing current plot as shown in Figure 4.10 was not so serious for the 0V setting, with the fall-off with analyser energy being less severe. However, this remained less suitable than the 2V setting and so on. The fact that the collimator misalignment increased the severity of the problem increased the possibility of field breakthrough occurrence, since when the electrons were directed closer to the spectrometer analyser entrance grid, the low energy flood gun electrons were more obviously impeded from reaching their target destination, the specimen being analysed.

It is interesting to note that problems have been encountered recently where the machining of spectrometer components can induce a level of magnetism into the material, causing it to generate undesirable fields within the analyser vacuum space. Such effects can also be seen
if an incorrect specification of material is supplied, such as ferritic (α) rather than austenitic (γ) stainless steel for in-vacuum components. Attention has been drawn to the possibility that stray fields within the analyser vacuum space may effect the current delivered to the specimen surface and hence distort the linearity of the spectrometer energy scale\(^{(126,127)}\). In particular, Jaegle and co-workers\(^{(128)}\) have commented upon the VG ESCA3 spectrometer, which is used in this study. The fact that accurate energy referencing is required across 3000eV when the monochromatic Ag La x-ray source is used further highlights the problem, since its range is twice that for conventional XPS.

Ideally, each individual specimen requires optimisation in its own right (through monitoring of the 1s-2p separation and the 1s resolution, for example). The application of such "optimised" settings for the compounds used previously for the repitition of Bechstedt's work produced results as shown in Table 4.8. These settings were either 4V or 6V accelerating potential, depending on the specimen sensitivity, with an emission current level of 0.2-0.25mA. The comparison with Bechstedt's data, as shown in Figure 4.12, was clearly more satisfactory than that achieved previously (Figure 4.7). These results were reproducible to \(\Delta R_{D}^{ea} \pm 0.2eV\), which was satisfactory. A linear relationship appears to exist between the silicon 1s and 2p extra-atomic relaxation energy values for this range of silicon compounds. The value for \(Si_3N_4\) from Bechstedt's work appears to be an estimate\(^{(129)}\), which implies that the value quoted here is probably more accurate.
<table>
<thead>
<tr>
<th>Sample</th>
<th>$-\Delta E(KLL)$</th>
<th>$\Delta E(1s)$</th>
<th>$\Delta E(2p)$</th>
<th>$-\Delta E(KLL)$</th>
<th>$-\Delta \alpha(KLL)$</th>
<th>$-\Delta R_0^{\text{ea}}(1s)$</th>
<th>$-\Delta R_0^{\text{ea}}(2p)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SiC</td>
<td>3.6</td>
<td>2.0</td>
<td>1.8</td>
<td>2.0</td>
<td>1.6</td>
<td>1.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Si$_3$N$_4$</td>
<td>5.4</td>
<td>3.2</td>
<td>3.2</td>
<td>2.2</td>
<td>2.2</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>3.2</td>
<td>-0.2</td>
<td>-0.6</td>
<td>4.2</td>
<td>3.4</td>
<td>2.9</td>
<td>2.1</td>
</tr>
<tr>
<td>K$_2$SiF$_6$</td>
<td>10.8</td>
<td>6.2</td>
<td>5.4</td>
<td>6.2</td>
<td>4.6</td>
<td>4.7</td>
<td>3.1</td>
</tr>
</tbody>
</table>

Table 4.8 Results of silicon chemistry study using optimised flood gun conditions

Figure 4.12 Extra-atomic relaxation energies for optimised flood gun settings
However, for general situations, if samples are unaffected by 6V electrons or greater, it appears that a general 6V+, 0.25mA+ setting is suitable for good results. For more accurate, reproducible work - particularly when using sensitive materials - it is better to determine an acceptable range of settings. An illustration of the way in which an optimum range can be found is shown in Figure 4.13, where the positions of the Cl 1s, Na 1s and Cl 2p peaks for sodium chloride are plotted as a function of flood gun accelerating potential, the emission current being held constant at 0.25mA. The range in which the lines become parallel
indicates the range of constancy for measurements such as the Auger parameter value. For sensitive materials, one would select an accelerating potential value at the lower end of this range, to minimise specimen damage effects. For less sensitive materials, where damage is less likely, the use of settings within this range of constancy is advised, to ensure confidence in experimental accuracy of results obtained.

4.3 A Study Of Alkali Metal Chlorides

The more detailed understanding of the operation of the electron flood gun allowed a further study of chloride compounds, for which the monochromatic Ag La source is potentially useful. Following the hydrolysis problems experienced during the previous study of chloride compounds (Section 4.1), a more restricted study was made of the alkali metal chlorides, which have been the subject of attention in previous work (69-73).

4.3.1 Experimental

Samples of LiCl, NaCl, KCl, RbCl and CsCl were dried in an oven at 120°C prior to imbedding into indium foil. On placement into the spectrometer, the sample probe was heated at 100°C for 24 hours, before baking the system at 100°C for 48 hours.

Narrow scan spectra were recorded using the following conditions:
Number of channels : 125
Channel width : 0.2eV
Total time in each channel : >6 mins
Analyzer energy : 50eV
Analyzer slit widths : 4mm
Electron take-off angle : 45°
X-ray anode settings : 14KV, 40mA = 560W
Spectrometer vacuum : 1-4 x 10^-9 mbar
Electron flood gun settings : 4V or 6V, 0.25mA

These are different from previous values quoted since the Apple VGS1000 datasystem was used to control the spectrometer, rather than the DEC PDP8e as in previous work.

Each chloride compound was run at least four times until four reproducible sets of data were recorded, from which Auger parameter and relaxation energies could be calculated. For the latter, an approach was adopted similar to that used for the optimisation of the electron flood gun settings, i.e. involving Bechstedt's approach. However, for the alkali metal chlorides the comparison is between different ionic crystals. The valence charge is described by the solid-state or Madelung potential, V(i), which can be accurately modelled by the "charged-shell" approach(69), as shown in Figure 4.14. For orbitals inside the shell, ΔBE will vary with q^2/r. For orbitals outside the shell, ΔBE varies with 1/(r - r0).
The reference point for the studies of silicon compounds was metallic silicon, which itself contains relaxation terms. However, a similar reference for chlorine cannot be used since it exists as a gas, and contains no relaxation terms. Thus solid chlorine would be necessary.

The binding energy of a chloride core level relative to the Fermi level will be:

\[ \text{BE (i)} = -E_{\text{HF}}(i) - R^a_D(i) - V(i) - R^e_D(i) - \phi \]

\[ \ldots.. 4.24 \]

Similarly, the kinetic energy of the KLL Auger electron \(KE \text{ (KLL)}\) will be:

\[ KE \text{ (KLL)} = \text{BE (1s)} - \text{BE (2p)} - \text{BE (2p)} - F(\phi, 2p) \]

\[ + R_s \]

\[ \ldots.. 4.25 \]
This allows two Auger parameters to be defined, as seen previously. The first is the sum of the 1s binding energy and the KLL kinetic energy peak positions:

\[ A = BE(1s) + KE(KLL) \]

\[ = 2BE(1s) - 2BE(2p) - F(2p,2p) + R_S \]

\[ = 2 \left\{ - \epsilon_{HF}(1s) - R_D(1s) - V(1s) - R_D(1s) - \phi \right\} - 2 \left\{ - \epsilon_{HF}(2p) - R_D(2p) - V(2p) - R_D(2p) - \phi \right\} - F(2p,2p) + R_S \]

\[ \ldots 4.26 \]

or, since, from the charged-shell model, \( V(1s) = V(2p) \):

\[ A = \varepsilon \left\{ E_{HF}(2p) - E_{HF}(1s) + R_D(2p) - R_D(1s) + R_D(2p) - R_D(1s) \right\} - F(2p,2p) + R_S \]

\[ \ldots 4.27 \]

For the comparison of chloride ions, terms defined for the isolated atom can be ignored, whilst the two-hole interaction energy \( F(2p,2p) \) can be assumed constant. Thus:

\[ \Delta A = 2\Delta \left\{ R_D^{ea}(2p) - R_D^{ea}(1s) \right\} + \Delta R_S \]

\[ \ldots 4.28 \]
Since $R_S$ is the difference between the total extra-atomic relaxation energy and that for the one hole state, i.e.

$$R_S = R_{T}^{ea}(2p,2p) - 2R_D^{ea}(2p) \quad \ldots \quad 4.29$$

and since classical theory suggests that relaxation energy is proportional to the square of change in charge, i.e.

$$R_S = 2R_D^{ea}(2p) \quad \ldots \quad 4.30$$

it follows that:

$$\Delta A = 4\Delta R_D^{ea}(2p) - 2\Delta R_D^{ea}(1s) \quad \ldots \quad 4.31$$

The second Auger parameter, $\zeta$, is defined as:

$$\zeta = KE(KLL) - BE(1s) + 2BE(2p)$$

$$- F(2p,2p) + R_S \quad \ldots \quad 4.32$$

Neglecting atom-like terms:

$$\Delta \zeta = 2\Delta R_D^{ea}(2p) \quad \ldots \quad 4.33$$

This produces:

$$\Delta R_D^{ea}(2p) = 1/2 \Delta \zeta \quad \ldots \quad 4.34$$

$$\Delta R_D^{ea}(1s) = \Delta \zeta - 1/2 \Delta A \quad \ldots \quad 4.35$$
Thus it is these equations that are used for calculation of extra-atomic relaxation energy values for this series of chlorides.

4.32 Results

The measured peak positions for chlorine in the alkali metal chlorides can be seen in Table 4.9. Figure 4.15 shows plots of the Auger parameters $\zeta$ and $A^1$ versus the metal-chlorine bond polarisability, which was calculated using the Lorentz-Lorenz relationship (equation 4.3).

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Cl1s B.E. (eV)</th>
<th>Cl2p B.E. (eV)</th>
<th>ClKLL K.E. (eV)</th>
<th>$\zeta$</th>
<th>$\Delta E_D$ (1s)</th>
<th>$\Delta E_D$ (2p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCl</td>
<td>2816.7</td>
<td>193.5</td>
<td>2391.4</td>
<td>38.3</td>
<td>5208.1</td>
<td>0.95</td>
</tr>
<tr>
<td>$\alpha = 2.98$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>2815.7</td>
<td>192.6</td>
<td>2391.2</td>
<td>39.3</td>
<td>5206.9</td>
<td>0.55</td>
</tr>
<tr>
<td>$\alpha = 3.38$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>KCl</td>
<td>2815.8</td>
<td>192.9</td>
<td>2391.4</td>
<td>38.6</td>
<td>5207.2</td>
<td>1.10</td>
</tr>
<tr>
<td>$\alpha = 4.30$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RbCl</td>
<td>2817.1*</td>
<td>194.7*</td>
<td>2389.2*</td>
<td>38.5</td>
<td>5206.3</td>
<td>1.65</td>
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<tr>
<td>$\alpha = 4.96$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsCl</td>
<td>2814.9</td>
<td>192.5</td>
<td>2392.4</td>
<td>37.5</td>
<td>5207.3</td>
<td>2.15</td>
</tr>
<tr>
<td>$\alpha = 6.04$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Flood gun set to 4V, 0.2mA

Table 4.9 Alkali metal chloride data
Values for refractive index were obtained from the literature\(^{130}\), as were values for unit cell parameters to determine crystal volumes\(^{131}\).

\[
\zeta = 40.33 + 0.397a \\
p = 0.744
\]

\[
\zeta (eV) = 40 - 33 + 0.397a
\]

\[
p (eV) = 0.744
\]

\[
\alpha = 5205.95 + 0.171a \\
p = 0.312
\]

\[
A = 5205.95 + 0.171a
\]

\[
p (a^3) = 0.312
\]

Figure 4.15 Variation of $\zeta$ and $A$ parameters with the metal-chlorine bond polarisability
The data for LiCl has been excluded from calculation of the regression lines shown, since substantial levels of oxygen were persistently found on the sample, indicating that hydrolysis was occurring. However, it is interesting that although the data for LiCl is different from that for the other materials, the scatter in this data is similar. Thus whilst water presence shifts these values, it does not affect the accurate control of charge effected by the electron flood gun. The hydrolysis of LiCl was difficult to overcome experimentally, and is a recognised problem (68). A similar problem was found when analysing the CsCl sample, though the problem in this case was less severe and was overcome by further drying.

The regression lines of Figure 4.15 have been extrapolated to \( a = 0 \), this giving base reference values for \( \zeta \) and \( A \). Consequently, the \( \Delta \zeta \) and \( \Delta A \) values are derived from the differences of data points from the \( a = 0 \) values. Though these values may not be identical to values obtainable for solid chlorine, the difference of the various metal chlorides with respect to the reference values will be relatable.

As experienced in the previous chlorides study, the scatter of results shown in Figure 4.15 is larger than would be desired. This is mainly due to two factors associated with the experiment:

1) the tendency of chloride materials to hydrolyse, and
2) the low count rates experienced by the use of monochromatic Ag L\( \alpha \) x-rays.
Any uncertainty in individual peak position value is further compounded on calculation of the Auger parameters since, in the case of \( \zeta \), four peak position values are involved. Thus it is a reflection on the quality of data produced that relationships are visible, since even slight experimental errors become magnified during data processing. The effect of specimen hydrolysis causes a shift in the line position, although the slope remains unaffected. However, on adjustment of the original data values by a value as small as 0.3eV any linear relationship is less evident.

Figure 4.16 shows plots of the extra-atomic relaxation energies \( \Delta R^\text{ea}_D(1s) \) and \( \Delta R^\text{ea}_D(2p) \) versus bond polarisability. Data for LiCl has been excluded in calculating the regression lines because of its overall shift.

### 4.33 Discussion

Following the work of Aitken et al\(^{67}\), who studied chlorine KLL and 2p energies to investigate the influence of initial-state and final-state effects on electronegativity, use can be made of the expression:

\[
R^\text{ea}_D = a (\Delta q)^2 / 2
\]

\((4.36)\)
Figure 4.16 Plot of extra-atomic relaxation energies versus bond polarisability

$\alpha = \text{the bond polarisability, and}$

$\Delta \rho = \text{the change in charge experienced on hole creation.}$

Thus $\zeta$ is related to the bulk polarisability of the medium. A relationship of this type provides the basis for interpretation of Figure 4.16. The slopes of the best fit lines will be given by:
This refers to the change in charge perceived by the bonding (i.e. 3p) electron on photoemission occurring from the 1s (Figure 4.16a) or the 2p orbital (Figure 4.16b).

Use can be made of the atomic shielding constants calculated by Slater(132), which involve the assignment of values for $n^*$, the effective quantum number, and $Z-s$, where $Z$ is the actual nucleus charge and $s$ is a screening constant, to the electrons of each shell in every atom or ion, so that a complete set of one-electron wave functions is produced. A set of rules was developed by Slater giving each subshell a separate screening constant and thus allowing prediction of the influence of the nucleus over different electrons. The rules are as follows:

Rule 1) $n^*$ values are determined by the table of real principal quantum number (n) values, as shown in Table 4.10,

Rule 2) To determine $Z-s$, electrons are separated into groups each possessing a different shielding constant, the groups being:

(1s)
(2s,p)
(3s,p) (3d)
(4s,p) (4d) (4f)
and so on.
<table>
<thead>
<tr>
<th>Value for n</th>
<th>1 2 3 4 5 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>n* value</td>
<td>1 2 3 3.7 4.0 4.2</td>
</tr>
</tbody>
</table>

Table 4.10 Real principal quantum number (n) values with respective n* values

This approach by Slater was similar to that taken by Zener\(^\text{153}\),

Rule 3) Values for s, the shielding constant, are calculated using individual contributions, as follows:

a) nothing for any shell outside the one considered,

b) 0.35 is subtracted for each other electron in the group considered (except for the 1s group, when a value of 0.30 applies),

c) if the shell is of the (s,p) type, 0.85 is subtracted for any electron with a total quantum number less by one, and 1.00 for each electron further in. But if the shell is a (d) or (f), an amount 1.00 is taken for every electron inside it.

Taking chlorine as an example (Z=17), since there are two 1s electrons, eight (2s,p) electrons and seven (3s,p) electrons, the effective screening constants, S, for each group can be deduced:
Thus σ for the 3p electron will be different from that for 1s photoelectron ejection to produce a change in the potential field which induces a rearrangement of electrons.

From Slater's work, it is clear that the value for Δq in equation 4.37 will depend on the source of photoemission, i.e. 1.0 for the loss of a 1s electron and 0.85 for the loss of a 2p electron. Though the intercepts for the best-fit lines in Figure 4.16 are chosen arbitrarily, the relative slopes of the different lines should be described by:

\[
\frac{\Delta R_{p}^{ea}(1s)}{\Delta R_{p}^{ea}(2p)} = \frac{f(\Delta q)^2(1s)}{(0.85)^2} = \frac{f(\Delta q)^2(2p)}{(1)^2} \quad \ldots \quad 4.38
\]

The ratio of the slopes gives a value, in fact, of 0.8^2. Considering the level of scatter present in the data, this value is satisfactory.

Figure 4.17 shows a plot of ΔR_{D}^{ea}(1s) versus ΔR_{D}^{ea}(2p) for this chloride data. The line predicted from Slater's screening coefficient work has also been plotted on the same axis, for comparison. It can be seen that the correlation is fairly good, whilst if one accounts for the wide scatter in the Li data through its rapid hydrolysis characteristic, the data for Na, K, Rb and Cs are more satisfactory. Such a plot is a good test of the experimental data obtained.
It would be interesting to study further chlorine, in an attempt to understand its behaviour more fully in natural environmental situations, such as its role in the pitting corrosion of stainless steels. This could be achieved by the use of perchlorate or hydroxychloride compounds, in which form chlorine often exists. However, problems exist, which need to be overcome, concerning the preparation of reliable samples since perchlorates when dry tend to be unstable (i.e. explosive) and hydroxychlorides preparation techniques are complicated.
4.34 Conclusions

1) The application of optimised electron flood gun parameters produced satisfactory results for this chloride study, although specimen hydrolysis remained a problem for LiCl.

2) The correlation between calculated extra-atomic relaxation energies for the Cl 1s and 2p orbitals with screening energy predictions of Slater is good, such that a linear relationship probably exists between (alkali metal) chloride extra-atomic relaxation with bond polarisability, the magnitude of such relaxation being partly determined by the change in nuclear charge screening on the occurrence of photoemission.

3) The data obtained was not accurate enough to conclude on the effects of change in structure from sodium chloride to caesium chloride types, for example. However, an approach similar to this in the future might be useful for the determination of relative screening coefficients for core-like orbitals.

4.4 Conclusions

1) The initial study of a series of chlorides produced disappointing results, due to the tendency of the materials to hydrolyse but also due to the failure of the electron flood gun to obtain uniformity of surface charging across the energy spectrum, when OV accelerating potential and 0.2mA emission current settings were used (as recommended by the manufacturer).
2) A study of the function of the electron flood gun in the ESCA3 MkII spectrometer revealed that applied parameters needed to be optimised for individual specimens, but if specimens are stable enough under electron bombardment a +6V accelerating potential and a +0.2mA emission current level is appropriate. This is the case due to the penetration of stray fields from the entrance to the analyser in this system, which can deflect lower energy electrons away to reduce neutralisation and increase non-uniformities in surface charging.

3) The discovery of such fields within the ESCA3 is pertinent to other systems since any sources of stray fields within the spectrometer vacuum space may cause non-uniformities of charging to be instigated.

4) On the use of such optimised flood gun settings, a study of the chlorides of the alkali metals produced satisfactory results, with good agreement between extra-atomic relaxation energies for the individual 1s and 2p core levels and bond polarisability.

5) The results of the alkali metal chloride study could be related to the breakdown of passive layers on steel through a study of chlorine in its perchlorate or hydroxychloride form in the future.

The successful optimisation of the electron flood gun achieved in this chapter highlighted the application of Ag La radiation to silicon-based materials, with calculation of Auger parameters and relaxation energies available for the identification of very small changes experienced by electrons when chemical environmental conditions are changed. Investigations particularly suitable for such studies include the growth of thermal oxides on silicon, which is pertinent to
the production of microchip devices, and the effect of cation exchange within zeolite cage structures utilised for catalysis in the petrochemical industry.

Additionally, the extra penetrating nature of the Ag Lα x-rays, together with its low intensity following monochromatisation, could make it suitable for the non-destructive depth-profiling of materials when combined with data obtained with conventional x-ray sources. This may be particularly useful for the studies of insulators such as polymers, which are usually too sensitive to allow the use of argon ion bombardment for the retrieval of depth information. One such system investigated involved a copolymer material used for the manufacture of contact lenses in the ophthalmic industry.
5.1 The Growth of Thermal Oxides on Silicon

The application of surface analytical techniques to the semiconductor industry has continuously increased over recent years (see Figure 1.1). Improvements in lithographic techniques for the fabrication of a micro-chip circuit have led to large scale integration, and techniques such as XPS and, more specifically, AES and SIMS, have been of use in the advancement of such high technology processes.

During the optimisation of the electron flood gun described in the previous chapter a study of silicon compounds was made, which led to the discovery of a linear relationship between the relaxation energies experienced by the 1s and 2p orbitals from silicon metal through $\text{Si}_3\text{N}_4$, $\text{SiC}$, $\text{SiO}_2$ to $\text{K}_2\text{SiF}_6$. Figure 5.1 shows an extended version of this original data, which includes data for different types of oxide on silicon. It is apparent that a thin layer of oxide, such as a native oxide, possesses considerably different characteristics from those of a thicker, thermally grown oxide layer of several hundred nm thickness. Furthermore, since the change from Si metal to $\text{K}_2\text{SiF}_6$ correlated with decreasing refractive index, it could follow that the various oxide thicknesses also have different refractive indices. This parameter is in fact used to control the manufacture of silicon-based electronics components as an indication of the quality of oxide formation.
Figure 5.1 Extra-atomic relaxation energies for silicon-based structures

The dielectric properties of SiO$_2$ are often used to isolate the various structures within a chip. In this study it was therefore examined whether refractive index correlated with any regular change in relaxation energies induced by thermal strains present in the oxide.
5.11 Previous Work

5.111 Oxidation kinetics

Studies of the formation of silicon dioxide layers by thermal oxidation of single crystal silicon have been numerous. Both thin (up to a few tens of nm) and thick (up to several hundred nm) films thermally grown in dry oxygen or steam (wet oxygen) have been used to determine oxidation kinetics and their dependence on such factors as temperature, pressure of oxidising species, substrate orientation, dopant type and concentration.

A notable contribution to this field has been made by Deal and Grove\(^{134}\) who, in accordance with experimental results, assumed that oxidation occurred by the inward movement of oxidant species rather than outward movement of silicon. This assumption applies today, and studies involving XPS\(^{135-137}\) and AES\(^{138}\) of the Si-SiO\(_2\) interface have sometimes shown the presence of non-stoichiometric oxide.

Thus Deal and Grove\(^{134}\) developed a simple model of oxidation that involves reactions occurring at the two boundaries of the oxide layer together with a diffusion process. This can be described by a linear-parabolic relationship and is shown in Figure 5.2, which is their plot of oxide thickness versus time for a temperature of 700°C. A period of rapid oxidation occurs initially, followed by a strictly linear process. This relationship was found to agree with experimental data over wide ranges of temperatures (700-1300°C), partial pressure of oxidising species (0.1-1.0atm) and oxide thickness (30-2000nm) for both oxygen and water oxidants. Adams et al\(^{138}\) confirmed the
linear-parabolic rate law in a study of very thin oxides, with a level of domination being shown by the parabolic term.

Figure 5.2 Oxide thickness versus time (T=700°C)

However, van de Meulen (140) and Ghez and van de Meulen (141) presented a kinetic model for the reaction of silicon and oxygen at the SiO₂-Si interface, in which two parallel competing reactions were postulated to occur:

1) Molecular oxygen reacts directly with silicon to form SiO₂ and atomic oxygen, and
2) The O₂ dissociates to form ions, which can react with silicon or recombine to form molecular oxygen.

Analysis of their data showed that a difference in activation energies associated with these competing reaction steps was responsible for the shift in their relative importance as a function of temperature,
the former reaction being dominant at high temperatures and the latter at lower temperatures.

5.112 Ellipsometry studies

Ellipsometry can provide an inexpensive, accurate and non-destructive method for the measurement of optical constants and thicknesses of films such as silicon dioxide, silicon nitride and alumina deposited on substrates such as silicon and gallium arsenide. Optical data has been obtained by several workers (139-144) for films of 80nm to several microns thickness, mostly at a wavelength of 5461Å, although Pliskin and Esch (145) used variable angle monochromatic fringe observation (VAMFO).

An ellipsometer measures the change in ellipticity of polarised light as it is reflected from the surface of the sample. This change in ellipticity, measured through changes in amplitude (W) and phase (Δ), is utilised (in conjunction with established optical theory) to calculate the required parameters. This is described mathematically by a complex reflection coefficient \( p \) given by:

\[
p = \tan \psi e^{i\Delta}
\]

This relationship between \( W \) and \( \Delta \) has been covered in depth by Archer(142). To compute the optical constants of a film, several fixed constants need to be known together with those measured by the ellipsometer. These are the angle of incidence of the light beam, its wavelength and the complex index of refraction \( n - ik \) of the silicon substrate, where \( k \) is the extinction coefficient of the \( \text{SiO}_2 \). In order
to simplify the analysis, the SiO₂ film has been assumed to be completely transparent, i.e. \( k_{\text{SiO}_2} = 0 \).

The fixed constants were taken to be:

- Angle of incidence: 70°
- Wavelength of radiation: 5461 Å
- Complex index of refraction of silicon: 4.050 - 0.028i

A graphical representation of the dependence of \( W \) and \( \Delta \) is shown in Figure 5.3. Since no two curves overlap or intersect, each point in the plane corresponds to a unique value for the index of refraction of the film.

![Graph](image)

Figure 5.3 Graphical dependence of amplitude (\( \psi \)) and phase (\( \Delta \))
Further work by So and Vadam(146) indicated that to obtain the true values of the optical constants for any system, it is not sufficient to have a selection of \((\psi, \Delta)\) measurements with arbitrary film thickness values. Though this data may be sufficient to yield values for the optical constants, they may not necessarily be the correct ones. Thus it is necessary to have enough data points on the \(\psi, \Delta\) curve to identify the true values of the optical constants. Both So and Vadam(146) and Smith and Carlan(147) concluded that the best values for the complex index of refraction of silicon were 4.065 - 0.028i and 4.05 - 0.028i respectively at 5461Å. The index values obtained for thermally grown SiO\(_2\) were 1.458 and 1.46. Differences in these values from those obtained by van de Meulen(140) and Raider et al(148) led Taft(143) to redetermine such optical constants. Rather than choose a value for the extinction coefficient from the available absorption data, as was done by most other workers, Taft established that \(k=0.031 + 5\%\) from absorption measurements on single crystal silicon at 5461Å. Using an ellipsometer, the real part of the refractive index of silicon was determined to be 4.086 at 5461Å. Having determined the complex refractive to be 4.086 - 0.031i, Taft also found the index of refraction of oxide films thermally grown on silicon in dry oxygen(143) and steam(144) to be a function of growth temperature. Figure 5.4 shows this relationship for oxides grown on silicon <100> oriented wafers in dry oxygen, with refractive index decreasing with oxidation temperature until a constant value is reached. Extrapolation of the straight line portion of the curves intersects the bulk fused quartz refractive index value of 1.460 at 1190°C. It is at this temperature and above that the index appears to remain constant at the higher value of 1.462. The high index suggested the presence of a film of density greater than that for bulk fused quartz, whilst the constant value indicated a stable material and the need for further
Taft accounted for the discrepancy between these limiting values and the refractive index of fused quartz by considering the compressive stresses that would be induced by differential thermal contraction in the plane of the film on cooling from the oxidation temperature. This would increase the density of the oxide film and hence increase the refractive index. It was concluded that at high temperatures (i.e. greater than 1190°C for dry oxygen oxides) the index of refraction of the oxide film is no different from that of pure fused quartz under a compressive stress. The higher refractive index values shown in Figure 5.4 would
require (for an 800 °C film) the equivalent of an isostatic pressure of more than 10kbar on quartz glass. Therefore, films grown at lower temperatures require a mechanism other than stress-strain for their high refractive indices.

However, Jaccodine and Schlegel\(^{(149)}\) determined stress levels in oxide films using two techniques:

a) A thin silicon sample was used as a beam and the amount of bowing under the strain exerted by oxide left on one surface was measured, and

b) An unsupported SiO\(_2\) window was used as a balloon and strain was measured as a function of air pressure inflating the balloon.

Results of their measurements were found to be in agreement with the stress expected from thermal mismatch of Si and SiO\(_2\), which contradicts with the work of Taft.

These findings, of course, rely on the assumption that refractive index is constant with changes in oxide thickness, an assumption that has been substantiated by the data of other workers\(^{(140,142,145-147)}\).

5.113 XPS studies

Most of the studies utilising XPS and AES have involved a study of the Si-SiO\(_2\) interface. For example, Johannessen et al\(^{(150)}\) used the chemical shifts in the Si KLL spectra to show that SiO\(_x\) (1 < x < 2) is a phase-separated system with Si particles finely dispersed in the SiO\(_2\) matrix. However, this remains an area of controversy. A Mg/Au anode has been used by Wagner et al\(^{(151)}\) to determine screening energy
variations in Si, SiO\textsubscript{2} and a range of silicides. The Auger parameter of silicon was found to be approximately 4eV larger than that for SiO\textsubscript{2}, corresponding to a greater screening energy for a singly-charged ion of 2eV, which confirmed previous work by Hollinger\textsuperscript{(152)}. It was concluded that relaxation effects at or near the interface make it unlikely that sharp peaks for intermediate oxidation species can be defined. Observations of sharp lines attributable to different species at the interface\textsuperscript{(153)} can only occur if three-dimensional aggregates of such species are in multi-atom dimensions, or two-dimensional layers exist in which the atoms of each lie in identical environments.

An XPS and ellipsometry study of the growth of thermal oxides on silicon was made by Raider et al\textsuperscript{(148)}, who concluded that the difference recorded between ellipsometric film thicknesses and estimated values from XPS data could not be accounted for solely by non-stoichiometry or densification of the oxide film, with the adsorption of impurities and oxide growth at room temperature being contributary factors.

In view of the above uncertainties and because of the level of interest it was felt that a study of relaxation energies which can only be achieved by use of a high resolution, high energy source would be a useful contribution to the subject.
5.12 Experimental

Specimens of size approximately 6mm x 6mm were cut from \(<100>\) single crystal silicon wafers (p-type), which had previously been mechanically polished. Throughout the literature a variety of sample cleansing methods have been utilised, with no single one being adopted for general use. Thus a method was devised similar to that used by Smith and Carlan\(^ {147} \), whose method appeared both thorough and effective. This involved the following stages:

a) immerse sample in concentrated \( \text{H}_2\text{SO}_4 \) saturated with \( \text{Cr}_2\text{O}_3 \) at a temperature of 80 to \( 85^\circ \text{C} \) for 4 minutes to remove organic material,

b) rinse sample in deionised water for 2 minutes,

c) immerse sample in 40% HF in water for 1 minute to remove the oxide, and

d) rinse sample in deionised water for 5 minutes.

After drying, the samples were stored in an evacuated dessicator prior to oxidation.

Samples to be oxidised were placed in quartz boats in a tube furnace, through which oxygen-free nitrogen gas was flowing, at the required oxidation temperature. A stabilisation period of 15 minutes was allowed for the attainment of a constant temperature level, before pure oxygen gas was introduced into the furnace. Samples were withdrawn from the furnace at intervals of between 10 and 80 minutes at oxidation temperatures of 700 to \( 900^\circ \text{C} \). These values were chosen for the growth of oxides of a sufficiently small thickness to allow the use of the monochromatic Ag \( \text{La} \alpha \) x-rays to penetrate to a depth close to the Si–SiO\(_2\)
The XPS analysis involved Mg Kα for the optimisation of sample cleansing procedure, a 100eV analyser energy being used, and monochromatic Ag Lα for the oxidised sample analysis. A 10V electron flood gun potential was adopted in the latter case, following the electron flood gun optimisation procedure described in Chapter 4. The oxides were stable enough to withstand electrons of this energy. The experimental conditions were as follows:

<table>
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<th>Parameter</th>
<th>Setting</th>
</tr>
</thead>
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<tr>
<td>Number of channels</td>
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</tr>
<tr>
<td>Channel width</td>
<td>0.2eV</td>
</tr>
<tr>
<td>Total time in each channel</td>
<td>&gt;3 mins</td>
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<td>Electron take-off angle</td>
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<tr>
<td>X-ray anode settings</td>
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</tr>
<tr>
<td>Spectrometer vacuum</td>
<td>&lt;10⁻⁹mbar</td>
</tr>
<tr>
<td>Electron flood gun settings</td>
<td>10V, 0.25mA</td>
</tr>
</tbody>
</table>

A Transistronics Ltd. Ellipsometer Mk II was used for refractive index and thickness measurements. This was based in the Department of Electronic and Electrical Engineering at the University of Surrey. The instrument configuration is shown in Figure 5.5. The detector unit was replaced by a photomultiplier and micro-ammeter unit, previously part of a Gaertner ellipsometer at the Kodak Research Centre, Harrow, Middx. The latter possessed a larger detection area and produced satisfactory results with standard silicon wafer specimens. The work was undertaken in a darkened room, this avoiding any interference by external sources of
light.

Figure 5.5 The ellipsometer experimental configuration

To measure $\psi$ and $\Delta$ the following method was adopted:

a) The specimen was placed onto the sample holder, the micro-ammeter being set to its lower sensitivity range. The analyser was set to 45 and the polariser varied from 45° upwards (in the range 45°-225°) to obtain a minimum point as indicated by the micro-ammeter. The analyser was then moved in the range 0-90° to obtain a better minimum,
b) With the micro-ammeter set to its more sensitive range and utilising alternate manipulation of the slow drives of the analyser and polariser a better minimum point was obtained. The values $P_1$ and $A_1$ could then be read off the polariser and analyser verniers respectively,
c) The analyser was set to $-A_1$ (i.e. 360°-A_1) and the polariser set
to \((P_1-90^\circ)\). An accurate minimum was then determined near to these settings and the values \(-A_2\) (i.e. \(360^\circ\) minus the angle shown on the analyser) and \(P_2\) recorded.

d) The values of \(\psi\) and \(\Delta\) were calculated using the equations:

\[
\psi = \frac{A_1 + A_2}{2} \quad \ldots \ldots 5.2
\]

\[
\Delta = 360^\circ - (P_1 - P_2) \quad \ldots \ldots 5.3
\]

A Basic computer program supplied with the instrument was modified to allow data to be filed. The University Prime computer system was then programmed so that values of refractive index and film thickness could be computed from values of \(\psi\) and \(\Delta\).

5.13 Results

5.13.1 Ellipsometry results

Optical measurements were made on each specimen up to four times and refractive index data computed, a selection of which is shown in Table 5.1. Figure 5.6 illustrates the high degree of scatter observed in the results. This bears little resemblance to the corresponding plot from Taft's work previously shown in Figure 5.4. The refractive indices for this data vary from 2.07 to 1.17 whereas comparable values extracted from Taft's data varied from 1.481 to 1.472. Thus the growth of such thin oxide films appears to induce a random jumping effect from line to line for \(n\) value (Figure 5.3) because of the closeness of the respective
lines. This limits the usefulness of ellipsometry for such measurements.

Figure 5.7 shows a plot of calculated oxide thickness versus oxidation temperature from this ellipsometry data, from which little clear trend is apparent. To confirm this ellipsometry data, which was considered disappointing, use was made of a fully computer-controlled Gaertner Dual Mode Waferskan ellipsometer based within the IBM (Winchester) microfabrication unit. Figure 5.8 shows a plot of the data obtained for the oxidation temperatures of 700 and 750°C. It was not possible to generate any refractive index values from these films, since they were of too low a thickness. Thus all the thickness measurements were obtained following the programming of the computer to an index value of 1.46, the value for SiO₂. This seemed reasonable. However, the fixing of n in this way negates the whole point of the experiment.

5.132 XPS results

The effectiveness of the cleansing procedures adopted can be seen in Figure 5.9, where the native oxide present on an original silicon wafer is removed satisfactorily following treatment.

The XPS results for the oxidised samples can be seen in Table 5.2. From the experimentally obtained peak positions for the Si 1s, 2p and KLL lines Auger parameters $A^I$ (1s+KLL) and extra-atomic relaxation energies for the 1s and 2p orbitals were calculated using the equations of Bechstedt et al (25), i.e.

$$\Delta R^e_a (i) = \frac{3}{2} \Delta \zeta (ijj) - \Delta \alpha (ijj) \quad \ldots \quad 5.4$$

$$\Delta R^e_a (j) = \frac{1}{2} \Delta \zeta (ijj) \quad \ldots \quad 5.5$$
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<th>T (°C)</th>
<th>t (mins)</th>
<th>ψ</th>
<th>Δ</th>
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</table>

Table 5.1 Ellipsometry results

Figure 5.6 Variation in oxide refractive index (obtained through ellipsometry) with temperature
Due to the low sensitivity factor for the Si 2p line in Ag Kα radiation (see Table 3.2), this region was acquired for lengthier periods to obtain reasonable quality spectra. Examples of a survey scan and high resolution narrow scan spectra are shown in Figure 5.10 and 5.11.
Figure 5.9 The effect of sample cleansing treatment

![Before and After Intensity Graphs](image)

Table 5.2 Thermal oxide on silicon results

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<th>Temp (°C)</th>
<th>Time (mins)</th>
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<th>KLL (KE)</th>
<th>2p (BE)</th>
<th>²f</th>
<th>Δf</th>
<th>ΔΔ²f (ls)</th>
<th>ΔR°²f (2p)</th>
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<td>-29.3</td>
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</table>
Figure 5.10 Survey scan of thermal oxide sample

Spectrum Number - M322C  Date - MON, 02 JUN 1986

XPS Analysis using magnesium radiation

THERMAL OXIDE ON SILICON

Intensity (Counts)

Binding Energy (eV.) x10^2

C = C  XPS PEAKS
O = o  AUGER PEAKS
SI = h

Intensity (Counts) x10^3

20
18
16
14
12
10
8
6
4
2
0

XPS PEAKS
AUGER PEAKS

Thermal Oxide on Silicon
Figure 5.11 Typical narrow scan spectra obtained
The growth of oxide thickness with oxidation time, seen via the Si (metallic)/ Si (oxidised) peak ratio, for a temperature of 700°C is shown in Figure 5.12, this being for the 1s region. Oxide thickness values can be calculated using these ratios, together with the estimate for the escape depth of the Si 1s (KE=1144) from Chapter 3 (Figure 3.10). Taking the sampling depth ($3\lambda$) to be approximately 75Å, values obtained are shown in Table 5.3.

Figure 5.13 shows a plot of the 1s relaxation energy versus the 2p relaxation energy for the thermal oxides on silicon over the temperature range used. The self-consistency in the shifts in relaxation energies compares favourably with data obtained via ellipsometry.

5.14 Discussion

Whilst the sample preparation technique was thought to be satisfactory, and the relationship between relaxation energies appeared reasonable (Figure 5.13), a closer examination of this data reveals discrepancies.

A correlation does appear to exist between the values of $\Delta R^\text{ea}_D(1s)$ and $\Delta R^\text{ea}_D(2p)$ for thermal oxides, but these do not correlate with temperature and time. The variation of times and temperature levels could be contributing to the difficulty in interpretation of results, whilst higher values of temperature could lead to increased plastic flow occurrence, and possibly even self-annealing, to dissipate any build up of stress level induced.
Figure 5.12 Variation of Si ls peak on growth of oxide (T=700°C)
Figure 5.13 Correlation of extra-atomic relaxation energies from thermal oxide data

Table 5.3 Calculated thicknesses from XPS data

<table>
<thead>
<tr>
<th>Oxidation T (°C)</th>
<th>Oxidation t (mins)</th>
<th>Oxide Thickness (nm)</th>
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</thead>
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<td>10</td>
<td>4.9</td>
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<td>40</td>
<td>7.4</td>
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<td>10.5</td>
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<tr>
<td>700</td>
<td>80</td>
<td>11.8</td>
</tr>
</tbody>
</table>
Figure 5.14 Variation in refractive index values obtained through ellipsometry

In Figure 5.14 refractive index values have been plotted against oxidation time for temperatures of 700 and 800°C. From the assumption that the index is constant with changes in thickness no dependence on time would be expected. Most of the data for each temperature appear to lie in bands. The values of $\psi$ and $\Delta$ for these temperatures are within the ranges 10-12° and 130-165° respectively. With reference to Figure 5.3, for these ranges of $\psi$ and $\Delta$ there is a large range of values possible for refractive index. Therefore, for a small difference in $\psi$ and $\Delta$ the computer program may carry out its iterative calculation based on one or another line of constant refractive index, as mentioned by So and Vedam (146). Thus the use of ellipsometry for the measurement of these film thicknesses appears unsuitable.
The wide scatter of the data (both XPS and ellipsometry) with temperature and time could be due to experimental error, which would be more likely a reflection of the heat treatent/oxidation stage than any other, although variation in adsorption of impurities and oxide growth at room temperature could also be influencing results obtained. It is also possible that the interface between the metal and the oxide may be dominating the strain presence for these films.

However, the XPS spectra (Figure 5.12) and calculated film thicknesses (Table 5.3) show a not unexpected change in ratio of oxidised to metallic silicon with time for the 700°C samples, where the thickness of oxide is small enough to allow some metallic silicon to be seen by the Ag La x-rays. This indicates that XPS is probably better able to characterise such thin films, in comparison to ellipsometry which is designed for thicker films.

A comparison can be made between the XPS data obtained here with that of West\(^{(28)}\) in his studies of aluminosilicate polarisabilities. A projection of his data is shown in Figure 5.15. Values for \(n\) are those predicted from Taft\(^{(143)}\), whilst \(\lambda\) values are taken from Table 5.2, being previously used for the calculation of extra-atomic relaxation energy values.

5.15 Conclusions

1) Ellipsometry is unable to provide reliable data on the refractive indices of thin (<10nm) films of thermal oxide on silicon.
Figure 5.15 Projection of West data onto thermal oxide data (XPS)

2) Relaxation energies obtained for the same films from the XPS data give a self consistent relationship between the shifts on the 2p and 1s levels.

3) The strong probability that these shifts correlated with the polarisability of electrons in the oxide could not be tested because of the lack of independent measurement of polarisability from the ellipsometer.
4) The polarisability derived from the XPS data did not correlate with temperature of oxidation or with thickness of the films measured by the peak ratio method; it is probable that this is because of the importance of interface effects in the thin films investigated.

5) Further work should seek to confirm the n/Auger parameter relationship using films thick enough to give reliable measurements of refractive index.
5.2 Zeolites For Catalysis

The surface chemistry of silicon and its compounds is of established importance in many areas of petrochemical technology and has been studied in the past by classical methods such as gas adsorption isotherms, calorimetry and the monitoring of swelling behaviour. Furthermore, diffraction methods and NMR have produced a wealth of structural information for the bulk materials. XPS has the ability to bridge these separate studies, and has for many oxide systems provided specific evidence of adsorption and catalytic sites.

![Figure 5.16 Typical zeolite structures (faujasite and ZSM-5)](image)

Naturally occurring zeolite materials have been known for 200 years. They are rich in water, which on heating is briskly liberated (the word zeolite is Greek for "the stone that boils"). The catalysts, which are physically similar to sponges, possess large internal surface areas (200-400 m²/g depending on crystallite size) and have regular pore sizes (unlike sponges) through which reactants and products may pass. Typical structures are shown in Figure 5.16, whilst the shape selectivity characteristic ability of zeolites is shown in Figure 5.17. Important
separations realised in this way include those of linear hydrocarbons from their branched-chain isomers.

![Diagram of shape selectivity of zeolites]

Figure 5.17 The shape selectivity of zeolites

Zeolites can also effect facile ion-exchange, being used for such processes as water softening, purification and general cleansing. They contain loosely bound cations such as Na\(^+\), K\(^+\) and Ca\(^{2+}\), which can be washed out and replaced by others such as Mg\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\) and Cs\(^+\). This has been found to be of great use for proposed radioactive waste disposal programmes.

5.21 The structure of zeolites

The zeolite atomic framework consists of Si or Al atoms tetrahedrally surrounded by O atoms, which in turn link other tetrahedrally bonded Si or Al atoms. This produces a porosity where cavities and channels can possess a diameter of 0.35–0.75nm, depending on
the topology of the particular system (see Table 5.4). They are derived from silica, SiO₂, from which some silicon atoms have been replaced by those of aluminium. Each substitution necessitates the introduction of a mono-valent exchangeable cation (or half a divalent one) to preserve electroneutrality, since Si is tetravalent and Al trivalent.

<table>
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<th>Number of Tetrahedra</th>
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<td>6</td>
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<tr>
<td>8</td>
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<td>10</td>
<td>0.6</td>
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<td>12</td>
<td>0.8</td>
<td>Y</td>
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<tr>
<td>18</td>
<td>1.5</td>
<td>Not yet observed</td>
</tr>
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Table 5.4 Zeolite internal porosities

Thus stoichiometrically, a zeolite is:

\[ M_x / n \cdot n \text{Al}_2 \cdot m \text{Si}_2 \cdot w \text{H}_2\text{O} \]

\[ \ldots \ldots 5.6 \]

where:

\( x = \) the valence of the cation \( M \),

\( n = \) the number of Al substitutions per \((n + m)\) Si atoms in the unit cell, and

\( w = \) the number of water molecules occluded in the structure.
By manipulating the complex atomic frameworks of zeolitic minerals, chemists have been able to develop catalysts that can transform low-grade fuels into petrol and other useful raw materials. For example, success has been achieved with H\(^+\)-ZSM-5, which converts small molecules such as methanol (CH\(_3\)OH) and large molecules such as hexadecane (C\(_{16}\)H\(_{34}\)) into a narrow spectrum of intermediate hydrocarbons, containing aliphatics of C\(_3\) and C\(_4\) and aromatics from C\(_6\)-C\(_{10}\), which in effect make up petrol. ZSM-5 also allows benzene and toluene to be produced from non-petroleum raw materials such as coal and biomass. The catalytic performance is related to the ease with which H\(^+\) ions are detached from the "active sites" where they are initially anchored. Catalyst pore inner walls are active sites for proton release, generating carbonium (or oxonium) ions in the presence of organic reactant molecules, which lose water and form C-C bonds to yield the hydrocarbons that constitute petrol.

Zeolites have been the subject of a number of studies in the past, these being reviewed in depth by McCarroll\(^{(154)}\) and Tompkins\(^{(155)}\). A notable contribution has been made by the work of Delgass et al\(^{(156)}\). When utilising XPS for the study of zeolites, the prime areas of interest are:

1) the degree of exchange of metal cations,
2) the changes in oxidation state experienced by the metal cations during development and use of the zeolite,
3) the extent of the interaction between the metal cations and the zeolite, and
4) any particular reactions experienced by the metal cations.
Studies have been made of zeolites possessing differing silicon-to-aluminium ratios by workers such as Tempere et al\(^{157}\), in which surface dealumination was found, this effect increasing with bulk Si/Al ratio increase. This work followed useful contributions by Lindsay et al\(^{158}\) and Brinen and Meloma\(^{159}\).

The XPS studies of Carberry et al\(^{160}\) showed that the use of \(\gamma\)-radiation induced the migration of alkali metal ions (such as caesium) to the surface. This involved a supported silver catalyst, whose properties were enhanced by this process for the oxidation of ethylene.

A study of the valence band spectra for both zeolites and clays has been made by Barr\(^{97}\), from which apparent selective degradation of the zeolite was seen through the broadening of \(1\)eV (in FWHM value) for \(\alpha\)-\(\text{Al}_2\text{O}_3\) to Ca Y zeolites respectively.

XPS has also been employed for the study of platinum and rhodium metal cations on zeolites. For example, Vedrine et al\(^{161}\) exchanged Pd and Pt ions into type Y zeolite, with the possible exchange of \(\text{Pd}^{2+}\) ions for \(\text{Na}^+\) ions occurring, whilst Okamoto et al\(^{162}\) exchanged \(\text{Na}^+\) ions with \(\text{Rh}^{\text{III}}\), which on reduction in vacuum produced a mixture of \(\text{Rh}^{\text{I}}\) and \(\text{Rh}^{0}\). \(\text{Rh}^{\text{I}}\) is possibly an active site for ethylene adsorption prior to subsequent hydrogenation. Evidence was also found for the migration of rhodium to the bulk on heating.
5.22 A zeolite study using low energy flood gun electrons

The monochromatic Ag L\textsubscript{\alpha} x-ray source was applied to a study of Na, Li and Mg cation-exchanged Y zeolites, since its ability to generate Auger parameter and individual core level relaxation energies for aluminium and silicon was thought to be useful.

5.221 Experimental

Samples of synthetic faujasite were supplied by the BP Research Centre at Sunbury-on-Thames, U.K. The zeolites were prepared with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios of between 2.47 and 4.79, involving the mixing of aluminate and silicate starting materials to produce a saturated solution which is then heated in an autoclave to a temperature in excess of 100 °C, to initiate product crystallisation. Y-Type faujasites, formed from a basic sodalite unit, involve the original sodium cations being replaced by a mixture of protons and rare earth or alkaline earth cations, which dramatically enhance the selection acidity of the system and permit it substantial activity over lengthy periods\(^{(163)}\).

The powder materials were dried in an oven at 120 °C before being imbedded into indium foil to form a compressed cake. They were then allowed to degas in the spectrometer preparation chamber for a 48 hour period, before being transferred to the analyser chamber for analysis at $10^{-9}$ mbar. The spectrometer was then baked at 100 °C for 26 hours, before repeated analysis using XPS. Finally, the samples were etched for 1 minute (Ar\textsuperscript{+} ions at 1KV energy and 0.5KV focus, with the analyser chamber backfilled to $10^{-5}$ mbar) before being examined for a third time. This was to establish an experimental protocol whereby these materials,
which are prone to the sorption of water, carbon monoxide and other species, could be brought to a condition so that meaningful comparisons could be made and the effects of cation exchange and Al content on the Si and Al Auger parameters elucidated.

Due to the sensitivity of the zeolite materials, charge neutralisation was effected initially by a flood gun accelerating potential of less than 2V, a value that was in line with the manufacturers and other workers recommendations. This level was increased in a separate study to overcome the field penetration problems discovered in Chapter 4, and is discussed in section 5.23. Other experimental conditions were similar to those described for the thermal oxide on silicon study (section 5.12).

5.22 Results

Using the sensitivity factors calculated earlier for monochromatic Ag Lα radiation use (Chapter 3), apparent surface compositions for the cation exchanged zeolites can be calculated. It is assumed that no concentration gradients exist within the surface region. The very low sensitivity factor for Li in x-radiation generally, together with its low concentration in these materials, made it virtually impossible to detect, although its presence could be inferred from the drop in levels of Na detected.

The results for the Na Y zeolite in the fresh, baked and etched conditions are shown in Tables 5.5 to 5.7, whilst the apparent compositions for Na and Mg zeolites are shown in Tables 5.8 and 5.9.
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Table 5.5 Na Y zeolite results: fresh condition

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<td>Na KLL</td>
<td>988.8 12.5</td>
<td>992.2 11.8</td>
<td>992.2 10.2</td>
<td>992.4 7.5</td>
<td>990.0 9.2</td>
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<tr>
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<td></td>
</tr>
<tr>
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<td>2948.2</td>
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<td>2948.0</td>
</tr>
<tr>
<td>A^Na)</td>
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<td>2062.2</td>
<td>2062.4</td>
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</table>

Table 5.6 Na Y zeolite results: baked condition
### Table 5.7 Na Y zeolite results: baked and etched condition

<table>
<thead>
<tr>
<th>$\text{SiO}_2/\text{Al}_2\text{O}_3$</th>
<th>As received</th>
<th>Baked</th>
<th>Baked and Etched</th>
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</tr>
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<td>1073.8</td>
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<td>$\text{C}$ 1s</td>
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<tr>
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<td>104.4</td>
<td>103.8</td>
</tr>
<tr>
<td>$\text{Al}_{2p}$ (MgKα)</td>
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<tr>
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<td>1609.4</td>
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<td>1386.4</td>
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<td>989.6</td>
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<td>3452.8</td>
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<tr>
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<td>2949.2</td>
</tr>
<tr>
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<td>76.4</td>
</tr>
<tr>
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<td>1609.4</td>
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<tr>
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<td>2063.4</td>
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### Table 5.8 Na Y zeolite: apparent compositions

<table>
<thead>
<tr>
<th>$\text{SiO}_2/\text{Al}_2\text{O}_3$</th>
<th>2.47</th>
<th>3.08</th>
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<th>4.23</th>
<th>4.79</th>
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<td>11</td>
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<td>2</td>
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<td>69</td>
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<tr>
<td>Excess $\text{O}$</td>
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<td>31</td>
<td>32</td>
<td>28</td>
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</tbody>
</table>

### Table 5.9 Mg Y zeolite: apparent compositions

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<th>2.47</th>
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<th>3.65</th>
<th>4.23</th>
<th>4.79</th>
</tr>
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<tbody>
<tr>
<td>$\text{Si}$ 1s</td>
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<td>16</td>
<td>20</td>
<td>22</td>
</tr>
<tr>
<td>$\text{Al}$ 1s</td>
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<td>11</td>
<td>11</td>
<td>11</td>
<td>11</td>
</tr>
<tr>
<td>$\text{Na}$ 1s</td>
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<td>3</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>$\text{Mg}$ 1s</td>
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<td>4</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>$\text{O}$ 1s</td>
<td>66</td>
<td>64</td>
<td>69</td>
<td>65</td>
<td>65</td>
</tr>
<tr>
<td>Excess $\text{O}$</td>
<td>32</td>
<td>26</td>
<td>31</td>
<td>32</td>
<td>28</td>
</tr>
</tbody>
</table>
The effect on the Auger parameter values of these ion-exchange processes can be seen in Figure 5.18.

![Figure 5.18 The effect of cationic exchange on Auger parameter](image)

5.2.2 Discussion

An excess of oxygen is apparent for the Na Y zeolite from Table 5.8. This is calculated as the observed value minus twice the Si and Al atomic percentages present. In comparison with the bulk composition for an idealised structure the surfaces as received are depleted in Si (and to a lesser extent in Al) and enriched in Na and O. This was thought to be a reflection of the composition of the solution in the final stages of zeolite synthesis. On baking the spectrometer, the surface concentration of O appears to increase at the expense of Al. Following the Ar\(^{+}\) ion etching process the zeolite composition approaches the theoretical values as the excess oxygen is depleted (i.e. desorbed).
The Mg exchanged zeolites (Table 5.9) have a surface composition close to the theoretical value. Some 2% of Na remains following the exchange process. On baking there is a large increase in excess O which can be attributed to the sorption of CO and CO$_2$ as the zeolite cools in the spectrometer (the excess O and C follow each other closely). On etching this sorbed material is removed and the apparent composition returns to closely mirror the theoretical values.

On analysing the Auger parameter data, which are displayed as boxes in Figure 5.18, it can be seen that despite variations in data reproducibility the Na and Li forms appear to follow each other closely, while the Mg form displays a significant shift in a negative direction. This may be attributable to the larger electronegativity of the Mg atom which will have a greater electron-withdrawing influence on the O atoms, thereby decreasing the availability of valence electrons to relax into the Si and Al atoms on the production of a core hole.

5.224 Conclusions

1) The use of a OV flood gun accelerating potential may not effect complete control of surface charging on zeolite materials. Their sensitivity to water absorption is a contributary factor to poor reproducibility of data.

2) The use of fresh, baked and etched XPS analyses improves the hydration problem for these materials. Indeed, the Auger parameters for Si and Al are possibly sensitive to the sorbed species in the zeolite and to the charge-balancing cation. However, there are two major factors which need to be considered further, both of which could account for the quality of
a) The effect of argon ion bombardment of zeolite samples must be viewed with extreme caution, since results obtained are at best confused. In addition to the removal of sorbed species at the surface, the surface being analysed can be physically and chemically altered by such action, which is undesirable, and

b) Following the electron flood gun optimisation procedure (Chapter 4) a level of at least 6V accelerating potential was recommended for use. Whilst the effect of these electrons could be detrimental to sensitive materials such as zeolites, with electron stimulated desorption and related effects being possible, it nonetheless required investigation since the reproducibility of results obtained could be subsequently enhanced.

Thus a study of zeolite materials utilising higher levels of electron flood gun accelerating potentials was proposed.

5.23 A zeolite study using higher energy flood gun electrons

In this case metal exchanged ions from a similar group in the periodic table were selected, to reduce levels of uncertainty on comparisons of data. A series of experiments were devised to investigate fully the effect of higher energy electrons impinging on samples of Na Y (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> 2.47 and 3.08), Li Y (2.47 and 3.08) and Cs Y (2.47) zeolites, for ease of comparison of any effects induced.
5.2.3.1 Sample decomposition

Samples were ground in a pestle and mortar and pressed into indium foil before being introduced into the preparation chamber of the spectrometer. They were heated on the specimen holder to 100 °C for 16 hours, this hopefully reducing any CO or CO₂ type effects as experienced in the low energy study outlined in section 5.22.

Spectra were recorded in monochromatic Ag Lα radiation using an electron flood gun potential of 10V which will accurately control any surface charge. Each analysis was immediately followed by analysis in Mg Kα radiation to promptly record the apparent composition, and monitor any differences incurred. Examples of results for Na and Li samples are shown in Table 5.10.

<table>
<thead>
<tr>
<th>Zeolite Sample</th>
<th>Si</th>
<th>Al</th>
<th>Na</th>
<th>O</th>
<th>C</th>
<th>Comments</th>
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<td>7.6</td>
<td>6.5</td>
<td>8.6</td>
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<td>Sample damaged</td>
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<td>9.8</td>
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<td>13.4</td>
<td>38.1</td>
<td>30.4</td>
<td>Sample damaged during previous experiment</td>
</tr>
<tr>
<td>LiY 2.47</td>
<td>9.8</td>
<td>7.7</td>
<td>6.1</td>
<td>46.1</td>
<td>30.1</td>
<td>No change</td>
</tr>
<tr>
<td>LiY 3.08</td>
<td>11.0</td>
<td>7.5</td>
<td>4.4</td>
<td>46.4</td>
<td>30.4</td>
<td>No change</td>
</tr>
</tbody>
</table>

Table 5.10 Results for Na and Li exchanged samples

It was observable through the spectrometer view port that certain samples (most notably the Na Y 2.47) discoloured whilst being analysed. This colouration (pink - red - purple - black, with time, see Figure 5.19) was lost on exposure to air within 10-15 minutes. For confirmation
of this result, a single sample of Na Y (SiO$_2$/Al$_2$O$_3$ =2.47) zeolite was oven dried at 120°C for 15 days before analysis with XPS as follows:

a) Prior Mg Kα analysis,
b) Ag La analysis: 10V flood gun electrons used,
c) Immediate "post" Mg Kα analysis, and
d) Mg Kα analysis after 60 hours "recovery" time, the sample remaining within the UHV system.

<table>
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<th>O</th>
<th>C</th>
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<td>13.2</td>
<td>50.3</td>
<td>16.9</td>
</tr>
<tr>
<td>After</td>
<td>8.2</td>
<td>6.4</td>
<td>25.1</td>
<td>41.2</td>
<td>17.7</td>
</tr>
<tr>
<td>60 hr. delay</td>
<td>9.1</td>
<td>6.6</td>
<td>21.7</td>
<td>41.1</td>
<td>19.7</td>
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</table>

Table 5.11 Analysis of Na Y 2.47 zeolite

Figure 5.19 Sample discolouration effects
The sample damaged as before, with a significant increase in sodium content being recorded between Mg Kα analyses. This is shown in Table 5.11 and Figure 5.20. The Al 2p peak at approximately 74eV can be seen in these spectra together with the Na 2s at 66eV. The changes in relative intensity and area show the increase in apparent Na content at the surface. Figure 5.21 is obtained following the subtraction of the height normalised spectra of Figure 5.20, and emphasises the presence of metallic sodium at 63.5eV. These results suggest that the sodium cations in the sample are being reduced to the metallic state and are also moving to the sample surface. Due to the clear chemical shift available from the photoelectron lines, occurring for the Na 2s with respect to the Al 2p, it was not considered necessary to apply the Auger parameter measurement in this instance.

Exposure to air re-oxidised the sodium metal to its cation state, with loss of colour resulting. This apparent instability of sodium is consistent with its position in the Ellingham oxidation/decomposition charts, i.e. it is less stable than Li (see Figure 5.22).

5.232 Decomposition dependence on time and energy

This apparent decomposition was investigated for dependence on time and energy of neutralising electrons. Na Y (2.47) and Li Y (3.08) samples were selected for more rigorous exposure. Both had been dried in an oven at 120°C for 15 days. Each sample was exposed to half hour regimes of flood gun potential from 0 to 10V at 2V increments, as shown in Table 5.12. The Li Y sample shows greater stability than the Na Y sample, which began to deteriorate after 20 mins at 8V (this being equivalent to a total exposure of 2 hours and 20 minutes).
Figure 5.20 Spectra obtainable for Na Y 2.47 zeolite

Figure 5.21 Subtraction of spectra
Figure 5.22 Ellingham diagram showing relative stabilities of oxides

Table 5.12 Stability of Na Y and Li Y samples
### Table 5.13 Results for Na Y zeolite: fresh (top) and dried (bottom) conditions

<table>
<thead>
<tr>
<th>Flood Gun Bias (V)</th>
<th>Peak Position (eV)</th>
<th>Peak Position (eV)</th>
<th>Peak Position (eV)</th>
<th>Peak Width (eV)</th>
<th>Apparent Composition At.% (MgKa)</th>
<th>Comments</th>
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</thead>
<tbody>
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<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>$A'$</td>
<td>$A'$</td>
<td>$01s$</td>
<td>$A'$</td>
<td>$S1s$</td>
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<td>-</td>
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<td>-</td>
</tr>
<tr>
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<td>1561.5</td>
<td>1385.8</td>
<td>2947.3</td>
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<td>*</td>
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<tr>
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<td>1692.1</td>
<td>1585.9</td>
<td>*</td>
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<td>2947.4</td>
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<td></td>
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<td></td>
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<td>1394.2</td>
<td>2947.1</td>
<td>521.7</td>
</tr>
</tbody>
</table>

* Lack of data due to computer problem.
For the determination of conditions under which reliable results might be obtainable, Na, Li and Cs samples of SiO$_2$/Al$_2$O$_3$ ratio 2.47 were dried for 1 week and in excess of one month respectively at 120 °C. These samples have been termed "fresh" and "dried" respectively.

To avoid damage when analysis of adjacent samples is in progress, which occurred in some experiments due to the large area illuminated by the flood gun electron beam (an ellipse of proportion 15 x 10mm), only one sample was mounted onto a specimen holder each time.

The experimental procedure involved the following steps:

1) Sample analysed in Mg K$_α$ radiation .......... at% recorded
2) ...... ...... Ag L$_α$ ...... ...... 0V flood gun
3) ...... ...... Mg K$_α$ ...... ...... at% recorded
4) ...... ...... Ag L$_α$ ...... ...... 2V flood gun
5) ...... ...... Mg K$_α$ ...... ...... at% recorded
6) ...... ...... Ag L$_α$ ...... ...... 4V flood gun
7) ...... ...... Mg K$_α$ ...... ...... at% recorded
8) ...... ...... Ag L$_α$ ...... ...... 6V flood gun
9) ...... ...... Mg K$_α$ ...... ...... at% recorded
10) ...... ...... Ag L$_α$ ...... ...... 8V flood gun
11) ...... ...... Mg K$_α$ ...... ...... at% recorded
12) ...... ...... Ag L$_α$ ...... ...... 10V flood gun
13) ...... ...... Mg K$_α$ ...... ...... at% recorded
This constituted seven days of spectrometer operation in total. Initially, samples were allowed to sit within the instrument over weekend periods, when no analyses were recorded, but this proved to be unsatisfactory since samples tended to "recover" from any physical and chemical changes during that time (as shown in Figure 5.23). Later experiments were run continuously.

The results of this study can be seen in Tables 5.13 to 5.15 and Figure 5.23. As noted previously, the function of an electron flood gun involves the accurate control of any surface charging effects present, these being shown as peak shift or peak broadening effects. From Figure 5.23 for the Na Y 2.47 sample a failure to execute this process occurs both in its fresh and dried conditions, with FWHM values for the Si 1s peak generally worsening once a certain level of potential is applied (>4V). However, for the Li and Cs Y samples this trend is not repeated, and some reductions in FWHM values are recorded.

It was shown for the case of NaCl in Chapter 4 (section 4.253) that the effects of non-uniformity in surface charging can be determined by plotting individual peak positions versus the level of flood gun potential, the separations between different lines hopefully remaining invariant. Such plots for the NaY zeolites are shown in Figures 5.24 and 5.25. Whilst some of these lines remain parallel, others tend to deviate, indicating some non-uniformity in charging (possibly due to changes in the sample surface chemistry). The degree of sample dryness appears to be a critical factor in this instance. This would suggest that correlation of the modified Auger parameters for Si and Al would be unlikely to give useful information.
<table>
<thead>
<tr>
<th>Flood Gun Bias (V)</th>
<th>Peak Position (eV)</th>
<th>A'</th>
<th>Peak Position (eV)</th>
<th>A'</th>
<th>Peak Position (eV)</th>
<th>A'</th>
<th>Peak Width (eV)</th>
<th>Apparent Composition At.% (MgKa)</th>
<th>Comments</th>
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<tr>
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<td>S1KL</td>
<td>S1s</td>
<td>S1KL</td>
<td>S1s</td>
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<td>525.1</td>
<td>3.0</td>
<td>3.0</td>
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<td>3452.1</td>
<td>1550.1</td>
<td>1396.8</td>
<td>2946.9</td>
<td>520.3</td>
<td>2.9</td>
<td>2.8</td>
</tr>
</tbody>
</table>

Table 5.14 Results for Li Y zeolite: fresh (top) and dried (bottom) conditions
Figure 5.26 shows such plots of the modified Auger parameter for Si and Al (flood gun potentials 10V and 6V respectively), and compares them with the original data (from the low energy electron study in section 5.22) which in this case involved a 0V level. On viewing the graphs for 6 and 10V levels it is evident that the Si Auger parameter shifts for dried Cs and Li Y zeolites are consistent with expectation, i.e. Auger

Table 5.15 Results for Cs Y zeolite: fresh (top) and dried (bottom) conditions
Figure 5.23 Variation of resolution (Si 1s) with flood gun accelerating potential (---- = dried, ------- = fresh)
parameter increasing with polarisability. However, it is disappointing that the shifts involved are extremely small, averaging 0.4 eV which is equivalent to the error boundary for the measurements themselves (since individual peaks can only be quoted to a ±0.1-0.2 eV accuracy). Conversely, the Al Auger parameter reveals a different trend by increasing from Cs to Li for the dried samples. This would imply an
opposite interpretation from that for the Si Auger parameter shifts, which confuses the situation.

Figure 5.26 Modified Auger parameter plot for 10, 6 and OV flood gun accelerating potential
5.24 Discussion

By their very nature, zeolites are extremely complex materials to analyse spectroscopically using monochromatic Ag L\textsubscript{α} radiation in the ESCA3 MkII spectrometer, since their insulating nature and the analyser field breakthrough effects necessitate the use of an electron flood gun whose product (i.e. electrons) ultimately effects the sample surface such that differences existing between different samples are obscured by detrimental effects induced. The extreme sensitivity of these samples to water content is another restricting factor.

The confidence in Auger parameter shifts obtained in these studies is less than satisfactory. This is due to the high reactivity and instability of the zeolite materials themselves, rather than any failings of the XPS analysis technique used. The calculation of individual relaxation energies, which could reflect the changes in species polarisability very accurately, would not aid the situation since the cross-section of the Si 2p is sufficiently low to lead to excessively long acquisition periods and thus further sample problems and resultant inaccuracies.

Nevertheless, the results from the study using higher energy electrons are of interest. The variation of the FWHM values for the Si 1s in Na Y and Li Y zeolites respectively is an example. The Li Y zeolite appears to be more stable than the Na Y sample, whose FWHM values increase by more than 4eV on increasing the flood gun accelerating potential from 0V to 10V. For a conducting sample the effect of any variation would be minimal, and the characteristic peak positions would remain constant with applied voltage. Conversely, for an insulating
sample the effect of any increase would be to shift the characteristic peak positions by an equivalent amount to the change in applied voltage. From Table 5.13 it can be seen that the FWHM value for the Na Y sample increases to a level of 6.8 when a 10V accelerating potential is applied, to produce a spectrum as shown in Figure 5.20. Thus a level of conductivity is being induced into the sample. This is evident at the surface through the reduction of $\text{Na}^+$ to Na metal, but is also a depth effect since a conducting pathway must be present between the sample and the spectrometer, to enable the conducting characteristic to be recorded. Whilst the zeolite is mounted onto indium foil (a conductor) it is present as a compressed cake, of thickness more than one particle, such that a pathway needs to exist through this medium.

Thus the reduction of the $\text{Na}^+$ cations in the structure to Na metal occurs concurrently with the sodium content increasing at the surface, the mobile ions diffusing towards the surface prior to their reduction. This action could be induced by the thermal energy generated via the electron flood gun which can effect sensitive materials such as polymers, and is equivalent to the solid state electrochemical reduction of sodium ions to the metallic state. Since such reduction is not possible in wet electrochemistry, this could be an important result. In the electrochemical series, the reaction:

$$\text{Na}^+ + e^- \rightarrow \text{Na} \quad \ldots \ldots \text{5.7}$$

requires a potential of -2.71V with respect to that for the Standard Hydrogen Electrode.
The apparent presence of such a strong reducing agent could be of interest for:

a) the use of fluidised beds, where the bombardment of a sample with electrons might induce a desirable level of conductivity into a structure to improve its characteristics,
b) the reduction of methane, and
c) the reduction of an acid to an alcohol,
each being of interest to the petrochemical industry.

5.25 Conclusions

1) The use of higher energy flood gun electrons for the charge neutralisation of zeolite materials produces unsatisfactory results, since some structures appear to be chemically and/or physically damaged. Such changes render the use of Auger parameters useless.

2) The electron flux appears to damage samples due to the energy of the incident electrons alone rather than through a cumulative effect. This is apparent since on the analysis of an Na Y sample at less than 6 volts for lengthy periods of time, no visual damage effects are induced, whilst an increase to a higher level of accelerating potential (such as 8 or 10V) leads to such damage in a relatively short time. Thus the changes in structure induced appear to be induced by a certain energy input to the system.
3) The chemical changes induced, predominantly in Na Y zeolites, involve the reduction of the Na\(^+\) cations to the metallic state, apparently following their diffusion from the bulk to the surface. The energy for this process appears to be provided by the flood gun electrons themselves.

4) The inducement of such a reaction indicates this to be an excellent reducing agent, for which application in the petrochemical industry could be wide.

5) In comparison to zeolites, which are hydrophilic due to the interaction of the dipole of the water molecules with the electrostatic fields of the anionic aluminosilicate framework and the balancing non-framework cations, aluminophosphates possess neutral frameworks and are only moderately hydrophilic due to the difference between the aluminium (1.5) and phosphorus (2.1) electronegativity values. Thus their affinity for water is lower, which should reduce any hydration problems as experienced in this study. A study of the role of phosphorus is within the capability of the monochromatic Ag La x-rays, the 1s core level being available, such that it could play an important part in the understanding of this new family of materials.
5.3 A Contact Lens Material Study

Although the monochromatisation of the Ag $L_\alpha$ x-rays leads to a severe decrease in count rate available due to a lower x-ray flux level, it also results in a lower level of electrons generated on x-ray impingement with the Al window. This can be of benefit for the XPS analysis of more sensitive materials such as polymers where, when combined with data from conventional sources, a non-destructive XPS depth profile can be obtained. However, it must be confirmed that the stability of the sample in question is sufficient to withstand the more substantial electron flux originating from the electron flood gun, particularly in the case of the ESCA3 spectrometer since the field penetration effect discussed in Chapter 4 makes the use of higher energy flooding electrons advisable.

Silicon finds itself playing an increasingly important role in the field of polymeric studies. One such example involves the role of siloxane groups present in gas permeable contact lens materials available today.

5.3.1 Background

It was during the 1940s that polymethylmethacrylate (PMMA) replaced glass as a material for contact lens manufacturing use. The attractiveness of PMMA, which remains today, was due to its:
1) refractive index, 
2) hardness, and 
3) biocompatibility.

However, PMMA is known to be poorly permeable to gases which inhibits the cornea-tear film gaseous exchange necessary for wettability and comfortable contact lens use. Thus over recent years gas permeable hard (GPH) contact lens materials have been introduced. These are normally copolymers consisting of:

a) a hydrophilic or hydrophobic alkyl acrylate, 
b) a siloxanyl alkyl acrylate monomer, and 
c) cross-linking agent additives.

The presence of organosiloxane pendent groups, which possess low intermolecular forces and a high degree of rotational freedom, leads to improved gas permeability to allow prolonged periods of lens wear. However, they also encourage poor lens wetting due to their inherent hydrophobicity.

Thus the wettability of the material needs to be improved, i.e. the hydrophilic/hydrophobic balance must be increased. One method of achieving this is to employ a plasma discharge treatment, where a stream of oxygen plasma is directed towards the sample in an attempt to modify its surface properties. This not only improves the surface wettability, but also retains the desirable bulk properties such as high gas permeability.
5.32 Experimental

Buttons of the proprietary contact lens copolymer material (code name BX3) were formed, of size 13mm diameter and 4mm thickness. These were then RF treated in a plasma asher using power levels of between 10 and 100W for time periods in the range 0-160 seconds.

The XPS analysis involved untreated and treated samples using three x-ray sources; Mg Kα, Al Kα and monochromatic Ag Lα. The electron flood gun accelerating potential used for the latter case was 8V, this being sufficiently high to overcome any effects outlined by the flood gun optimisation procedure (Chapter 4) but not high enough to induce any detrimental effects in the polymeric samples themselves, following an initial study. Other experimental conditions were similar to those described for the thermal oxide on silicon study (section 5.12).

5.33 Results and discussion

Table 5.16 shows the variation of carbon, oxygen and silicon over various treatment times and two power loadings (10W and 100W), this data being obtained by the use of Al Kα radiation. The general observations from this data were that a reduction of C occurred with treatment time, with both O and Si being increased. The use of a higher power loading appeared to increase the effect.

On deconvolution of the C 1s narrow scan spectra, both the C=O and the C-O functionalities increase with respect to the C-H, as shown in Figures 5.27 and 5.28, which are for before and after the plasma treatment process (the treatment condition being 10W for 80 seconds).
<table>
<thead>
<tr>
<th>Treatment time (s)</th>
<th>Carbon 10W</th>
<th>Carbon 100W</th>
<th>Oxygen 10W</th>
<th>Oxygen 100W</th>
<th>Silicon 10W</th>
<th>Silicon 100W</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>68.8</td>
<td>68.8</td>
<td>26.7</td>
<td>26.7</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>10</td>
<td>54.6</td>
<td>48.3</td>
<td>39.8</td>
<td>43.3</td>
<td>5.3</td>
<td>7.8</td>
</tr>
<tr>
<td>40</td>
<td>49.1</td>
<td>37.8</td>
<td>43.0</td>
<td>50.0</td>
<td>7.4</td>
<td>11.1</td>
</tr>
<tr>
<td>160</td>
<td>40.2</td>
<td>20.6</td>
<td>50.0</td>
<td>61.7</td>
<td>9.2</td>
<td>17.4</td>
</tr>
</tbody>
</table>

Table 5.16 Al Kα results

Similarly for the Si 2p narrow scan spectra, a gradual change occurs in the chemical environment of the silicon atoms with treatment from the organic polysiloxane component to an inorganic silica-like species, as shown in Figures 5.29 and 5.30 which are again for before and after the plasma treatment process. In this case the treatment condition was 10W for 320 seconds. Thus the replacement of Si–C groups by Si–O groups occurs with degree of treatment, the oxygen plasma altering the chemical environment of the silicon atom substantially. The silicones of the polysiloxane groups originally present are not removed from the surface, but become enhanced in oxygen due to the formation of a silica-like species.

Table 5.17 shows the variation of carbon, oxygen, nitrogen and silicon elemental compositions for untreated and treated (power loading 100W) samples using the three different x-ray sources. On comparison of this data it is clear that near surface concentration gradients exist, since the untreated sample shows 65.3% C in Mg Kα, 64.3% C in Al Kα and 72.7% C in monochromatic Ag La. It is evident that the extra penetrating
Figure 5.27 C 1s peak prior to plasma treatment

Figure 5.28 C 1s peak following plasma treatment
**Figure 5.29** Si 2p peak prior to plasma treatment

**Figure 5.30** Si 2p peak following plasma treatment
depth of the Ag Lα x-rays is probing nearer to the bulk composition than the conventional x-rays.

<table>
<thead>
<tr>
<th>X-ray source</th>
<th>C</th>
<th>O</th>
<th>N</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>U</td>
<td>T</td>
<td>U</td>
<td>T</td>
</tr>
<tr>
<td>Mg</td>
<td>65.3</td>
<td>20.2</td>
<td>27.1</td>
<td>58.9</td>
</tr>
<tr>
<td>Al</td>
<td>64.3</td>
<td>21.2</td>
<td>29.0</td>
<td>60.3</td>
</tr>
<tr>
<td>Ag</td>
<td>72.7</td>
<td>41.4</td>
<td>20.6</td>
<td>39.2</td>
</tr>
</tbody>
</table>

100W 160s calculated using Si 1s; sampling depth ≈ Si 2p in MgKα

Table 5.17 Results for the x-radiations used

The non-destructive depth-profiling capability using this range of photon sources can be seen in Table 5.18. The sampling depths, taken as $3\lambda$ ($\lambda$ = inelastic mean free path), have been calculated using the formalism of Seah and Dench (165). It is interesting to note that the sampling depth of the Si 2p in Mg Kα is approximately equal to that for the Si 1s in monochromatic Ag Lα (since their respective kinetic energies are approximately 1154eV and 1153eV). Thus it is pleasing that the atomic percentages derived for these separate analyses are very similar, being 6.1%Si for the untreated and 20.1%Si for the treated sample in Mg Kα and 6.7%Si for the untreated and 19.4%Si for the treated sample in monochromatic Ag Lα radiation. These results support the accuracy of the sensitivity factors measured experimentally for the latter x-ray source (see Chapter 3), and will hopefully encourage their reliable use in the future, when quantitative XPS is to be carried out using this novel source.
X-ray energy (eV) | Photoelectron sampling depth (nm)  
---|---
| Si2p | Cls | O1s | Si(1s) |
1253.6 | 7.9 | 7.2 | 6.2 | - |
1486.6 | 8.7 | 8.1 | 7.2 | - |
2984.3 | 12.5 | 12.1 | 11.5 | 7.6 |

Table 5.18 Sampling depths for the x-radiations used.

Figure 5.31 Variation of C/Si ratio with treatment time

The data for the 10W RF treatment is presented graphically in Figure 5.31. The C/Si ratio for Al Kα use increases with treatment time indicating the surface enhancement of silicon. This is confirmed by the offset shown by the Mg Kα results, the more sensitive surface analysis consistently recording a lower C/Si value. If energy is considered as
the product of the level of power and treatment time it is possible to produce a universal curve for all power and treatment times. The data for the C/O and C/Si ratios are shown in this form in Figure 5.32, where a logarithmic relationship appears to apply.

Figure 5.32 Plots of C/O and C/Si ratios versus log energy

The XPS results quoted here have been supported by both contact angle measurements, microscopy and SIMS studies, and is currently in the process of being compiled(165)
5.34 Conclusions

This study has shown that, at the chemical level, plasma-discharge treatment of the contact lens copolymer BX₃ material results in a surface grossly depleted in carbon but enriched with silicon and oxygen atoms. The oxygen appears to displace carbon from the surface but remains chemically bonded to that component remaining. The extent of this interaction, seen through the increase in C=O and C=O functionalities, varies with the energy level of plasma treatment. The silicon from the polysiloxane is not displaced from the surface on treatment. However, there is evidence of additional oxygenation of the silicon bearing molecules.

The consistency in XPS analyses obtained, together with later microscopy work, indicated that the copolymer samples remained unaltered by flood gun electrons when monochromatic Ag Lα radiation was applied. The results gained in this study are important since they:

a) demonstrate that sensitive materials can be successfully analysed quantitatively using monochromatic Ag Lα x-rays, and 
b) demonstrate that this x-ray source can be applied with conventional x-ray sources to generate a reliable non-destructive depth-profile of sensitive materials without changing the physical or chemical structure, as would be the case on ion etching.
5.4 Conclusions

1) The monochromatic Ag Lα x-ray source has been successfully applied to the studies of silicon chemistry by use of its ability to generate Auger parameter and extra-atomic relaxation energy information, and also its extra penetrating nature for the attainment of non-destructive depth-profiles, when combined with data from conventional x-ray sources.

2) XPS was shown to be more appropriate than ellipsometry for the characterisation of very thin films (<10nm). The calculation of individual extra-atomic relaxation energy values together with the independent measurement of oxide refractive index is a promising analytical combination for the measurement of strain induced on thermal contraction following device processing.

3) The analysis of zeolite materials proved difficult, due to the sensitivity of these materials, particularly with regard to water, CO and CO₂ absorption. On the use of less severe neutralisation conditions, these being below those recommended for use in Chapter 4, some relative differences for cation-exchanged zeolites could be found, but the degree of reproducibility obtained was poor due to insufficient charge control. However, on gaining control of non-uniformities in surface charging by use of the optimised electron flood gun parameters as discussed in Chapter 4, the samples proved sufficiently unstable to physically and chemically change on analysis. This rendered the use of Auger parameters useless.
4) The changes induced in samples involved the diffusion of mobile Na\(^+\) ions to the surface, followed by their solid state electrochemical reduction to Na metal, which produced a change in colour. This effect was reversible on exposure to air. The presence of such a strong reducing agent could be of interest to the petrochemical industry.

5) For the successful optimisation of monochromatic Ag L\(_\alpha\) x-rays to zeolite-type materials within the ESCA3 spectrometer system, greater stability of structure under electron bombardment is required. This could involve a study of aluminophosphate materials.

6) The application of monochromatic Ag L\(_\alpha\) to polymer systems is promising. The x-ray flux excites a sufficiently small number of secondary electrons from the aluminium window to cause little, if any, change in surface composition with analysis time. The sensitivity factors for elements such as nitrogen, carbon and oxygen in this radiation are respectable when compared to those for conventional XPS sources, whilst the extra penetrating nature can yield both useful depth information within a sample and excite new 1s core level peaks for elements involved in polymeric systems. The possibility of non-destructive depth-profiling using monochromatic Ag L\(_\alpha\) with conventional XPS sources is useful, since near surface concentration gradients can be measured for sensitive materials without physically changing their structure, which is a facility less available when utilising conventional sources in isolation.
Since the energy of the monochromatic Ag L\alpha x-ray source is higher than that for conventional sources, any new photoelectron lines generated possess no reference values in the literature with which to compare. Thus a method for the accurate determination of individual peak positions is required. It has been shown in Chapter 4 that the successful optimisation of the electron flood gun counteracts the effects of differential charging and non-uniformities in surface charging which can hinder experimental accuracy. However, this does not produce binding energy values of electrons referenced to a particular energy level for insulators, whereas for conductors all measurements are relative to the spectrometer Fermi level. Thus an internal energy referencing technique is required, utilising a standard material peak for calibration purposes.
Chapter 6. Internal Referencing

6.1 Previous Work

The successful application of XPS for the analysis of insulators can involve both the use of an electron flood gun and an internal referencing technique. This has been found to be the case when Auger parameters are obtained with the assistance of an electron flood gun and when secondary features of a peak are analysed, as exemplified by the catalysis work of Barr.\(^{166}\)

A potentially useful internal referencing method has been investigated by Stephenson and Binkowski.\(^{167}\) They conducted a theoretical and experimental XPS study of silica which involved a unique method for apparently "pinning" the Fermi levels of insulators to those of a metal calibrant and thus measuring absolute binding energies for the electronic levels in wide band-gap insulators.

Previous studies of clean silica surfaces using deposited gold as a reference had yielded errors of 1.5eV for the Si 2p line, since no electronic equilibrium existed between the two Fermi levels, there being no allowed states below the insulator's conduction band into which conduction electrons from the metal could tunnel. However, Stephenson and Binkowski speculated that the forcing of an electronic equilibration across the metal-insulator junction, by "pinning" the Fermi levels to a common value, could permit the absolute energy calibration of any insulator with respect to the Fermi level of a metal. By addition of the work function of the metal, a binding energy value with respect to the vacuum level is derived, the vacuum level defining the energy at which an
electron sits on being excited into vacuum. For insulating materials, this is the accepted level to which peak positions can conventionally be referenced, since the Fermi levels for such materials are difficult to define.

The philosophy envisaged by Stephenson and Binkowski for this "biased referencing" technique can be seen in Figure 6.1, and consists of two parts: a) conduction needs to be established in the insulator to ensure uniformity of energy levels throughout its surface. The metal electrons cannot enter the insulator conduction band due to the presence of the metal-insulator energy barrier. Thus some source of energy is required to overcome this barrier, and is provided in their study by the exciting x-radiation itself (monochromatic Al Kα x-rays being used) through the generation of a large number of low energy secondary electrons within the sample which are capable of being internally injected into the insulator conduction band, and b) the energy levels of the insulator need to be aligned with a well defined level in the metal. Following the legend of Figure 6.1a, a typical energy-level diagram for a metal-insulator junction would appear as in Figure 6.1b. On the build-up of charge at the specimen surface, "band bending" of the valence and conduction bands will occur since insulators and semiconductors can support an internal electric field, whereas metals cannot. Figure 6.1c represents such bending when an electron flood gun is used to introduce electrons of sufficient energy to overcome the surface potential present, these bending towards lower potential energy.
Figure 6.1 Stephenson and Binkowski energy level diagrams

For the attainment of exact Fermi level equilibration, it is proposed that the insulator bands need to be bent by an amount equal to the work function difference between the metal and insulator, which also requires a lowering of the metal Fermi level by the same work function difference, this involving virtual transfer of electrons from the metal to the insulator.

On increasing the energy of the impinging flood gun electrons, it is thought that the metal Fermi level is lowered by the corresponding amount of induced insulator band bending until the work function difference can be supported by the space charge near the insulator surface, as shown in Figure 6.1d. The energy required to obtain this condition is difficult to determine, since the metal-insulator contact potential difference will vary with insulator type and surface cleanliness conditions. Thus to "guarantee" that Fermi levels are aligned, the flood gun voltage (or
bias) is driven to a high value. This is depicted in Figure 6.1e. Since the insulator is assumed intrinsic, its Fermi level will bend in exact accordance with the additional level of band bending induced by the bias level.

On measuring the kinetic energies from an artificial level obtained by adding the work function of the metal to its apparent Fermi level under high negative bias, one obtains the same values as would be obtained under zero bias (Figure 6.1b). This shown in Figure 6.1f. This implies that the Fermi levels are "pinned", and according to Stephenson and Binkowski permits the ready determination of binding energies in insulators.

It was found that the surface potential oscillated by approximately \( \pm 0.2 \text{eV} \) during the time of analysis, which was attributed to instabilities in the x-ray flux and/or flood gun electron flux. This must be regarded as an additional contribution to the instrumental broadening function, \( W_{\text{Sp}} \), as discussed in Chapter 1 (Section 1.2).

An investigation of the biased referencing technique was made by Landis and Martin\(^{168}\), who used it for biological mineral standards for the identification of chemical species associated with a calcified bone matrix. The technique of biased referencing as interpreted by these authors is shown schematically in Figure 6.2.

Following Stephenson and Binkowski, it is assumed that the insulating sample possesses a wide band gap and is absent of any surface states. They argue that virtual transfer of electrons from the flood gun is unnecessary to establish Fermi level alignment, since the rectifying
Figure 6.2 Landis and Martin energy level diagrams

contact allows Fermi level equalisation between gold and the insulator under non-excited conditions (Figure 6.2b). On analysis with XPS, a process of surface charge build-up occurs, and all levels rise (Figure 6.2c). Reference of insulator levels to corrected values of the metal levels now gives vacuum level alignment, as shown in Figure 6.2c. This according to Landis and Martin is the normal means of charge correction. It compares with the proposal of Stephenson and Binkowski for Fermi level alignment as shown in Figure 6.1e. Attempts to utilise the situation given in Figure 6.2c have problems since photoelectron cross sections,
electron mean free paths and other factors that can effect the electron yield are different for the insulator and the Au dot, and thus a potential difference will result around the decorated area. This "double potential" is shown by dotted lines in Figure 6.2c. Landis and Martin therefore successfully employed the use of biased referencing for biological materials, without space-charge problems, but in accord with Figure 6.2d assumed Fermi level alignment.

A major contribution has also been made by Lewis and Kelly, whose work involved Al and Au evaporated onto silica. They showed how the surface potential is dependent upon the flux and energy of incident electrons and on the resistance between the sample and the spectrometer over a wide range, and how the surface potential of a sample can be fixed to a known value by completely insulating the sample from the spectrometer and compensating for the residual positive charge solely with the use of low energy electrons. However, the use of a conducting material in contact with an insulating sample for binding energy referencing with respect to the Fermi level was open to question in their opinion, since good contact cannot be presumed or experimentally verified. They maintained that for conducting samples the reference position was the Fermi level whilst that for insulating samples would be the vacuum level.

Whilst each of these contributions had outlined the potential usefulness for the biased referencing method in the analysis of aluminosilicate materials, its practical suitability for use in the ESCA-MkII needed verification. This instrument operates without a lens which in other instruments shields the specimen from the field arising from the retarding potential, which in the case of Ag Lα can sometimes be very
high. Thus an investigation was planned to determine experimental accuracy and reproducibility of data when using the biased referencing technique.

6.2 The Application Of Biased Referencing

To establish a full background to the energy referencing issue, several points need to be considered before experimental procedures can be developed and investigated.

6.21 The electron flood gun bias

One such factor involves an understanding of the effect of the flood gun accelerating potential (or bias). The primary purpose of an electron flood gun is to neutralise the build-up of surface charge created by the loss of photoelectrons during an XPS experiment. It is relatively easy to imagine that on a specimen becoming positively charged (e.g. following photoemission), oppositely-charged electrons will be attracted towards the specimen to cause neutralisation of this charge. However, as has been highlighted by Hunt et al\(^{(119)}\), electron flood gun operation does not work quite so simply.

With reference to Figure 6.3, consider a flood gun biased at a voltage \(-V_f\). This determines that electrons will leave the filament with energy:
Figure 6.3 The operation and function of the electron flood gun

\[ e(\phi_f - V_f) \] ....... 6.1

relative to ground, where:

\( \phi_f \) = the work function of the filament.

The electrons so produced can subsequently arrive at the specimen providing that the specimen surface potential \( \phi_e \) is less than \( \phi_f - V_f \). Therefore, the surface potential of the specimen \( \phi_e \) would rise to:

\[ \phi_e = (\phi_f - V_f) \] ....... 6.2

as long as the flood gun can provide a current at least equal to the photo-current. (This is strictly only true for a flood gun mounted normally to the specimen surface; for other angles the surface
potential is related to the normal component of the beam energy).

The Fermi level of the specimen is at a lower potential than the surface, and thus the potential of the Fermi level relative to ground is:

\[-V_s = -V_f + (\phi_s + \phi_f)\]  

..... 6.3

where:

\(\phi_s\) is the work function of the specimen.

It is interesting to consider that even when the electron flood gun bias is set to 0V, the specimen surface potential, \(\phi_e\), and its Fermi level may each exist at some finite voltage relative to ground, due to the effects of work function differences. Of course, in the majority of situations there will be several sources of currents toward and away from the specimen, which will play a role in the determination of the specimen surface potential. These include the photoelectrons emitted from the sample and electrons originating from x-ray source windows, ion gauges and other filaments present in the vacuum system. Changes in the flow of electrons into the spectrometer may subsequently also influence the specimen. The use of the electron flood gun enables the surface potential (or local vacuum level) of an isolated specimen to be defined, assuming that the possible current from the flood gun towards the specimen exceeds all other possible currents, and no other higher energy electrons are present in a large enough number to cause the surface potential to be driven more negative than that instigated by the potential of the flood gun itself.
6.22 Experimental

As a preliminary investigation of the potential usefulness of the combined experimental technique involving the use of the electron flood gun and an internal referencing method such as biased referencing, gold was selected as the standard reference material, since its 4f⁷/₂ photoelectron peak position at 84.0eV is universally accepted and a reliable point from which to compare data for insulators.

Initial experiments involved the simple vacuum evaporation of a single Au dot, approximately 3mm in diameter, onto samples. The procedure for metal deposition was as follows:

a) prepare substrate material (abrade, degrease etc.) to give fresh surface,
b) prepare mask (Al plate with 0.3mm holes drilled),
c) accurately place the mask over the intended area for deposition on the sample,
d) place specimen and mask within SEM/TEM sample preparation coating unit,
e) evacuate coating chamber,
f) evaporate/sputter metallic reference,
g) remove from coating unit, remove mask, and place in electron spectrometer, and
h) analyse with XPS.
Following the successful optimisation of the electron flood gun (Chapter 4), the emission current level was held constant at 0.3 mA throughout each experiment, with only the bias being changed.

The conditions for XPS analysis were as follows:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of channels</td>
<td>125</td>
</tr>
<tr>
<td>Channel width</td>
<td>0.2 eV</td>
</tr>
<tr>
<td>Total time in each channel</td>
<td>&gt;2 mins</td>
</tr>
<tr>
<td>Analyser energy</td>
<td>50 eV</td>
</tr>
<tr>
<td>Analyser slit widths</td>
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</tr>
<tr>
<td>Electron take-off angle</td>
<td>45°</td>
</tr>
<tr>
<td>X-ray anode settings</td>
<td>14 KV, 40 mA = 560 W</td>
</tr>
<tr>
<td>Spectrometer vacuum</td>
<td>1 - 3 x 10^-9 mbar</td>
</tr>
<tr>
<td>Electron flood gun settings</td>
<td>0 - 14 V, 0.3 mA</td>
</tr>
</tbody>
</table>
6.23 Results

6.23.1 Au dot on copper

One experiment involved the evaporation of a gold dot (≈3mm diameter) onto a freshly ion-cleaned copper substrate. This was then mounted onto insulating tape, causing the specimen to be completely isolated electrically from the spectrometer. The results for this experiment are shown in Table 6.1, from which the Cu 2p3/2 peak position, when referenced to the Au 4f7/2 peak, is generally constant over the 0-10V bias range used for the electron flood gun. Similarly, the Au 3d5/2-Au 4f7/2 peak separation is also fairly constant, as would be expected since non-uniformities of charging should be minimal. Typical errors in the measurement of individual peak positions are ±0.1-0.2eV, and thus for peak separations this error will be increased to ±0.2-0.4eV.

6.23.2 Au dot on SiO₂

To compare "insulated conductor" and "insulator" type behaviour, a Au dot was deposited onto a SiO₂ substrate (vitreosil, derived from quartz crystal). The results of this investigation are shown in Table 6.2. The FWHM for the Si 1s peak is improved on increasing the bias level from 0 to 14V. The Auger parameter \( A^{1}(1s + KLL) \) and \( A^{II}(2p + KLL) \) values appear to stabilise at 10V bias and above, as does the Si 1s when referenced to the Au 4f7/2. The 0V and 2V settings are clearly unsatisfactory, even for a relatively uncomplicated insulating specimen such as vitreosil. This agrees with the conclusions of Chapter 4 following the flood gun optimisation procedure. The variation in measured peak position and parameter can be seen in Figures 6.4 and 6.5,
Table 6.1 Results for Au dot on copper
with a 10V bias level producing peak constancy across a wide energy range. These results tend to support previously-outlined theories, since regions of rapid change exist before the onset of a plateauing effect. Thus the binding energies of the silicon and gold photoelectron peaks are following each other, and can apparently be referenced to the same energy level, this possibly being the Fermi level.

The differences apparent in the Au $3d_{5/2}$ and Au $4f_{7/2}$ peak energies as a function of potential shows that the surface charge on the specimen is changing with electron kinetic energy during XPS measurement when using low flood gun bias levels. This is probably due to the problem outlined in Chapter 4, due to the penetration of stray fields originating from the analyser entrance grids into the vacuum space.
Table 6.2 Results for Au dot on SiO₂

<table>
<thead>
<tr>
<th>Flood Gun Bias (V)</th>
<th>S11s</th>
<th>S1KL</th>
<th>S1zp</th>
<th>$\Delta S_1^1$ (1s+KLL)</th>
<th>$\Delta S_1^2$ (2p+KLL)</th>
<th>S1 (1s-2p)</th>
<th>O1s</th>
<th>Au3d5/2</th>
<th>Au4f7/2 (s)</th>
<th>Au (3d-4f)</th>
<th>Au shift (6d-x)</th>
<th>S11s (ref.to Au4f)</th>
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<tr>
<td>0</td>
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<td>108.1</td>
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<td>93.2</td>
<td>3452.7</td>
<td>1712.4</td>
<td>1740.3</td>
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<td>13.9</td>
<td>1843.6</td>
</tr>
</tbody>
</table>

Figure 6.4 Au dot on SiO₂: peak position variation with flood gun bias

Figure 6.5 Au dot on SiO₂: parameter variation with flood gun bias
Figure 6.6 Plot of applied and measured flood gun potentials

It is evident from these results that the effect a sample experiences on increase of the bias level is not necessarily equal to that added at source, as seen by the Au values in Tables 6.1 and 6.2, i.e. if the flood gun is manually switched from its 0V to 2V setting the difference in potential experienced by the sample, seen through the shifting of the Au $^{4f_{7/2}}$ peak, will not necessarily be 2V.
Instabilities in the power supply for the flood gun can lead to some inaccuracies, but this situation is also dependant on the field penetration problem originating from the analyser entrance grids. Figure 6.6 shows a plot of "applied" electron flood gun volts versus physically "measured" volts, the measurement involving use of a Keithley 504 electrometer, as for the landing current measurements in Chapter 4. A copper specimen holder was used, since it will not suffer from any charging effects but will reflect the field penetration problem. The acceptability of higher levels of electron flood gun bias is reflected in Tables 6.1 and 6.2, with the Au values reflecting the performance of the electron flood gun.

A logical extension of the evaporation of Au dots onto silica and copper substrate materials involved the deposition of both Au and Cu dots onto silica, since such independent referencing should produce similar results.

6.233 Au and Cu dots on SiO$_2$

Dots of Au and Cu were vacuum-deposited of 3mm size and 4mm separation (to allow a reasonable signal to be obtained from metals and substrate on XPS analysis) onto a vitreosil substrate material. This experiment also permitted the biased referencing technique to be used with Cu together with Au as the reference metal.

The results of this experiment can be seen in Table 6.3. Material parameters such as the Si (1s-2p) and Au (3d5/2-4f7/2) stabilise on the application of an 8V bias, as before. Individual peak position variations are shown in Figures 6.7 and 6.8. When referenced to the Au
Table 6.3 Results for Au and Cu dots on SiO$_2$

4f$^7$/2 line, both the Si 1s and Cu 2p$^3$/2 peaks can be seen to vary rapidly in position before reaching a plateau at around 10V Au shift level (≈ 10V flood gun bias). However, when the Si 1s and Au 4f$^7$/2 peaks are referenced to the Cu 2p$^3$/2, minimal variation of the Si 1s peak position occurs on increasing the bias level whilst the Au 4f$^7$/2 peak position varies rapidly at the lower levels of bias before stabilising at around 10V bias. This difference between Si 1s peak position variation when measured with respect to Cu and Au is again probably due to the stray fields problem. The energy separation between the Si 1s and Cu 2p$^3$/2 peaks is approximately 912eV (KE), which is considerably lower than that for the Si 1s and Au 4f$^7$/2 peaks (approximately 1760eV). Thus any field

<table>
<thead>
<tr>
<th>Flood Gun Bias (V)</th>
<th>Si1s</th>
<th>Si2p</th>
<th>Si (1s-2p)</th>
<th>Au3d5/2</th>
<th>Au4f7/2 (x)</th>
<th>Au4f7/2 (84-x)</th>
<th>Cu2p3/2 (y)</th>
<th>Cu2p3/2 (932.7-y)</th>
<th>Au (3d-4f)</th>
<th>Si1s (ref.to Au4f)</th>
<th>Si1s (ref.to Cu2p)</th>
<th>Cu2p3/2-Au4f</th>
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<tbody>
<tr>
<td>0</td>
<td>1843.2</td>
<td>106.2</td>
<td>1737.0</td>
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<td>848.7</td>
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</table>

Table 6.3 Results for Au and Cu dots on SiO$_2$
penetration effects across the 3000eV energy range will be more evident when comparing more widely separated peaks, with the Si 1s referenced to Au producing a more obvious effect.

However, when the plateau regions are considered there is found a level of contradiction with the Stephenson and Binkowski model for the explanation of how biased referencing might work. The first evidence for this is shown in Table 6.3, where a slight disparity exists between the plateau values obtained for the Si 1s referenced to Au and Cu respectively. The differences obtained are in the range 0.4-0.5eV, which is not substantial when one considers that an accuracy of ±0.2eV can generally be placed on the individual photoelectron peak positions. However, this experiment and similar ones involving isolated single dots of Au and Cu placed onto silica-based materials found that this disparity, however slight, was consistently present and appeared to be a
It was possible that this difference in referencing to Cu and Au could be due to experimental error, varying levels of surface oxide present, instabilities in the electron flood gun power supply or other similar effects. However, the possibility also existed that Fermi level alignment was not being attained on the use of biased referencing, since such a difference should not occur if one adheres to the logic of the Stephenson and Binkowski approach. If vacuum level alignment rather than Fermi level alignment was occurring, for instance, one would expect to see the different values of the reference metal work functions taking effect in the calculations (see Figure 6.10b).
Table 6.4 shows a list of work function values\(^{(169)}\). The values for parent Cu and Au metals are 4.65 and 5.1 respectively, with a difference between them of 0.45. This separation is within the range of the "error" apparent previously.

<table>
<thead>
<tr>
<th>Element</th>
<th>Work Function</th>
</tr>
</thead>
<tbody>
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<td>Au</td>
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</tr>
<tr>
<td>Cr</td>
<td>4.5</td>
</tr>
<tr>
<td>Cu</td>
<td>4.65</td>
</tr>
<tr>
<td>Fe</td>
<td>4.5</td>
</tr>
<tr>
<td>Pt</td>
<td>5.65</td>
</tr>
</tbody>
</table>

Table 6.4 Table of work function values

6.24 Fermi level and vacuum level alignment

Thus an important factor to be considered is the fundamental difference between Fermi level and vacuum level alignment. This issue has been discussed by many workers concerned with the differences between XPS analysis of insulating and conducting samples. As has been emphasised by Barr\(^{(166)}\), it is the existance of Fermi level alignment (or lack thereof) that determines precisely what is being measured experimentally. From the work of Lewis and Kelly\(^{(114)}\), outlined earlier, this can be envisaged through the consideration of three separate types of situation that can exist when two metallic dots are placed onto a sample for XPS analysis. These are as follows:

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Situation 1: The metal dots are in contact with each other and with the spectrometer (e.g. separated or connected Al and Au dots placed onto a copper substrate),

Situation 2: The metal dots are not in contact with each other or the spectrometer (e.g. separated Al and Au dots placed onto a silica substrate) and

Situation 3: The metal dots are not in contact with the spectrometer but are in contact with each other (e.g. connected Al and Au dots placed onto a silica substrate).

Each of these situations is idealised, but can experimentally exist. However, a combination of them can make the situation much more complicated. If the physics of each situation is investigated more closely, a semi-quantitative insight can be gained into their similarities and/or differences.

**Situation 1**

When the metal dots are in contact with each other and the spectrometer, this exemplifies the "standard" situation of metal analysis with XPS. As described in Chapter 1, during analysis a photon of energy $h\nu$ causes a photoelectron to be emitted from the sample, and its kinetic energy can be given by:

$$E_{KE} = h\nu - e\phi_b - e\phi_s$$

..... 6.4
where:

\( E_{KE} \) = the kinetic energy of the electron outside the metal surface,

\( \Phi_b \) = the binding energy of that electron referenced to the Fermi level of the metal, and

\( \Phi_s \) = the work function of the metal.

On measuring the energy of the electron by the application of a voltage between the specimen and the spectrometer, the voltage, \( V \), required to just prohibit the electron from reaching the spectrometer is defined by:

\[
eV - e\Phi_s + e\Phi_{sp} = E_{KE}
= h\nu - e\Phi_b - e\Phi_s
\]

where:

\( \Phi_{sp} \) = the work function of the spectrometer.

This is demonstrated in Figure 6.10a.

Since equation 6.5 applies to both metal dots any differences existing between voltages measured for photoelectron peaks from Metals 1 and 2 can be given by:

\[
V_1 - V_2 = \Phi_{b1} - \Phi_{b2}
\]
Thus the difference between the voltages equals the difference between the binding energies.

**Situation 2**

When the metal dots are in contact with the spectrometer but not in contact with each other, the situation is more complex. Due to differences in factors such as the x-ray yield and x-ray flux to the two regions, the actual potentials of the dots may not be easily defined or necessarily the same. As described earlier, the potential of the specimen can be defined by the energy of the flood gun electrons themselves. In this case the vacuum levels of the metals and the insulating surface are aligned to the level defined by the flood gun $\Phi_e$, as shown in Figure 6.10b. The kinetic energy of the photoelectron emitted from Metal 1 can be described by:
\[ E_{KE1} = h\nu - \phi_{b1} - \phi_{s1} \] ...... 6.7

where:

\[ \phi_{b1}, \phi_{s1} \] and \[ E_{KE1} \] are the energies and work function referring to Metal 1.

However, in this case the voltage, \( V_1 \), required to prohibit the electron from reaching the spectrometer is:

\[ eV_1 - e\phi_e + \phi_{sp} = E_{KE1} \]
\[ = h\nu - e\phi_{b1} - e\phi_{s1} \] ...... 6.8

Similarly, for Metal 2, the voltage, \( V_2 \), required to prohibit its electron from reaching the spectrometer can be given by:

\[ eV_2 - e\phi_e + \phi_{sp} = E_{KE2} \]
\[ = h\nu - e\phi_{b2} - e\phi_{s2} \] ...... 6.9

where:

\[ \phi_{b2}, \phi_{s2} \] and \[ E_{KE2} \] are the energies and work function referring to Metal 2.

Combining equations 6.8 and 6.9 gives:
\[ V_1 - V_2 = \phi_{b_2} - \phi_{b_1} + (\phi_{s_2} - \phi_{s_1}) \] ...... 6.10

Hence for this situation the difference in measured voltage is not accurately defined by the difference in electron binding energies alone, since it contains an extra term involving the work functions of the two metals.

**Situation 3**

When the two metal dots are in contact with each other but not with the spectrometer, the Fermi levels are aligned even though the metals are not connected to ground. This combined Fermi level will exist at some potential \( \phi_{fe} \) relative to earth. The voltage required to prohibit the electron from reaching the spectrometer can in this case be given by:

\[ V_1 - \phi_{fe} + \phi_{sp} - \phi_{s_1} = E_{KE1} \]
\[ = h\nu - \phi_{b_1} - \phi_{s_1} \] ...... 6.11

As for Situation 1, since equation 6.11 applies to both metal dots any differences existing between voltages measured for photoelectron peaks from Metals 1 and 2 can be given by:

\[ V_1 - V_2 = \phi_{b_1} - \phi_{b_2} \] ...... 6.12

Thus, as found for Situation 1, the difference between the voltages is equal to the difference between the binding energies.
This simple methodology describes the use of an electron flood gun for the analysis of isolated or completely insulating specimens, and defines the measured voltage only to values within possible differences in the work function values themselves (unless, from the model of Stephenson and Binkowski, the Fermi levels are aligned). However, a complex insulating specimen rather than the idealized and simplistic ones described above might have metal particles both in contact with each other and isolated so that two or more binding energies might be observed.

6.241 Au, Cu and Pt dot experiments

To investigate this issue, reference metals were sought consisting of more widely separated work function values. It can be seen from Table 6.4 that whilst the values of Cu and Au differ by less than 0.5eV, which can be within the XPS experiment error bar assignments, the difference between those for Cu and Pt (whose work function = 5.65) is 1.0, which is outside reasonable XPS error. Thus platinum was selected for use in a confirmatory experiment, it also being sufficiently unreactive and easily sputter deposited to be practically suitable. Although the position of the Cu 3p at 74eV would superimpose onto the position of the Pt 4f_{5/2}, the Pt 4f_{7/2} peak at 70eV remains unaffected, and thus easily measurable.

Thus for this experiment, three types of condition were created in accord with the three types of situation proposed earlier. These were as follows:
a) A copper specimen with Au and Pt dots deposited,
b) An SiO$_2$ specimen (vitreosil) with isolated Cu and Pt dots deposited, and
c) An SiO$_2$ specimen (vitreosil) with connected Cu and Pt dots deposited

This is shown in Figure 6.11.

![Figure 6.11 Situations 1, 2 and 3 (Fermi and vacuum level alignment)](image)

The results of this investigation are summarised in Table 6.5, and indicate that the work functions of the reference metals appear to be playing a role in the energy referencing procedure. The experiment involving the deposition of Au and Pt dots onto copper produces a Cu 2p$_{3/2}$-Pt 4f$_{7/2}$ peak separation of 861.7eV, which is essentially identical to that measured for the connected Pt and Cu dots on silica (861.6eV), whereas the value for the separated dots is different by approximately 1eV (860.7eV). As found in the previous experiments, stability at the higher levels of bias is obtained for parameters such as the silicon Auger parameter, the Pt (3d$_{5/2}$-4f$_{7/2}$) peak separation and the Pt 3d$_{5/2}$ and 4f$_{7/2}$ individual peak separations from the Cu 2p$_{3/2}$, so that this difference is not due to any other spectrometer variations.
For the isolated dots on silica, the position for the Si 1s is 1845.7 eV when referenced to copper and 1842.8 eV when referenced to platinum, the difference between them being predicted by the work function differences of the two metals. However, when the reference dots are in contact, the Si 1s position referenced to copper becomes 1843.0 eV whilst that referenced to platinum is 1843.1 eV. Thus their values are approximately equal, as would be expected if vacuum level alignment was occurring. The drift of the "connected Si 1s value" to 1843.1 eV reflects...
a greater movement from the reference value to Cu than to Pt in the separated condition, since the Si 1s drifts towards 1842.8eV rather than 1843.7eV. This could be due to the ability of the copper 3s electrons to enter the vacant orbitals present in the Pt 4f levels, which is behaving as a transition metal.

The completion of the biased referencing experiments for vitreosil SiO$_2$ with respect to metal deposits of Cu, Au and Pt enables a quantitative measure for the energy of the Si 1s photoelectron peak in this material. The value can be accurately defined as that referenced to the vacuum level, plus $\Delta w$, where $w$ is the difference in work function between the reference metal and the spectrometer itself. The spectrometer work function value is equal to the individual values for Fe and Cr (from Table 6.4) metals that make up the spectrometer vacuum chamber itself. Thus:

when referenced to the Au 4f7/2 :

$$\text{Si 1s} = 1843.6 + (5.1 - 4.5)$$

$$= 1844.2\text{eV}$$

when referenced to the Cu 2p3/2 :

$$\text{Si 1s} = 1844.0 + (4.65 - 4.5)$$

$$= 1844.2\text{eV}$$
when referenced to the Pt 4f\(^{7}/2\) :

\[
\text{Si 1s} = 1843.0 + (5.65 - 4.5) = 1844.2\text{eV}
\]

Thus the binding energy of the Si 1s in vitreous Si\(_{2}\) can be accurately defined to be 1844.2eV. This demonstrates a useful feature of the biased referencing technique, since it enables energy definition of levels previously unobtainable. This is of particular use for high energy x-ray sources, such as monochromatic Ag L\(_\alpha\), since it overcomes the lack of reference data for such orbitals in the available literature.

6.3 The Applicability of Biased Referencing

Since one of the useful applications of high energy monochromatic Ag L\(_\alpha\) x-rays involves the study of materials of interest to the petrochemicals industry, the biased referencing technique has been investigated using powdered zeolite catalysts. As demonstrated in Chapter 5 these materials can be difficult to successfully charge-neutralise using an electron flood gun, when monochromatic Ag L\(_\alpha\) radiation is used with the ESCA3 MkII spectrometer, since the use of higher bias levels sometimes causes the inducement of chemical and/or physical changes. Thus this represented a significant challenge to the combined electron flood gun/biased referencing technique.

One such study involved a sample of Na Y (Si\(_{2}\)/Al\(_{2}\)O\(_{3}\) = 3.08) zeolite which was impressed into indium foil to produce a flat surface prior to the careful deposition of a Au dot onto its surface. The results of this study are shown in Table 6.6. Peak position stability is
Table 6.6 Results for Au dot on Na Y zeolite

obtainable for the Si 1s photoelectron peak, and is shown in Figure 6.12. The behaviour of this sample under such high levels of electron bias is encouraging. In this instance the Na Y zeolite sample appears to be successfully charge-neutralised by the use of higher levels of bias with no evidence of surface damage to the structure as described in the study of zeolites in Chapter 5.

Thus for the Na Y zeolite \((\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.08)\) the binding energy of the Si 1s peak can be accurately given by:

\[
1843.5 + (5.1 - 4.5) = 1844.1 \text{eV}
\]

<table>
<thead>
<tr>
<th>Flood gun bias (V)</th>
<th>SI 1s</th>
<th>SII K LL</th>
<th>Au 5d 5/2</th>
<th>Au 4f 7/2</th>
<th>Au (3d-4f)</th>
<th>O 1s</th>
<th>Au shift (84-x)</th>
<th>SI 1s BE Au</th>
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<td>3453.1</td>
<td>2205.4</td>
<td>84.9</td>
<td>2120.5</td>
<td>532.1</td>
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<td>1613.2</td>
<td>3453.6</td>
<td>2204.0</td>
<td>81.5</td>
<td>2122.5</td>
<td>528.9</td>
<td>2.5</td>
</tr>
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<td>1614.5</td>
<td>3453.6</td>
<td>2202.6</td>
<td>79.2</td>
<td>2123.6</td>
<td>527.1</td>
<td>4.8</td>
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<tr>
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<td>1837.4</td>
<td>1616.3</td>
<td>3453.7</td>
<td>2200.4</td>
<td>77.0</td>
<td>2123.4</td>
<td>525.5</td>
<td>7.0</td>
</tr>
<tr>
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<td>1835.3</td>
<td>1618.1</td>
<td>3453.4</td>
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<td>75.9</td>
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<td>522.1</td>
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<td>3453.3</td>
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<td>72.0</td>
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<td>12.0</td>
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<td>1623.8</td>
<td>3453.3</td>
<td>2192.5</td>
<td>70.1</td>
<td>2122.4</td>
<td>518.1</td>
<td>13.9</td>
</tr>
</tbody>
</table>

251
Due to the inherent problems associated with the XPS analysis of zeolite-type materials, their large surface areas making them very sensitive and thus difficult to accurately control, the success of the biased referencing technique in this case is of interest since:

a) it demonstrates the energy referencing technique to be suitable for use when analysing sensitive materials, and

b) it is possible that the future analysis of zeolite materials, and other physically similar materials, could be considerably improved through the application of biased referencing, since it enables meaningful binding energies to be obtained.
6.4 The Inducement of a New Transition

It is noticeable in Figure 6.12, and has been evident in other studies (see Figure 6.4) that immediately prior to the onset of a peak plateau position for the Si 1s and other peaks, a region is observed where the sample appears to be temporarily overcompensated for its surface charging effects to exhibit a different type of behaviour. For vitreosil, the band gap energy is approximately 9.8eV. Since the overcompensation appears to occur between 8V and 10V bias application, it is possible that the action of the higher energy electrons may be inducing a physical effect, such as entering unoccupied atomic orbitals (e.g. the conduction band of the insulator). This is due to a process known as inverse photoemission and if so would be accompanied by the emission of light from the sample as the electron enters the level:

\[
\text{photoemission} : M + h\nu \rightarrow M^+ + e^- \\
\text{inverse photoemission} : M^+ + e \rightarrow M + h\nu
\]

Unfortunately, since the specimen is already illuminated due to the action of the electron flood gun, this effect is difficult to experimentally record.

If the energy of the incident electrons was sufficient to occupy previously-empty orbitals on the raising of electron flood gun bias value, it is possible that on the lowering of the bias value from 14 to 0V a hysteresis effect might be recorded. Evidence was found for such hysteresis occurrence, but not for all photoelectron peaks, such that its presence was not conclusive. This remains an area for further investigation.
To investigate whether an internal transition, such as an Auger transition across the band gap, was being instigated on a certain level of bias use, the spectrum of the reflected and emitted secondary electrons was measured using the vitreosil sample. Thus no x-rays were used. On scanning the region of interest from 0 to 25eV (KE) using 4mm slits and an analyser energy of 20eV the spectrum obtained can be seen in Figure 6.13, this being for a flood gun bias of 14V. It is evident that saturation of the channeltron is occurring at the position of the primary peak (17V), but a large background (i.e. energy loss) structure is apparent in the spectrum. Since one is attempting to measure the position of a "new" transition induced at this level of bias, the intensity of which could be very weak, the background of the spectrum needs to be as low as possible. Figure 6.14 shows the results of an attempt to overcome the channeltron saturation problem through the use of 0.5mm slits and a 2eV analyser energy. It is apparent that, at a level
of bias between 6 and 8V, a "new" transition appears. Whilst the primary peak due to the flooding electrons changes in position as the energy of the flood gun is changed from 0V to 14V, the transition appears to be fairly constant in position once it is excited. Other peaks which track and follow the position of the primary peak are energy loss features due to plasmons. The peak present at between 4 and 6eV is due to the work function of the spectrometer, and in effect represents the beginning of a spectrum normally gained with XPS. This remains invariant.

The presence of the induced transition at around 8V can be seen more clearly in Figure 6.15a, which involves the use of an 8V flood gun bias, following which the signal due to the background has been removed. The position of the peak is close in energy to the area of interest before the plateauing effect seen in the biased referencing of vitreosil. The effect of differentiating the original spectrum is shown in Figure 6.15b, and again highlights this presence.

Following consultation with Messrs VG Scientific, one possible source of this "new" transition that could be attributable to the spectrometer itself would involve the internal generation of this peak within the energy analyser, from the collision of higher energy electrons with the internal walls of the hemispheres. This is shown in Figure 6.16. Thus if the retard potential of the analyser is set to 3eV and the pass energy set to 2eV a flood gun electron of 10eV energy will produce a primary peak of 7eV energy, for example. This possesses too much energy to traverse the hemispheres and be recorded by the channeltron and will thus impinge with the outer hemisphere to produce a cascade of secondary electrons of varying energy. These are characteristic of the difference in energy between the analyser energy and the retard potential. Thus the
Figure 6.14 Energy loss structure for vitreous sample (0-14V bias, 0.5mm slits, E_p = 2eV)
7eV electron could traverse the hemispheres to be recorded as a peak of 5eV on the energy spectrum, and so on.

Since the energy of such peak generation will be a characteristic of the analyser energy employed, the analyser energy was varied for vitreosil from 2eV to 20eV using an electron flood gun bias of 8V. This can be seen in Figure 6.17. The alteration of analyser energy causes a shifting of a large component of this "new" transition, which appears to be a function of the difference in analyser energy applicable. Indeed, on the use of a 20eV analyser energy the induced peak is present at a higher energy than the primary peak itself.

Thus it appears that the transition induced at around 8eV energy on the use of a 2eV analyser energy for the biased referencing of vitreosil is due to an artifact of the spectrometer itself, it being unfortunate that this analyser energy was useful for the counteraction of the channeltron saturation affect outlined previously.
However, the presence of the "hump" immediately prior to the onset of a stable peak plateau position in the biased referencing experiments remains to be further investigated in the future, possibly with the use of a dedicated LEELS spectrometer, since it could be due to the inducement of a physical affect of some kind in non-conducting materials.

6.5 Conclusions

1) Biased referencing, involving the vacuum-deposition of a metallic reference onto an insulating substrate material, leads to accuracy in peak position measurement to a possible ±0.1eV accuracy. The level of
Figure 6.17 Effect of variation of analyser energy on transition position

bias generally necessary is at least 8V, at which peak position consistency is obtained with respect to the metal deposited. Thus peak energies can be accurately defined in monochromatic Ag Lα radiation, despite the absence of reference values in the literature.

2) Binding energy measurements so produced appear to be referenced to the vacuum level, rather than the Fermi level of the spectrometer as suggested by some other workers. This is apparent since the work function values of the reference metals play a role in the internal referencing technique.

3) The reproducibility of data obtained appears to be satisfactory, such that the use of biased referencing as an internal referencing technique should become more widespread within the surface science community, since it offers considerable improvements when compared with normal XPS
procedures for insulating materials, when monochromatic x-rays are used.

4) Since the experimental preparations for the use of this technique are not complex, it is likely that as the use of biased referencing becomes more widespread in the future an in-situ sample preparation unit will be developed. This might involve the attachment of a metal evaporator to the electron spectrometer and an easily positionable mask for the selective deposition of reference dots onto the sample substrate. In certain cases, it could permit the measurement of work function changes whilst monitoring surface composition, this method instigating less surface damage than higher energy electron beam techniques such as AES.
Chapter 7. Summary and Future Work

This investigation has outlined the useful properties of monochromatic Ag Lα x-rays for use as a high energy source to complementary conventional Al Kα and Mg Kα for general XPS applications. The resolution and sensitivity for this novel source have been shown to be satisfactory, allowing confidence in both qualitative and quantitative results obtained, although the signal intensities do lead to more lengthy acquisition times than usual. Experimental sensitivity factors recorded were in good agreement with theoretical values quoted by Yarzhemski (5). The transmission function for the ESCA3 MkII obeys an E(-1/2) dependence up to 3000eV, which is beyond its design specification.

When utilising a monochromatic XPS source for insulating materials, the use of an electron flood gun to counteract surface charging effects is obligatory. On the use of the monochromatic Ag Lα x-ray source within the ESCA3 MkII spectrometer difficulties were experienced in effecting uniformity of charge compensation across the energy spectrum. This was found to be due to the breakthrough of fields from the entrance to the energy analyser. The use of higher levels of accelerating potential for these electrons avoided this problem. Thus the VG LEG51 electron flood gun was optimised successfully for future application within this and similar systems.

In this investigation, the monochromatic Ag Lα source has been applied to zeolites for catalysis, silicon surface chemistry and studies of chlorides, together with a method for internal energy referencing known as biased referencing. Each of these areas remains open to further development in the future, particularly on different instrumentation from
In the case of the zeolites, the necessity for use of high levels of flood gun accelerating potential produced a risk of specimen chemical and/or physical damage occurrence in some instances. Thus the stability of samples under such conditions needs verification prior to detailed experimentation. The damage effects induced involved the mobilisation and reduction of Na⁺ ions to Na metal at high accelerating potentials. The presence of such a strongly reducing environment might be of interest for future application in the petrochemical industry. The greater stability of aluminophosphate materials, which possess similar structures to zeolites, could be a useful application of Ag La in the future.

The thermal oxide on silicon study is an area of interest to the spectroscopist, since the independent measurement of individual extra-atomic relaxation energies produces a physical term for subsequent correlation with separate measurements such as that for the material refractive index. The oxides grown in this study were not thick enough to allow measurement of refractive index values for comparison with XPS data, though XPS was shown to be better able to distinguish between very thin oxides. Thus thicker oxide layers need to be grown, which will hopefully lead to the generation of useful information concerning the surfaces present on photovoltaic devices.

The use of this source when based within the geometry of the ESCA₃ MkII spectrometer appears to be more difficult than would be the case on more modern instrumentation, which involve more efficient analysis procedures by use of 6 inch diameter energy analysers and multichannel detection systems (rather than the 4 inch diameter energy analyser and
single channeltron detection system as for the case of the ESCA3 MkII). This would considerably reduce the acquisition times required and thus further improve confidence in data produced. Furthermore, the presence of a lens between the sample and the analyser precludes the effects of stray fields from the analyser as found for the ESCA3, so that lower levels of electron energy may effect uniform neutralisation. However, the effect of fields from other sources present within the vacuum space could produce a similar effect.

The applicability of the high energy monochromatic Ag La x-ray source as a complementary analytical tool to conventional XPS anode materials was highlighted by a study of a contact lens copolymer material. The combination of Mg Kα, Al Kα and monochromatic Ag La enables a non-destructive depth-profile to be obtained, which can give useful information concerning elemental concentration gradients at a specimen surface without the need for destructive argon ion bombardment. This will be of particular use for sensitive materials such as polymers, for which the latter facility is unreliable. Together with the possibility of increased analysis depths on variation of electron take-off angle, this may constitute a significant application of this x-ray source in the future.

The energy of the monochromatic Ag La x-ray source produces 1s core level accessibility up to chlorine in the periodic table. The study of alkali metal chlorides outlined in this study was successful, despite problems experienced with the handling of these sensitive materials. A correlation of the extra atomic relaxation energies for the 1s and 2p orbitals was in good agreement with that predicted from theoretical work of Slater(132). As a direct continuation of this work, the preparation
of basic chlorides and a study of material properties thereof might give useful information concerning the role of chloride ions in the breakdown of passive films on stainless steels, for example. The Ag L\_\alpha source could also be applied to the surface chemistry studies of sulphur and phosphorus (which could be related to possible aluminophosphate studies). Sulphur, in particular, is of great interest due to its association with a variety of materials problems, including pitting corrosion of stainless steels and biodegradation due to SRB (sulphate reducing bacteria). The use of Ag L\_\alpha for calculation of individual orbital relaxation energies for the identification of changes in polarisability could help to develop an understanding of the role played by sulphurous species in these processes.

The development of the biased referencing technique, involving the vacuum deposition of a metallic reference onto insulating materials, produced accuracies in reproducibility of data for insulators similar to those commonly accepted for conducting materials in XPS, which was encouraging. Such values obtained were found to be referenced to the vacuum level for insulators, rather than the Fermi level as for conductors, since the work function values of the metallic references affected the binding energies consequently obtained. The application of this technique for zeolite samples was particularly encouraging, since binding energies obtained were reproducible to ±0.1eV and no specimen damage effects were recorded. It is likely in the future that this method of energy referencing, particularly with respect to gold, will be widely used as interest in this method is being shown by many workers in the field. The possible presence of a new transition prior to the production of peak position constancy is worthy of future investigation, since this possibly represents a threshold energy prior to the occupation
of a forbidden energy level for an electron, this energy being supplied by the flood gun electrons themselves.

The aluminosilicate field remains an area of prime interest and Ag La suitability, and there are a variety of areas of interest with respect to the petrochemical industry, in particular, that may be usefully studied using this novel x-ray source. Among these include:

a) The role of ion exchange on the adsorption/desorption behaviour of surfactants on minerals present in oil well formations,

b) The identification of aluminosilicate minerals present in coal and a study of their potential use as ion-exchanged catalysts in liquefaction processes,

c) Studies of the effect of grinding medium and of flotation collectors in the coal/mineral flotation separation of aluminosilicate material from coal or metal ores during coal beneficiation,

d) More advanced applications of zeolite materials themselves, such as for the production of novel paint formulations, and

e) Studies of polymeric materials generally, where the useful non-destructive depth-profiling capabilities of monochromatic Ag La x-rays, when used in conjunction with conventional XPS sources, could be beneficial.
Thus the prospects for this x-ray source appear to be good. The excitation of widely differing photoelectron and Auger line energies affords measurement of near surface concentration gradients in materials without the need for destruction of the sample in any way, whilst the application of Auger parameters and extra-atomic relaxation energies available on the use of Ag La should ensure its application to a wide range of materials of interest to materials science, chemistry, corrosion, microelectronics and many other fields.
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HIGH ENERGY XPS USING A MONOCHROMATED Ag Lα SOURCE: RESOLUTION, SENSITIVITY AND PHOTOELECTRIC CROSS SECTIONS

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ABSTRACT

Resolution, sensitivity and calibration data are presented for a novel high energy XPS source, monochromated Ag Lα radiation (hν = 2984.3 eV). Adequate resolution is attainable for good signal/noise spectra, whilst values for experimental sensitivity factors agree well with theoretical cross section values calculated by Nefedov. This allows an evaluation of ESCA 3 Mk. II transmission function up to 3000 eV, which appears to obey an approximate E^−1/2 dependence. Monochromated Ag Lα (linewidth 1.3 eV) overcomes the problem of broad natural linewidths for high energy sources, such that chemical state information can be gained. Various new core level and Auger peaks are developed, a notable feature being the 1s core level and KLL Auger transition capability from Al through to Cl. Improved sensitivity is experienced for elements whose major peaks occur in the 1500—3000 eV BE range, whilst there is no serious reduction of sensitivity in the conventional XPS energy range.

INTRODUCTION

The search for higher energy X-ray sources for XPS has been intensified in recent years [1—10], with a wide variety of anode materials being considered for use (Table 1).

Both Si Kα [2,4] and Zr Lα [7,8] have been used in this laboratory, and these represent the useful limit of the unmonochromated Kα and Lα X-ray series, respectively.

High energy X-rays have the ability to excite new core level peaks, together with new Auger series (Figs. 1 and 2). However, their application has been hindered by the possession of comparatively broad natural linewidths which reduce the resolution available to the spectroscopist. Hence, accurate chemical state information has been difficult to obtain.
TABLE 1
LIST OF HIGH ENERGY XPS ANODE MATERIALS

<table>
<thead>
<tr>
<th>X-Ray</th>
<th>Photon Energy (eV)</th>
<th>Linewidth (eV)</th>
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<tr>
<td>Si Kα</td>
<td>1739.4</td>
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<td>Zr Lα</td>
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</tr>
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<td>Au Mα</td>
<td>2122.9</td>
<td>2.15</td>
</tr>
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<td>Mo Lα</td>
<td>2293.2</td>
<td>1.9</td>
</tr>
<tr>
<td>Ag Lα</td>
<td>2984.3</td>
<td>2.6 (1.3)</td>
</tr>
<tr>
<td>Ti Kα</td>
<td>4510.9</td>
<td>2.0</td>
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<td>Cr Kα</td>
<td>5417</td>
<td>2.1</td>
</tr>
<tr>
<td>Cu Kα</td>
<td>8055</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Fig. 1. Photo- and Auger-electron lines from the deepest 1s orbitals accessible with the five radiations used in the The Surface Analysis Laboratory (relative positions).

This article highlights the suitability of monochromated Ag Lα radiation for high energy XPS applications. The natural linewidth of 2.6 eV for Ag Lα would be prohibitive for chemical state analysis. However, it has been shown [9] that the wavelength of Ag Lα X-rays is approximately half that for Al Kα X-rays (energy 1486.6 eV), and satisfies a second order Bragg condition rather than the first order reflection for Al Kα. This permits the use of standard Al Kα monochromator geometry as present on recent VG Scientific spectrometers, easing construction considerably. Consequently, the linewidth is reduced to approximately 1.3 eV.

It has been postulated [1] that Ag Lα might be the hardest X-ray suitable for XPS from all elements in the Periodic Table, since for higher energy X-rays there is a fall in the photoemission cross sections of orbitals of low binding energies, and in the case of the first row elements this loss is not compensated by access to new high energy orbitals. Thus, the light element sensitivity of XPS is lost at energies above \( \approx 3 \) keV.
Fig. 2. Photo- and Auger-electron lines from the deepest 2p orbitals accessible with the five radiations used in The Surface Analysis Laboratory (relative positions).

The major advantages achieved through the use of a monochromator are the removal of Bremsstrahlung radiation and interfering satellites, an improved signal-to-background ratio and a lower level of X-ray beam damage.

Resolution and sensitivity data, for elements up to Z = 30, have been collected using this novel source, allowing an evaluation of the mean free path x transmission function product covering a range of 0—3000 eV. The energy scale has also been calibrated up to 3000 eV.

EXPERIMENTAL

The spectra were acquired using a VG ESCA3 Mk II spectrometer (VG Scientific Ltd., East Grinstead, Sussex, Gt. Britain) fitted with a standard twin Mg/Al anode and a monochromatic Ag Lα source, operating at 14 kV, 40 mA, and flood gun setting of 2 A filament current and 0.2 mA emission current (energy mode 0 V) for the study of insulators. The spectrometer ran at a normal operating pressure of 1—4 x 10^{-9} mbar, being controlled in CAE mode with programme switch in, thereby keeping the total effective voltage across the multiplier constant, regardless of any change in retarding potential. Analyser entrance and exit slits were set to 4.0 mm.

Resolution data for the monochromated Ag Lα source was collected using a sample of Au evaporated onto Si, gold (or silver) being the usual reference materials when commissioning commercial spectrometers.

All compounds used for standardisation were the purest commercially available, obtained from Koch-Light Laboratories Ltd., Colnbrook, Bucks, Gt. Britain, Fisons Scientific Apparatus, Loughborough, Leics., Gt. Britain, and BDH Chemicals Ltd., Parkstone, Poole, Dorset, Gt. Britain.
A similar practice to that used previously for the identification of reliable standard materials for analysis was followed [4], the use of simple fluorides rather than complex salts reducing peak overlap problems. If a fluoride of a particular element proved to be insufficiently stable, a secondary standard was taken, as, for example, sodium in the case of chlorine or oxygen in the case of zinc. Chemically, the use of fluoride standards poses a problem in that they are often unstable in air, leading to rapid hydrolysis, or sometimes unstable under X-ray bombardment, though with the low intensity monochromated Ag La source the latter proved to be less of a problem.

Powdered samples were dried at 120°C for 72 h, mounted onto indium
Fig. 5. Variation in signal intensity on improving resolution for monochromated Ag $L\alpha$ radiation; Au $4f_{9/2}$ line.

Fig. 6. Plot of sensitivity factors for 1s photoelectrons in monochromated Ag $L\alpha$ radiation.

foil [11], and occasionally baked in situ within the spectrometer — the bake-out temperature being limited to 100°C to avoid damage to the quartz crystal in the monochromator assembly. Alternative methods of sample preparation were investigated, such as mounting onto double-sided adhesive
tape or sample pelletisation under pressure, but these invariably led to less satisfactory results with regard to hydrolysis or longer periods for pump down of the preparation chamber than was acceptable.

Indium foil, being malleable and able to grip fine powders, proved a suitable substrate material. The foil could be wrapped and crimped around recesses in special stainless steel sample holders, thus fixing the foil without the use of adhesive tape. The fine powders were then impressed into the surface, rather than between leaves of foil [11] which was found to be unnecessary in this case.

The in situ sample baking procedure did not affect the chemical state of the element(s) being analysed. Hydrocarbon contamination was extremely low on most samples, being 2–3% of the F 1s signal intensity. The oxygen signal was monitored as an indication of sample hydrolysis, and was kept below 5% of the F 1s intensity. Samples not satisfying these conditions were rejected, and subsequently reanalysed. Very occasionally it was necessary to etch slightly the surface with argon ions. The usual conditions were 3 kV energy and 1.5 kV focus voltage, for a period of 5–15 s. No changes in chemical state were detected following this process. Sample coverage of the substrate was good, the indium 3d_{5/2} signal being 1% of that for F 1s.
Due to the low count rates experienced with the monochromated Ag La source, samples being analysed at the highest resolution of $E_p = 50$ eV were examined until reasonable ($\approx 40$) signal-to-noise ratios were achieved — some photoelectron peaks of poor cross section did not reach this ratio, these being counted for lengthier times, without any noticeable growth in contamination. Despite lengthy acquisition periods no problems were experienced with the overheating of the X-ray anode, since silver possesses the highest thermal conductivity of any material at room temperature.

Following previous work [12], a study was made of the excitation of Auger peaks both directly, using monochromated Ag La, and indirectly through Bremsstrahlung radiation, using Mg Kα, in an attempt to calibrate the spectrometer up to 3000 eV range. Silicon and aluminium foil were chosen as reference materials, since they provide standards across the range of aluminosilicate materials to be studied in the future.

RESULTS

Resolution data

Figure 3 shows a plot of variation in resolution with analyser energy for monochromated Ag La radiation using the Au 4f line, while Fig. 4 compares this novel source with some others used in this laboratory.
<table>
<thead>
<tr>
<th>Z</th>
<th>Element</th>
<th>Compound</th>
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<th>2s orbitals</th>
<th>2p orbitals</th>
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<td>Area</td>
<td>Height</td>
<td>Area</td>
<td>Height</td>
<td>Area</td>
</tr>
<tr>
<td>3</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>B</td>
<td>NaF4B</td>
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<td>0.099</td>
<td></td>
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</tr>
<tr>
<td>6</td>
<td>C</td>
<td>(C₂F₄)ₘ</td>
<td>0.20</td>
<td>0.16</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>N</td>
<td>KNO₃</td>
<td>0.37</td>
<td>0.38</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>8</td>
<td>O</td>
<td>Na₂SO₄,</td>
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<td>0.58</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al₂O₃</td>
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<td></td>
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</tr>
<tr>
<td>9</td>
<td>F</td>
<td>NaF</td>
<td>1.00</td>
<td>1.00</td>
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</tr>
<tr>
<td>11</td>
<td>Na</td>
<td>NaF</td>
<td>2.32</td>
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<td>0.15</td>
<td>0.03</td>
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<td>12</td>
<td>Mg</td>
<td>MgF₂</td>
<td>2.71</td>
<td>2.75</td>
<td>0.15</td>
<td>0.12</td>
<td>0.05</td>
</tr>
<tr>
<td>13</td>
<td>Al</td>
<td>AlF₃</td>
<td>3.84</td>
<td>4.14</td>
<td>0.20</td>
<td>0.24</td>
<td>0.09</td>
</tr>
<tr>
<td>14</td>
<td>Si</td>
<td>K₂SiF₆</td>
<td>4.81</td>
<td>4.92</td>
<td>0.28</td>
<td>0.30</td>
<td>0.11</td>
</tr>
<tr>
<td>15</td>
<td>P</td>
<td>NaPO₃</td>
<td>6.37</td>
<td>6.52</td>
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<td>0.36</td>
<td>0.18</td>
</tr>
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<td>16</td>
<td>S</td>
<td>Na₂SO₄</td>
<td>6.81</td>
<td>6.78</td>
<td>0.45</td>
<td>0.45</td>
<td>0.29</td>
</tr>
<tr>
<td>17</td>
<td>Cl</td>
<td>NaCl</td>
<td>8.55</td>
<td>8.25</td>
<td>0.54</td>
<td>0.51</td>
<td>0.40</td>
</tr>
</tbody>
</table>
## Table 3
Sensitivity Factors Relative to F 1s for Elements in Monochromated Ag La Radiation: Period 4

<table>
<thead>
<tr>
<th>Z</th>
<th>Element</th>
<th>Compound</th>
<th>2s orbitals</th>
<th>2p orbitals</th>
<th>3s orbitals</th>
<th>3p orbitals</th>
<th>3d orbitals</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Area</td>
<td>Height</td>
<td>Area</td>
<td>Height</td>
<td>Area</td>
</tr>
<tr>
<td>19</td>
<td>K</td>
<td>KF</td>
<td>0.83</td>
<td>0.77</td>
<td>0.66</td>
<td>0.63</td>
<td>0.09</td>
</tr>
<tr>
<td>20</td>
<td>Ca</td>
<td>CaF₂</td>
<td>0.97</td>
<td>0.92</td>
<td>0.90</td>
<td>0.85</td>
<td>0.12</td>
</tr>
<tr>
<td>21</td>
<td>Sc</td>
<td>ScF₃</td>
<td>1.04</td>
<td>0.98</td>
<td>0.75</td>
<td>0.68</td>
<td>0.15</td>
</tr>
<tr>
<td>22</td>
<td>Ti</td>
<td>TiF₃</td>
<td>1.24</td>
<td>1.16</td>
<td>0.95</td>
<td>0.98</td>
<td>0.18</td>
</tr>
<tr>
<td>23</td>
<td>V</td>
<td>VF₃</td>
<td>1.42</td>
<td>1.32</td>
<td>1.20</td>
<td>1.12</td>
<td>0.19</td>
</tr>
<tr>
<td>24</td>
<td>Cr</td>
<td>CrF₃</td>
<td>1.67</td>
<td>1.51</td>
<td>1.52</td>
<td>1.56</td>
<td>0.22</td>
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<tr>
<td>25</td>
<td>Mn</td>
<td>MnF₂</td>
<td>1.78</td>
<td>1.68</td>
<td>1.78</td>
<td>1.70</td>
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<td>1.86</td>
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<td>CoF₂</td>
<td>2.01</td>
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<td>2.54</td>
<td>1.53</td>
<td>0.30</td>
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<tr>
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<td>NiF₃</td>
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<td>1.50</td>
<td>2.99</td>
<td>1.55</td>
<td>0.36</td>
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<tr>
<td>29</td>
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<td>CuF₂</td>
<td>2.38</td>
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<td>3.42</td>
<td>2.87</td>
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<tr>
<td>30</td>
<td>Zn</td>
<td>ZnO</td>
<td>2.62</td>
<td>2.08</td>
<td>4.16</td>
<td>4.25</td>
<td>0.40</td>
</tr>
</tbody>
</table>
The effect on intensity of monochromating the Ag $L\alpha$ radiation can be seen in Fig. 5.

**Sensitivity data**

The F 1s line was taken as primary standard for comparison of peak area [13,14] and peak height [15] intensities of subshells up to $Z = 30$. S-shaped background signals were removed using an iterative routine [16], this method giving peak areas which are much less dependent on the selection of window position. Tables 2 and 3 show the intensity ratios obtained, these being displayed graphically in Figs. 6 and 7 for which the peak area values are plotted. The points plotted are experimental sensitivity factor values, whilst the continuous lines are drawn from values calculated theoretically by Nefedov and co-workers [17].

**Instrument transmission function**

Possession of experimental sensitivity factor and theoretical cross section values allows evaluation of the instrument transmission function [18], as seen in Fig. 8 which is a plot of $G_x \lambda_x / G_f \lambda_f$, derived from the ratio $F_x / \sigma_x$ as a function of kinetic energy, where $G$ is the instrument transmission function, $F_x$ is the experimentally determined sensitivity factor relative to F 1s for element $x$ and $\sigma_x$ the corresponding theoretically calculated cross section value, whilst $\lambda$ is the inelastic mean free path. The subscript $x$ refers to the element whose sensitivity is being determined, whilst $f$ refers to the reference values taken for fluorine.

**Energy scale calibration**

The results for aluminium foil studied in Mg $K\alpha$ and monochromated Ag $L\alpha$ radiations are shown in Tables 4 and 5, allowing a measurement of energy scale uniformity from 1254 eV up to 2984 eV.

**DISCUSSION**

The resolution capabilities of monochromated Ag $L\alpha$ radiation compare favourably with conventional sources (Fig. 4), from which it can be seen that this source is suitable for the retrieval of chemical state information, since FWHM (full peak width at half maximum height) values of up to 2 eV are generally acceptable, and that its resolution limitation is similar to that for unmonochromatic Al $K\alpha$. The resolution for other high energy XPS sources, being unmonochromated, is limited by the separations between components in the X-ray line. Hence, certainly for high energy XPS, the best resolution is obtainable with monochromated Ag $L\alpha$ since this source does not suffer in this respect.

A study of Figs. 4 and 5 can explain why lengthy acquisition periods can
TABLE 4
METALLIC AND OXIDISED ALUMINIUM DATA

<table>
<thead>
<tr>
<th>Radiation</th>
<th>Region</th>
<th>( E_{B} \text{Al}^{0} ) (eV)</th>
<th>( E_{B} \text{Al}^{3+} ) (eV)</th>
<th>( \Delta E_{B} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg K( \alpha )</td>
<td>2( p )</td>
<td>73.6</td>
<td>76.2</td>
<td>2.6</td>
</tr>
<tr>
<td>KLL</td>
<td>1392.8</td>
<td>1385.5</td>
<td>7.3</td>
<td></td>
</tr>
<tr>
<td>Ag L( \alpha )</td>
<td>2( p )</td>
<td>69.9</td>
<td>72.5</td>
<td>2.6</td>
</tr>
<tr>
<td>KLL</td>
<td>1396.5</td>
<td>1389.5</td>
<td>7.0</td>
<td></td>
</tr>
<tr>
<td>1s</td>
<td>1556.7</td>
<td>1559.3</td>
<td>2.6</td>
<td></td>
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</tbody>
</table>

TABLE 5
AUGER PARAMETER DATA FOR ALUMINIUM METAL AND OXIDE

<table>
<thead>
<tr>
<th>( A' )(Al)</th>
<th>( A' \text{Al}^{0} )</th>
<th>( A' \text{Al}^{3+} )</th>
<th>( \Delta A' )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg K( \alpha ) (2p \ldots \ldots KLL)</td>
<td>212.8</td>
<td>208.1</td>
<td>4.7</td>
</tr>
<tr>
<td>Ag L( \alpha ) (2p \ldots \ldots KLL)</td>
<td>-1517.9</td>
<td>-1522.3</td>
<td>4.4</td>
</tr>
<tr>
<td>Ag L( \alpha ) (1s \ldots \ldots KLL)</td>
<td>-31.1</td>
<td>-35.5</td>
<td>4.4</td>
</tr>
<tr>
<td>1s–2( p ) separation</td>
<td>1486.8</td>
<td>1486.8</td>
<td>0.0</td>
</tr>
</tbody>
</table>

be necessary, since, for a FWHM value of 2 eV (equivalent to an analyser energy of 50 eV) a signal of only 200 counts s\(^{-1}\) is obtainable with the Au 4\( f \) line. Of course, when analysing powders such as for standards work a further drop in signal intensity can occur, depending on the sample preparation technique employed. It then becomes of vital importance for any powdered specimen to be rendered in as fine a state as possible, to reduce losses both in X-ray and photoelectron shading.

A direct result of the improved resolution gained by the monochromatisation of Ag L\( \alpha \) X-rays is that accurate chemical state information can be obtained by way of Auger parameters, the theoretical background for their use having been outlined previously [19]. Although in the study of insulators, e.g., silicates, the presence of a flood gun helps in equilibrating specimen charging, it nonetheless does not remove it. The Auger parameter being sensitive to chemical state but insensitive to specimen charging, assuming this to be uniform with kinetic energy, is a reliable and meaningful quantity in such studies. Figure 9 shows a survey scan for mica, the high signal-to-noise ratio obtained using a 20 eV analyser energy (20 scans at 1000 s/scan) being evidence of monochromated Ag L\( \alpha \) radiation capability, and the low background level allowing much clearer definition at high binding energies. Mica is a notoriously difficult material to analyse, as is sodium fluoride (Fig. 10), being both a powder and charge-sensitive. Survey
scans were not recorded for all standards analysed, due to the length of time this would involve, but regular ones such as this were run, involving 100 eV analyser energies and 20 scans at 1000 s/scan.

However, Fig. 11 gives, perhaps, the most informative survey scan for
monochromated Ag $L\alpha$ radiation — that for gold. Using similar conditions to those for mica, the Au 3$d$ doublet generates a good photoelectron cross section, whilst the $MNN$ Auger series derived from it are clearly discernible. On reducing the analyser energy to 10 eV the Au 4$f$ doublet becomes resolvable.

The higher energy possessed by monochromatic Ag $L\alpha$ radiation allows an extension of sensitivity factors beyond that measured in this laboratory before, indeed up to Cl in the 1$s$ series. It can be seen from Figs. 6 and 7 that a general exponential increase occurs in subshell peak intensity with increasing atomic number. (The signal strength for the high energy range is much better, the gold 3$d$ peaks yielding over $10^3$ counts per second.) The apparent anomaly shown at $Z = 21$, when a decrease in intensity occurs, is because of the possibility of distinguishing between the separate spin states ($2p_{1/2}$ and $2p_{3/2}$) in the 2$p$ atomic orbital. Above $Z = 21$, only the 3/2 component is plotted, whereas below the areas of the combined peaks are used.

The experimentally determined sensitivity factors are approximately equal to the theoretically calculated cross section values, within a ± 10% error. This has been accounted for over shorter ranges of kinetic energy than used here by an energy-independent product of the instrument transmission function ($G$) and the electron mean free path ($\lambda$). $\lambda$ itself has previously been shown to obey an approximate square root dependence with kinetic energy over normal [20] and extended [10] XPS ranges. This implies, as has often been suggested, that the transmission function varies as $E^{-1/2}$ [4, 21–24], at least.
over ranges typically up to 1500 eV. The present data suggest that a similar dependence applies up to 3000 eV.

Since for VG ESCA 3 Mk II instruments pre-retardation is used [4, 25–27], it is expected that G would vary inversely with kinetic energy, from the electron optics brightness law [28]. However, this law is only obeyed if each aperture and slit between the sample and detector is filled with photoelectrons originating from the sample. Below a definite level of retardation, acceptance angles are not filled and G becomes independent of kinetic energy — this change occurring at approximately 200 to 0 eV below the photon energy.

Nevertheless, it should be noted that this “transition point” is dependent on:
(a) analyser pass energy,
(b) entrance and exit slit separations, and
(c) X-ray irradiated sample size.

In the case of the monochromated Ag Lα line source, its electron optics are different from conventional sources. Though the maximum acceptance angles are similar to those for Mg Kα and Al Kα, the actual angles are determined by the irradiated sample area. The monochromatisation gives a line source (6 x 1 mm) and hence the angles are very much smaller. This significant difference probably accounts for the G value being constant at retardations up to 3000 eV.

It can be seen from Tables 4 and 5 that the energy scale has been calibrated up to 3000 eV, which is a considerable extension from the range for conventional sources. Subtracting the Auger parameter (A1) value for Al 2p–KLL Auger in monochromated Ag Lα radiation from that for Mg Kα radiation should produce the difference in photon sources used (i.e., 2984.3 – 1253.6 eV) and this is found to be so. Furthermore, the separation between the Al 2p–KLL and 1s–KLL A1 values using monochromated Ag Lα radiation should be equal to the energy of the Al Kα X-ray energy. This is shown in Table 5, and is acceptable when one considers the limits of chemical shifts on the X-rays themselves.

The great potential for the use of higher energy unmonochromated X-ray sources for extending depth profiling scales has been indicated recently [10] with the particular advantage for application to fibrous or powdered samples. Monochromated Ag Lα radiation, with its improved resolution capabilities, might also prove to be a useful tool for XPS, its low beam damage characteristic being of such benefit that this source could become complementary to conventional Mg Kα and Al Kα sources, giving a different sampling depth due to its more penetrating nature.

CONCLUSIONS

The novel high energy monochromated Ag Lα source is a reliable and useful analytical tool, possessing adequate resolution for good signal/noise spectra.
Relative sensitivity factors have been experimentally determined, with the extended 1s core level and KLL Auger series potential being a particular feature. The agreement with theoretical cross section values calculated by Nefedov is good.

The instrument transmission function for the ESCA 3 Mk. II using high energy and conventional sources has been shown to vary with $E^{-1/2}$ within the range 0–3000 eV.

ACKNOWLEDGEMENT

It is a pleasure to thank B.P. Research for their assistance through an EMRA award.

REFERENCES

THE USE OF MONOCHROMATIC Ag $\text{L}_\alpha$ RADIATION TO STUDY RELAXATION ENERGY DIFFERENCES IN X-RAY PHOTOELECTRON SPECTROSCOPY OF ALKALI METAL CHLORIDES

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(First received 11 May 1985; in final form 31 October 1985)

ABSTRACT

Monochromatic Ag $\text{L}_\alpha$ radiation has been used to measure the Cl $1s$, Cl $2p$ and Cl $KLL$ Auger energies by XPS in a series of alkali metal chlorides. The extra-atomic relaxation energies derived from these data were found to be linearly related to the polarizability of the metal—chloride bond. The magnitudes of the extra-atomic relaxation energies associated with photoemission from the Cl $1s$ and Cl $2p$ levels conformed with the Slater screening coefficients for these orbitals.

INTRODUCTION

Following the comprehensive work of Wagner [1], the study of the Auger lines which appear in XPS spectra as a de-excitation process is assuming increasing importance. The positions and shapes of these lines are often valuable indicators of chemical state. In particular the so-called 'Auger parameter' in its various forms has been utilized in the study of a wide variety of compounds [2] and has proven especially useful for insulators since, being essentially an energy interval, it is independent of sample charging and work function.

Furthermore, changes in the Auger parameter going from one compound to another have been identified with changes in the 'extra-atomic relaxation energy' and hence the polarizability of the atomic bond. The applications of this approach have included the study of magnesium [3], transition metals [4–8], sodium compounds [9, 10], chlorine compounds in the gas phase [11], alumino silicates [12], sulphur compounds [13], silicon compounds [14, 15] and alkali metal halides, both crystalline [16–19] and frozen in solution [20, 21].

The Auger parameter measurement may be used as a 'fingerprint' for
chemical state. This straightforward approach often makes use of ‘mixed’ Auger parameters, for example using the 2\textit{p} binding energy and the \textit{KLL} Auger kinetic energy, the latter being excited by the Bremsstrahlung component of unmonochromated X-radiation [22]. Of interest in this paper is the use of the Auger parameter to determine changes in relaxation energy following photoemission from chlorine in alkali metal chlorides.

Several approaches to this problem have been taken [21, 23–28]. We follow the method of Bechstedt et al. [14], which is outlined below.

The method is to measure an Auger peak energy along with the binding energies of the core levels involved (in this case the Cl \textit{KL}_{2,3}\textit{L}_{2,3} Auger peak, and the Cl 1s and 2\textit{p} peaks). The binding energy of a chloride core level relative to the Fermi level, BE(\textit{i}), will be

\begin{equation}
\text{BE}(\textit{i}) = -E_{HF}(\textit{i}) - R_0^D(\textit{i}) - V(\textit{i}) - R_s(\textit{i}) - \phi
\end{equation}

\text{E}_{HF} is the Hartree–Fock orbital energy for the isolated atom with zero defined at the vacuum level. \textit{R}_0^D is the ‘dynamic’ intra-atomic relaxation energy for the isolated atom. This energy represents the re-arrangement of the electrons following photoemission in the new potential field created by the departure of the photoelectron [29]. The effect is to lower the total electronic energy in the post-emission state compared to freezing the orbitals, increasing the photoelectron kinetic energy and hence decreasing the binding energy determined. \textit{V} is the solid-state (or Madelung) potential, that is, the shift in the pre-photoemission orbital energy due to moving from an isolated atom into the ionic solid. It is essentially due to the acquisition of a valence charge in bonding, and can be simply and accurately modelled by the ‘charged-shell’ approach [16]. \textit{R}_s^D is the ‘dynamic’ extra-atomic relaxation energy, and relates to the movement of bonding electrons towards the core hole following photoemission. Finally, \textit{\phi} is the sample work function.

The kinetic energy of the \textit{KLL} Auger electron, KE(\textit{KLL}), is given by

\begin{equation}
\text{KE(\textit{KLL})} = \text{BE}(1\textit{s}) - \text{BE}(2\textit{p}) - F(2\textit{p}, 2\textit{p}) + R_s
\end{equation}

\textit{F}(2\textit{p}, 2\textit{p}) is the interaction energy of the two final-state holes in the 2\textit{p} level. \textit{R}_s is the ‘static’ relaxation energy, which arises in this model from the shift in the 2\textit{p} orbital binding and relaxation energies following the initial photoemission from the 1\textit{s} orbital.

Now two Auger parameters are defined. The first is the sum of the 1\textit{s} binding energy and the \textit{KLL} kinetic energy

\begin{equation}
A = \text{BE}(1\textit{s}) + \text{KE(\textit{KLL})}
\end{equation}

\begin{equation}
= 2\text{BE}(1\textit{s}) - 2\text{BE}(2\textit{p}) - F(2\textit{p}, 2\textit{p}) + R_s
\end{equation}

\begin{equation}
= 2(-E_{HF}(1\textit{s}) - R_D(1\textit{s}) - V(1\textit{s}) - R_D(1\textit{s}) - \phi) - 2(-E_{HF}(2\textit{p}) - R_D(2\textit{p}) - V(2\textit{p}) - R_D(2\textit{p}) - \phi) - F(2\textit{p}, 2\textit{p}) + R_s
\end{equation}
In the charged-shell model, \( V(1s) = V(2p) \) so
\[
A = 2\{E_{HF}(2p) - E_{HF}(1s) + R_D(2p) - R_D(1s) + R_D(2p) - R_D(1s)\} \]
\[- F(2p, 2p) + R_s \quad (6)
\]
Comparing chloride ions in one crystal with those in another, we can drop terms which are defined for the isolated atom. Also the two-hole interaction energy \( F(2p, 2p) \) can be assumed constant, so that
\[
\Delta A = 2\Delta\{R_D^{\infty}(2p) - R_D^{\infty}(1s)\} + \Delta R_s \quad (7)
\]
\( R_s \) is the difference between the total extra-atomic relaxation energy for the two-hole state and twice the extra atomic relaxation energy for the one-hole state, i.e.
\[
R_s = R_{D}^{\infty}(2p, 2p) - 2R_{D}^{\infty}(2p) \quad (8)
\]
From classical theory where the relaxation energy is proportional to the square of the change in charge,
\[
R_s = 2R_{D}^{\infty}(2p) \quad (9)
\]
giving
\[
\Delta A = 4\Delta R_{D}^{\infty}(2p) - 2\Delta R_{D}^{\infty}(1s) \quad (10)
\]
The other Auger parameter is defined as
\[
\xi = KE(KLL) - BE(1s) + 2BE(2p) \quad (11)
\]
\[= F(2p, 2p) + R_s \quad (12)\]
so that
\[
\Delta \xi = 2\Delta R_{D}^{\infty}(2p) \quad (13)
\]
hence
\[
\Delta R_{D}^{\infty}(2p) = \frac{1}{2} \Delta \xi \quad (14)
\]
\[
\Delta R_{D}^{\infty}(1s) = \Delta \xi - \frac{1}{2} \Delta A \quad (15)
\]

**EXPERIMENTAL**

Samples of LiCl, NaCl, KCl, RbCl and CsCl were obtained in powder form from BDH Chemicals Ltd., Parkstone, Poole, Dorset, Gt. Britain, and Koch-Light Laboratories Ltd., Colnbrook, Buckinghamshire, Gt. Britain. They were dried in an oven at 120°C prior to mounting for XPS analysis by pressing them into indium foil. The sample probe was heated to 100°C for 24 h in the spectrometer vacuum and then the system was baked at 100°C for 48 h before sample analysis.
### TABLE 1
PEAK POSITION, AUGER PARAMETER AND RELAXATION ENERGY DATA

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cl 1s BE (eV)</th>
<th>Cl 2p BE (eV)</th>
<th>Cl KLL KE (eV)</th>
<th>$-\xi$</th>
<th>$A$</th>
<th>$\Delta R_{\text{Cl}}^{1s}$ (1s)</th>
<th>$\Delta R_{\text{Cl}}^{2p}$ (2p)</th>
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<tbody>
<tr>
<td>LiCl $\alpha = 2.98$</td>
<td>2816.7</td>
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<td>1.22</td>
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<td>2391.3</td>
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<td>5208.3</td>
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<td>0.62</td>
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<td></td>
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<td>38.5</td>
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<td>NaCl $\alpha = 3.38$</td>
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<td>39.3</td>
<td>5206.9</td>
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<td>0.52</td>
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<td>38.6</td>
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<td>0.87</td>
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<td>2391.0</td>
<td>38.6</td>
<td>5206.4</td>
<td>1.50</td>
<td>0.87</td>
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<td>KCl $\alpha = 4.30$</td>
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<td>2391.2</td>
<td>38.7</td>
<td>5206.5</td>
<td>1.35</td>
<td>0.82</td>
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<tr>
<td></td>
<td>2815.0</td>
<td>192.5</td>
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<td>38.8</td>
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<td>0.77</td>
</tr>
<tr>
<td></td>
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<td>37.5</td>
<td>5207.7</td>
<td>1.95</td>
<td>1.42</td>
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</table>

* Flood gun set to 4 V, 0.2 mA.
The instrument used was a VG ESCA 3 mk.II with a monochromatic Ag Lα X-ray source [30] running at 14 kV anode potential and 40 mA emission current. 4 mm slits were used at the analyser entrance and the pass energy was set to 50 eV in the CAE mode. Typical operating pressures were in the $1-4 \times 10^{-9}$ Torr range. To effect control of the specimen surface charge, a VG LEG 51 electron flood gun was employed. The emission current was constant at 0.2 mA and the accelerating potential was 6 V, which has been found to minimize differential charging across the kinetic energy range of the spectrum [31].

Spectra were recorded digitally by a VGS1000 data system over periods of 8–16 h per specimen. Each chloride material was run at least four times until four reproducible sets of data were taken (hydration being the major problem).

RESULTS

The measured peak positions for chlorine in the alkali metal chlorides studied are presented in Table 1. These are referenced to the vacuum level

![Graph](image)

Fig. 1. Auger parameter vs. bond polarizability for chloride ions in alkali metal chlorides.
and are shifted (by the same amount) from the ‘true’ values by the action of the flood gun. In Fig. 1, the values for the Auger parameters $\xi$ (Fig. 1a) and $A$ (Fig. 1b) are plotted against the metal—chlorine bond polarizability, $\alpha$. This was calculated using the Lorentz—Lorenz relationship \cite{12, 32} from literature values of refractive index \cite{33} and unit cell parameters \cite{34}. The data for LiCl have been excluded from the calculation of the regression lines shown, as these samples were found to exhibit substantial oxygen peaks, indicative of hydrolysis, a persistent problem with this material \cite{18}. CsCl also exhibited some oxygen, which may bear on the anomalous $A$ values, but the data are included in the calculation of the regression lines nonetheless. The regression lines have been extended to $\alpha = 0$ to provide base values of $\xi$ and $A$; $\Delta\xi$ and $\Delta A$ values are calculated from the data points as differences from the $\alpha = 0$ values.

In Fig. 2, values of $\Delta R_D^{\text{ex}}(1s)$ and $\Delta R_D^{\text{ex}}(2p)$ calculated from $\Delta\xi$ and $\Delta A$

![Graph](image)

**Fig. 2.** Change in extra-atomic relaxation energy associated with photoemission from (a) 1s and (b) 2p orbitals vs. bond polarizability for chloride ions in alkali metal chlorides.
are plotted against the bond polarizability. Again, the data for LiCl have been excluded from the calculation of the regression lines.

DISCUSSION

The variability of the data is of the order of the differences observed between chlorides. This is mainly due to two experimental difficulties. The first is the tendency of these samples to hydrolyse. We have noticed in a wider study of chlorides that hydration causes an increase in relaxation energy of a few eV. It proved difficult to keep absolutely dry the outermost few nm of material probed by XPS. The second difficulty lies in the rather low count rates we experienced with the monochromatic Ag La source (a few tens of c.p.s. at most). The resultant uncertainty in the individual peak positions is further compounded when the Auger parameters are calculated (for example δ contains four peak positions).

In keeping with other studies from this laboratory [12] we have chosen to correlate relaxation energy with polarizability. Our calculated values for α correspond well to determinations made by a variety of methods [35]. A linear relationship of relaxation energy with bond polarizability is a central feature of the theoretical treatment of the effect. In the study of sodium salts Kuroda et al. [21] used the following expression

\[ E_p = \frac{-n\Delta q}{r^2} + \frac{nb\mu^2}{2r^3} + \frac{n\mu^2}{2\alpha^*} + \frac{nB}{r^5} \]  \( (16) \)

where \( E_p \) = polarization (relaxation) energy, \( n \) = number of nearest neighbour ions, \( \Delta q \) = change in charge upon hole creation, \( r \) = interatomic distance, \( b \) = structure factor, \( \mu = \text{induced dipole} = \alpha^*\Delta q(1 + b\alpha^*/r^3)/r^2 \), \( \alpha^* \) = polarizability of neighbouring ion, and \( B \) = constant so that \( dR/dr = 0 \) at equilibrium.

Aitken et al. [11], in the study of Cl compounds in the gas phase, successfully applied the simpler relationship

\[ R_{D}^a = \alpha(\Delta q)^2/2 \]  \( (17) \)

where \( \alpha \) is related to the bulk polarizability of the medium.

A relationship of this type provides a basis for an interpretation of Fig. 2. The slopes of the best fit lines will be given by

\[ \frac{\Delta R_{D}^a}{\Delta \alpha} = f[(\Delta q)^2] \]  \( (18) \)

which refers to the change in core charge perceived by the bonding (3p) electron on photoemission from the 1s (Fig. 2a) or 2p (Fig. 2b) orbital. From Slater’s screening coefficients [36] it is to be expected that \( \Delta q \) will be different in each case; viz., 1 on the loss of a 1s electron and 0.85 on the
loss of a 2p electron. Although the intercepts of the best fit lines in Fig. 2 have been chosen somewhat arbitrarily, the relative slopes should be given by

\[
\frac{\Delta R_{1s}^P(2p)}{\Delta \alpha} / \frac{\Delta R_{1s}^P(1s)}{\Delta \alpha} = \frac{f(\Delta q)^2(2p)}{f(\Delta q)^2(1s)} = \frac{(0.85)^2}{(1)^2}
\]

In fact the ratio of slopes gives \( \Delta q^2(2p)/\Delta q^2(1s) \equiv 0.8^2 \) which is satisfactory in view of the scatter in the data. A plot of \( \Delta R_{1s}^P(1s) \) vs. \( \Delta R_{1s}^P(2p) \) and the line predicted from the Slater screening coefficients is given in Fig. 3.

**CONCLUSIONS**

In view of the experimental difficulties experienced in this study it is impossible to draw conclusions from these data with confidence. The indications are that in the alkali metal chlorides the extra atomic relaxation energy increases linearly with bond polarizability. The data were not of sufficient precision to determine any effect of the structure changes going from the NaCl to CsCl types. The magnitude of the relaxation appears to be determined in part by the change in screening of the nuclear charge on photoemission, and the approach outlined here may be useful in determining relative screening coefficients for core-like orbitals.
ACKNOWLEDGEMENT

The authors acknowledge with thanks an EMRA award from BP Research.

REFERENCES

The Use of an Electron Flood Gun When Adopting Monochromatic AgLα Radiation for the XPS Analysis of Insulators

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To combat the problem of specimen charging when analysing insulators with a high energy monochromatic AgLα x-ray source for XPS in the VG ESCA3, the application and use of a low energy electron flood gun is investigated. It is found that individual specimens can require widely differing ‘optimum’ conditions for the satisfactory management of surface charging. However, the use of an accelerating voltage of at least 6 V, together with an emission current of at least 0.25 mA, appears to be satisfactory for the majority of specimens. It is concluded that an electron flood gun, when properly set-up, can play an important role in gaining chemical state information from non-conducting materials using XPS, though it is noted that the use of secondary binding energy referencing may still be necessary.

INTRODUCTION

It has been recognized for some time that the XPS analysis of non-conducting materials differs from analysis of conducting species in that the ejection of photoelectrons from the sample leads to the build-up, with time, of a significant degree of surface charge. The flow of electrons from the spectrometer to the sample that is available for conductors and which minimizes charging effects is unavailable for insulators, for which large changes in both peak position and shape result.1

The tendency to charge is counteracted, when monochromatic radiation is used, by the flux of low energy electrons originating from the window of the x-ray source. Thus any shifts produced are generally less than one electronvolt.2-4 However, the situation becomes much more serious when monochromatic radiation is employed, as in this study, where the loss of the Bremsstrahlung component results in a much less intense x-ray beam, unable to excite sufficient secondary electrons from the x-ray set window to compensate fully for any sample charging. The resulting peak shifts can be of the order of hundreds of electronvolts, which is clearly unsatisfactory.

Since the technique of XPS depends on the ability to measure accurately individual peak positions for chemical state information, several methods have been employed in an attempt to overcome this problem, the more popular ones being:

(a) To assign a fixed value to the C 1s peak produced by the presence of adsorbed adventitious carbonaceous material, and reference all other peaks to this.5 This method remains popular despite misgivings.5,7

(b) To assign a fixed value to a key peak in the support material, e.g. Al 2p in Al₂O₃, and use this as a reference.6 This method can be of use, but oversimplifies the problem.

(c) To make use of quantities such as the Auger parameter, which, being a measure of separation between photoelectron and Auger peaks, allows characteristic values to be assigned for individual systems, these values being both sensitive to chemical state and insensitive to specimen charging, presuming the latter to be constant across the energy spectrum. This parameter has become popular following development work by Wagner10,11 and Castle and West,12 and is used in this and many other laboratories as a readily portable standard measurement for insulators.

(d) The removal of charging shifts by the application of an electron flood gun, first demonstrated by Huchital and McKeon.13

Essentially the electron flood gun consists of a tantalum filament which feeds electrons to a cylindrical cathode assembly, such that both the current and electron energy may be controlled. The use of this device allows the specimen surface charge to be managed and made uniform. The latter facility is important in the study of powders, particularly catalysts, as uneven surface charge (seen as peak broadening) may be eliminated.14-19

Although the use of an electron flood gun can prove successful, it has been noted by several workers10,15,16 that this arrangement is not always satisfactory for discontinuous systems (e.g. powders), and even for contiguous systems where there is no Fermi-level coupling, in which case determination of the sample work function, forced Fermi edge pinning20 or binding energy referencing are still required to achieve accurate binding energy values.

Furthermore, attention has been drawn to the possibility that stray fields within the analyser vacuum space may be capable of affecting the current delivered to the sample surface and hence distorting the linearity of the spectrometer energy scale.21,22 In particular, Jaegle and co-workers23 have commented upon the VG ESCA3 spectrometer, which we use for our studies with the monochromatic AgLα source.24 We need to ensure the linearity of the energy scale up to ~3000 eV, which is twice the normal operating range.

In this paper the performance of the instrument in this respect will be evaluated and procedures developed...
for optimizing the flood gun settings to ensure energy scale linearity over 3000 eV.

EXPERIMENTAL

Powder samples of Si₃N₄, K₂SiF₆ and NaCl were obtained from Koch-Light Laboratories Ltd., Colnbrook, Buckinghamshire, UK. SiC was obtained from the Carborundum Company Ltd., Trafford Park, Manchester, UK. Both Si (100) (n-type) and SiO₂ (thermally grown ~2000 Å thick) were found in house, whilst thanks are due to Kodak Research, Harrow, UK., and BP Research Centre, Sunbury-on-Thames, UK. for supplies of mica and NaY zeolite, respectively.

All powdered samples were dried in an oven at 120 °C prior to mounting for XPS analysis by embedding them into indium foil. The planar samples were mounted on double-sided adhesive tape.

The instrument used was a VG ESCA3 Mk. II with a monochromatic AgLa x-ray source (6 mm x 1 mm x-ray line) operating at 14 kV anode potential and 40 mA emission current. 4 mm slits were used at the analyser entrance and the pass energy was set to 50 eV in the CAE mode. Operating pressures varied with sample, but remained in the range 1-8 x 10⁻⁹ mbarr. For the normalization of specimen surface charge, a VG LEG51 electron flood gun was used, the accelerating potential of which can be varied from 0 to 14 V. Flood gun emission currents were held at a value of at least 0.25 mA (see Fig. 2). The target area produced on collimation of the flood gun electrons is approximately 1 cm in diameter.

A VGS1000 datasystem recorded the spectra digitally for periods of time ranging from 4 hours up to 20 hours, depending upon the specimen. All spectra were recorded at a sample to analyser entrance angle of 45 degrees.

RESULTS

Figure 1 shows a plot of 'landing current', measured using a Keithley model 600B electrometer and an ion-cleaned copper specimen, produced by impinging flood gun electrons of varying energy over a 3000 eV retard (analyser) potential. Figure 2 demonstrates how this measured 'landing current' varies with the emission level in the flood gun filament when the retard potential is 2900 eV.

Figure 3 shows the variation in resolution of the Si Is peak (FWHM) with the applied flood gun voltage for a range of materials at constant emission current (0.25 mA), this being a reasonable setting following the results shown in Fig. 2. The points plotted were reproducible over four experiments. The source of the variation in FWHM for these materials, in which silicon has a single chemical state, is most probably due to the presence of potential gradients in the near surface region which are minimized by correct optimization of the electron flood gun. (The increase shown by the NaY zeolite is against the trend and probably results from partial decomposition). Figure 4 demonstrates the Si Is peak position and shape variation with applied flood gun potential for Si₃N₄.
Table 1 shows for silicon-based materials how the measured Si 1s–2p separation, i.e. the Si Kα x-ray transition, appears to change as a function of flood gun potential. This is clear evidence of an unacceptable non-linearity of the energy scale when the flood gun is used at its 0 V setting.

Figure 5 shows a plot of relaxation energies for silicon compounds acquired using a flood gun accelerating voltage of 0 V and an emission current of 0.20 mA. The poor correlation of these data, obtained with the monochromatic source, with those obtained with polychromatic sources emphasizes that the Auger parameter does not behave satisfactorily when differential charging is present. Figure 6 shows the same samples examined using 'optimized' settings, whereby the flood gun settings have been adjusted to give a minimal peak width coupled with a realistic 1s–2p separation. The raw data for these plots are given in Tables 2 and 3, respectively.

**Table 1. Variation of Si (1s–2p) separation with flood gun setting for silicon and silicon nitride**

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<table>
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**DISCUSSION**

We believe that the variation in landing current with analyser energy (Fig. 1) for a given set of flood gun parameters is due, in the case of the VG ESCA3 used in this study, to 'breakthrough' of fields from the retarding grid into the sample area. It would appear that the very low energy flood gun electrons (0 V energy) are deflected more readily than the higher energy electrons. We have found that this effect can be reduced somewhat by trial-and-error re-alignment of the flood gun. The point of concern here is that if the flood gun settings are inappropriate or the flood gun is misaligned, then the landing current (and hence the shift in surface charge) will vary as the analyser scans from 0 to 3000 volts—that is the peak shift applied by the flood gun to, say, the Si 2p peak will differ from that applied to the Si 1s peak. Even the Auger parameter will be affected and rendered meaningless under these conditions. Instruments utilizing a transfer lens will not suffer from this particular field breakthrough. However, variable stray fields may arise from a variety of sources and would give similar effects.

Clearly, the importance of using the optimum setting of accelerating voltage for the control of surface charge with a flood gun cannot be overstated. It is our
Figure 4. Variation of Si 1s peak position and shape with flood gun acceler­
ing potential, (Si$_3$N$_4$ sample).
experience that each sample needs to be ‘optimized’ individually in this respect. This is well demonstrated in Fig. 5 and Fig. 6, which follows the silicon chemistry study conducted by Bechstedt and co-workers, in which they calculated extra-atomic relaxation energies for both 1s and 2p orbitals from peak position shifts for 1s, 2p and KLL Auger lines. Their protocol has been followed in previous work from this laboratory, and only the equations themselves will be given here:

$$\Delta R_D^{(2p)} = 1/2\Delta \zeta$$

and

$$\Delta R_D^{(1s)} = 3/2 \Delta \zeta - \Delta A$$

where

$$\Delta R_D^{(2p)} = \text{extra atomic relaxation energy following creation of hole in 2p orbital}$$

$$\Delta R_D^{(1s)} = \text{extra atomic relaxation energy following creation of hole in 1s orbital}$$

$$\Delta A = \text{change in Auger parameter \textit{zeta}}$$

$$\Delta A = \Delta [BE(1s) + KE(KLL)]$$

$$\Delta = \text{change in the Auger parameter \textit{zeta}}$$

$$\Delta = \Delta [KE(KLL) - BE(1s) + 2BE(2p)]$$

Figure 5. 1s and 2p extra-atomic relaxation energy values for silicon compounds using OV flood gun accelerating potential and 0.20 mA emission current level.

Figure 6. 1s and 2p extra-atomic relaxation energy values for silicon compounds using optimized flood gun settings.
Thus through the measurement of 1s, 2p and KLL Auger peak positions, extra-atomic relaxation energies can be calculated as in Tables 2 and 3 from which the plots in Figs. 5 and 6 derive. The Bechstedt data is shown as crosses, with these data as circles, each circle being the average of five recorded values. A straight-line relationship appears to exist for 'corrected' silicon extra-atomic relaxation energy values of differing compounds. (It should be noted that the value for Si₃N₄ from Bechstedt's work appears to be an estimate, so that the value quoted here is probably more accurate.) Clearly, from behaviour such as shown in Figure 3, the application of a single flood gun accelerating voltage, be it 0 V or 10 V, is unsuitable, with each sample needing optimization in its own right. However, an acceptable range can be found once a certain level of bias is applied. An illustration of the way in which the optimum range can be found is shown in Fig. 7, where the positions of the Cl 1s, Na 1s and Cl 2p peaks for sodium chloride are plotted as a function of flood gun accelerating potential, the emission current being constant at 0.25 mA. The range in which the lines become parallel indicates the range of constancy for measurements such as the Auger parameter value. For sensitive materials, one would select a value for flood gun potential at the lower end of this range, to minimize specimen damage due to electron stimulated desorption etc. From the work conducted to date, if an arbitrary value is to be taken as capable of managing surface charge on all insulating samples, it would need to be at least 6 V. Such a level involves the use of low energy electrons, such that any specimen damage caused should be minimal, though we have noticed some beam-sample interaction, an example of which is the NaY zeolite shown in Fig. 3. However, in general there has been little or no effect—even after the lengthy periods of time necessitated by the low count rates experienced with the monochromatic AgLa source. The positioning of the electron flood gun in the VG ESCA3 appears to be critical. It must be far enough away from the sample being analysed to minimize contamination and heating effects, and needs to be directed accurately onto the sample to cause stabilization of the surface potential.

It can be seen in Fig. 1 that the current produced by the monochromatic AgLa x-rays themselves is very small and is, not surprisingly, a factor of 100 down from values expected for conventional XPS sources. Thus any specimen damage due to the x-rays themselves must be considered minimal, even for the periods of time for analysis outlined previously. This plot again demonstrates the suitability of higher accelerating potentials, certainly at least 6 V for flood gun electrons. It can also be seen from Fig. 2 that any instability present can be overcome by use of a flood gun emission current of at least 0.25 mA, together with the application of a 'correct' accelerating voltage. This is demonstrated well in Fig. 4 where the problem of peak broadening due to specimen charging can be seen, the 0 V setting for silicon nitride
being clearly unsatisfactory. Adjustment of the accelerating voltage can be seen to overcome the problem.

The achievement of the conditions necessary to give accurate internal standards, e.g. the Auger parameter, paves the way for a study of the relation of photoelectron peaks to those of applied reference materials. This can aid discussion of Fermi-edge pinning and the extent of band-bending in insulators. Preliminary results of this study will be presented elsewhere.28

XPS analysis of insulators. In the VG ESCA3 Mk. II spectrometer, when monochromatic AgLα radiation is employed, an accelerating voltage of at least 6 V, with an emission current of at least 0.25 mA, gives reproducible results (assuming the specimen to be sufficiently stable).

However, the use of secondary binding energy referencing by any of the methods outlined previously may still be appropriate, as noted by other workers, and this is currently being investigated.

CONCLUSIONS

The use of an electron flood gun has a role to play in the total management of surface charge build-up during XPS analysis of insulators. In the VG ESCA3 Mk. II spectrometer, when monochromatic AgLα radiation is employed, an accelerating voltage of at least 6 V, with an emission current of at least 0.25 mA, gives reproducible results (assuming the specimen to be sufficiently stable).

Acknowledgements

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REFERENCES

BIASED REFERENCING EXPERIMENTS FOR THE XPS ANALYSIS OF NON-CONDUCTING MATERIALS

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A method of “biased referencing”, involving the use of an electron flood gun and an internal reference such as a metal dot, is investigated for the XPS analysis of non-conducting materials. Methods of Cu, Au and Pt dot referencing are used for silica, copper and zeolite substrate materials, from which binding energy measurements accurate to ±0.1 eV can be obtained. Such binding energy values are not independent of the work function of the measured materials, such that vacuum level alignment rather than Fermi level alignment appears to be induced by the action of the electron flood gun.

1. Introduction

It is well known that the use of X-ray photoelectron spectroscopy (XPS) or ESCA for analysis of non-conducting materials can be hindered by the development of a surface charge which shifts the measured binding energies and can broaden peak widths [1]. When monochromatic X-ray sources are used, the shifts can be up to hundreds of electron volts. Even when standard polychromatic sources are used, which provide a source of low energy electrons from a nearby window, the charging shifts are often in the 1 to 10 eV range. In either situation, accurate measurements of electron binding energies for chemical state information are made much more difficult.

Since analysis of non-conducting materials is important in a wide variety of basic and industrial research areas, a number of different methods are used to try to circumvent the difficulties in obtaining useful information. Most of the

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methods can be placed in one of two categories:  
(1) charge compensation to minimise the influence of charging, or  
(2) use of internal standards, not sensitive to charging.  
Each of these methods have both advantages and disadvantages. 

Low energy electron flood guns, first reported by Huchital and McKeon [2] provide a method that compensates for charge build-up on the specimen. The required conditions for neutralisation appear to vary from specimen to specimen. This popular method has been used in this laboratory [3] for the compensation of built up charge on specimens analysed using a monochromatic high energy Ag La X-ray source (hv = 2984.3 eV). However as indicated by Barr [4] the use of an electron flood gun is not sufficient for attainment of accurate chemical state information. Other supporting methods, usually to relate the measured binding energies to the Fermi level of the spectrometer, must be included.

A variety of methods may be used instead of, or in addition to, a flood gun [5] to produce some type of internal standard to which measurements can be referenced. These methods include: adventitious carbon referencing [6]; layer deposition of Au [7–10] or organics [11,12]; production of mixtures with a known component; reference to a common chemical state in a series of compounds [13]; or use of charge independent parameters such as the Auger parameter [14,15].

As already suggested, some successful uses of XPS for analysis of insulators involve both use of a flood gun and an internal reference. This is so when Auger parameters are obtained with the assistance of a flood gun [3] and when secondary features of a peak are analysed, as for the catalysis work of Barr [4]. One potentially very useful method was introduced by Stephenson and Binkowski [10], and has recently been used by Landis and Martin [16]. For this “biased reference method” a gold dot is applied to an insulating specimen which is then flooded with electrons at a potential of 10 eV so that the Au 4f peak is shifted from 84 eV to an experimentally measured binding energy of 74 eV. According to refs. [10,16], this procedure allows the Fermi level of the insulator surface to align to that of gold and accurate relative electron binding energies can be obtained.

The purpose of the present study was to investigate the accuracy of the combined use of a low energy electron flood gun and an internal standard, such as Au, for the measurement of the binding energy of electrons emitted from specimens isolated from the spectrometer. Particular attention has been given to measurements of the relative binding energies of metal dots evaporated onto insulating specimens. With dots both in contact with each other and isolated, these specimens provide a severe test of the Stephenson and Binkowski model [10] and the results do not fully support their analysis. However, the method is, nonetheless, very useful as it provides a reproducible measuring procedure.
2. Background

Adequate understanding of the results of this paper involves several different factors which will be covered separately before they are combined in discussion of the results. These items include: effect of flood gun bias; Fermi level and vacuum level alignment; and the Stephenson and Binkowski model.

2.1. Flood gun bias – charge neutralisation and stabilisation of the surface potential

The primary purpose of an electron flood gun is to neutralise charge build-up created by electron loss during an experiment. The flood gun arrangement used for this work is shown in fig. 1. It is relatively easy to imagine that if a specimen is positively charged, electrons will be attracted to the specimen and the charge build-up will be neutralised. However, it has been pointed out by Hunt et al. [17] that flood gun operation does not work quite so simply.

Consider a flood gun biased at a voltage \(-V_f\) (fig. 2). Electrons will leave the filament with energy \(e(\phi_f - V_f)\) relative to ground, where \(\phi_f\) is the work function of the filament. These electrons can arrive at the specimen as long as

![Fig. 1. The experimental arrangement of sample, analyser and electron flood gun (latter in same plane as monochromatic X-rays).](image-url)
After Ref 15

e \Phi_e \equiv -eV_f + e \Phi_f

Fig. 2. The function of the electron flood gun.

the specimen surface potential \( \phi_s \) is less than \( (\phi_f - V_f) \). Therefore, the surface potential of the specimen \( \phi_e \) would rise to \( \phi_e = (\phi_f - V_f) \) as long as the flood gun can provide a current at least equal to the photo-current. Now the Fermi level of the specimen is at a lower potential than the surface so that the potential of the Fermi level relative to ground is \(-V_s = -V_f + (\phi_f + \phi_f)\) where \( \phi_f \) is the work function of the specimen.

It is interesting to note that even if the flood gun bias is 0 V, the specimen surface potential, \( \phi_s \), and its Fermi level may both be at some finite voltage relative to ground, due to the effects of different work functions. In most real situations there will be several sources of currents toward and away from the specimen that will determine the actual potential of the specimen surface. In addition to the photoelectrons lost, there may be electron currents from the X-ray source, ion gauges or other filaments in the system. Changes in the flow of electrons into the spectrometer could also influence the specimen. The flood gun potential defines the surface potential (or local vacuum level) of an isolated specimen when the possible current from the flood gun to the specimen can exceed other possible currents, and no other greater energy electrons are present in enough quantity to drive the surface potential more negative than the flood gun.

2.2. Fermi level and vacuum level alignment

The differences in XPS measurements made on insulating and conducting specimens have been considered by many workers. Much of the discussion
below follows the arguments of Lewis and Kelly [18] who considered Al and Au evaporated onto SiO₂. As emphasised by Barr [4], Fermi level coupling or lack thereof determines what is measured. For the purpose of this discussion consider a wafer of quartz with two dots of different metals deposited. Three situations will be examined where the metal dots are: (1) connected to each other and in contact with the spectrometer; (2) not connected to each other and not in contact with the spectrometer; (3) not in contact with the spectrometer but in contact with each other.

(1) When the metal dots are connected to each other and in contact with the spectrometer, we have the standard case of metal analysis by XPS. When a photon of energy $h\nu$ causes a photoelectron to be emitted the kinetic energy of that photoelectron is:

$$E_{KE} = h\nu - e\phi_B - e\phi_s,$$

where $E_{KE}$ is the kinetic energy of the electron outside the metal surface, $\phi_B$ is the binding energy of that electron referenced to the Fermi level of the metal and $\phi_s$ is the work function of the metal. If we consider measuring the energy of that electron by applying a voltage between the specimen and the spectrometer the voltage, $V$, required to just prohibit the electron from getting to the spectrometer (fig. 3A) is defined by:

$$eV - e\phi_s + e\phi_{sp} = E_{KE} = h\nu - e\phi_B - e\phi_s,$$

where $\phi_{sp}$ is the work function of the spectrometer. This equation applies to

---

Fig. 3. Energy level diagrams for metal dots: (A) in contact with each other, and (B) isolated.
both metal dots so that the differences between voltages measured for photopeaks from metals 1 and 2 is:

\[ V_1 - V_2 = \phi_{B1} - \phi_{B2}, \]  

or that the difference between the voltages equals the difference between the binding energies.

(2) When the metal dots are not in contact with the spectrometer and not in contact with each other, the situation is more complex. Due to differences in X-ray yield and flux to the two regions the potentials of the dots may not be easily defined or the same. The use of the flood gun as described earlier allows the potential of the specimen to be defined by the energy of the flood gun electrons. In this case the vacuum levels of the metals (and the insulating surface) are aligned to the level defined by the flood gun \( \phi_e \) (fig. 3B). For a photoelectron emitted from metal 1 we still have:

\[ E_{KE1} = h\nu - e\phi_{B1} - e\phi_{S1}, \]  

where \( \phi_{B1}, \phi_{S1} \) and \( E_{KE1} \) are the energies and work function referring to metal 1. However, the voltage, \( V_1 \), required to keep the electron from reaching the spectrometer is now:

\[ eV_1 - e\phi_e + \phi_{sp} = E_{KE1} = h\nu - e\phi_{B1} - e\phi_{S1}. \]  

A similar equation applies to metal 2 so that:

\[ V_1 - V_2 = \phi_{B2} - \phi_{B1} + \phi_{S2} - \phi_{S1}. \]  

In this case, the difference in measured voltage is not the difference in electron binding energies, but contains a term involving the work functions of the two metals.

(3) When the two metal dots are in contact with each other the Fermi levels are aligned even when the metals are not connected to the ground or the spectrometer. This combined Fermi level will be at some potential \( \phi_{fe} \) relative to earth and the voltage required to stop the electron will be:

\[ V_1 - \phi_{fe} + \phi_{sp} - \phi_{S1} = E_{KE1} = h\nu - \phi_{B1} - \phi_{S1}, \]  

and for both metals we have:

\[ V_1 - V_2 = \phi_{B2} - \phi_{B1}. \]  

This analysis tells us that the use of a flood gun for analysis of isolated or overall insulating specimens defines the measured voltage only to values within possible differences in the work function values themselves (unless, from the model to follow, the Fermi levels are aligned). A complex insulating specimen might have metal particles both in contact with each other and isolated from each other so that two or more binding energies might be observed.
2.3. Biased Fermi level alignment

In the course of an XPS study of SiO₂, Stephenson and Binkowski [10] presented an argument to show that in certain conditions it was possible to force the Fermi levels at the surface of silica to align to those of Au (or any other metal) evaporated on the surface. In their model, for such alignment to occur several conditions must be present including an external potential applied to the surface (via the electron flood gun) and a source of electrons for the conduction band of the SiO₂ (X-ray excited electrons within the X-ray penetration depth of the SiO₂). According to this approach, when the bias voltage of the electron flood gun is sufficiently large (roughly equal to the difference between the work functions of the two materials) the Fermi level of the metal is lowered to that of the insulator. The X-ray excited electrons provide a source of electrons that allows the Fermi levels to be pinned. A much more complete discussion is found in their paper [10].

Although some of their argument is presented in terms of a metal-insulator junction, it is really the whole surface of the material from which XPS electrons are detected. In some sense it is a material-vacuum junction where a potential at the vacuum level might cause the Fermi levels of the surface components under the electron beam to align. To support their model Stephenson and Binkowski show that the voltage measured for Au 4f and Si 2p peaks vary independently with flood gun energy, until the flood gun voltage is 4 V or greater.

If their argument is correct it would enable XPS binding energy measurements of insulators to be referenced to the Fermi level of a deposited metal producing binding energy measurements referenced in the same way for both metals and insulators. This would avoid the differences in measurements discussed above for situations (1), (2) and (3) where only the vacuum levels of isolated materials were aligned, while Fermi level alignment occurred for the metals in contact.

3. Experimental

The instrument used for XPS analysis was a VG ESCA3 MkII spectrometer with a monochromatic AgLα X-ray source [19] working at 14 kV anode potential and 40 mA emission current. The spectrometer pass energy was set to 50 eV in the CAE mode, whilst 4 mm slits were used throughout. Spectrometer operating pressures remained in the range (1–3) × 10⁻⁹ mbar.

For control of specimen surface charge a VG LEG51 electron flood gun was employed, with a range of accelerating potentials available from 0–14 V. The emission currents used were 0.3 mA, following a previous study [3].
Spectra were recorded digitally by a VGS1000 data system over periods of up to 18 h per specimen because of the low X-ray flux. The system was calibrated by examining Cu lines at 932.7 BE (2p₁/₂), 75.1 BE (3p₁/₂) and 919.1 KE (LMM Auger).

Specimens used included fused silica (Vitreosil, derived from quartz crystal), copper and NaY zeolite on which copper, gold and/or platinum dots were deposited. The 2–3 mm dots were placed singly or in various combinations to test the accuracy with which binding energies can be referenced for various cases of metals in contact with each other and/or the spectrometer. The dots needed to be carefully positioned in the X-ray beam since the beam dimensions were only 6 mm × 1 mm.

4. Results

As an initial test of the gold biased referencing method for our experimental arrangements, Au dots were evaporated onto copper and silica substrates. The copper was mounted with an insulating tape so that both specimen surfaces were isolated from direct electrical contact with the spectrometer. For the metal specimen the Cu 2p binding energy when referenced to the Au 4f is generally constant over the 0–10 V bias range of the electron flood gun and the Au 3d–4f separation is also nearly constant (table 1). (Typical errors in the measurement of individual peak positions are ±0.1–0.2 eV, whilst for peak separations the error is ±0.2–0.4 eV.)

In contrast, the data for silica shown in fig. 4 (and table 2) show a region of rapid change before the onset of a plateau region for Si 2p, Si 1s, O 1s and Si KLL peak positions, indicating that accurate referencing is only achieved for applied bias voltages of 6 V and greater. These results tend to reproduce the results of Stephenson and Binkowski [10] and support the biased referencing method by showing that with an appropriate bias of an insulating surface, the binding energies of the Si and Au photopeaks are following each other and can referenced to the same energy level.

However, the data shown in fig. 5 (and table 2) also shows the existence of a trend that appears to contradict or at least confuse the model proposed [10] to explain why biased referencing works. Not only do the Si 1s and Si 2p photopeaks track the Au above 6 eV, but the same trend is followed by the material parameters which should be charge independent, i.e. the Auger parameters (A' and A''), the Si 1s–2p peak separation and even the Au 3d–4f peak separation. These later results suggest that the use of a flood gun does something more than just cause the Fermi levels of SiO₂ and Au to align when a sufficiently large flood gun potential is applied. Differences in the Au 3d and Au 4f peak energies as a function of potential show that the surface charge on the specimen changes with electron kinetic energy during XPS measurement
Table 1
Results for Au dot placed onto copper substrate

<table>
<thead>
<tr>
<th>Flood gun bias (V)</th>
<th>Cu2p3/2</th>
<th>CuLMM</th>
<th>$A_{Cu}$</th>
<th>O1s</th>
<th>C1s</th>
<th>Au3d5/2</th>
<th>Au4f7/2 (x)</th>
<th>Au3d–4f</th>
<th>Au_shift (84 – x)</th>
<th>Cu2p3/2 (ref. to Au 4f7/2)</th>
<th>Cu2p3/2 – Au4f7/2</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>931.6</td>
<td>–</td>
<td>–</td>
<td>530.5</td>
<td>–</td>
<td>2205.3</td>
<td>83.1</td>
<td>2122.2</td>
<td>0.9</td>
<td>932.5</td>
<td>848.5</td>
</tr>
<tr>
<td>2</td>
<td>930.1</td>
<td>919.2</td>
<td>1849.3</td>
<td>528.9</td>
<td>282.1</td>
<td>2203.9</td>
<td>81.3</td>
<td>2122.3</td>
<td>2.7</td>
<td>932.8</td>
<td>848.8</td>
</tr>
<tr>
<td>4</td>
<td>928.5</td>
<td>922.4</td>
<td>1850.5</td>
<td>526.5</td>
<td>280.0</td>
<td>2201.7</td>
<td>79.1</td>
<td>2122.6</td>
<td>4.9</td>
<td>933.0</td>
<td>849.0</td>
</tr>
<tr>
<td>6</td>
<td>926.3</td>
<td>923.2</td>
<td>1849.5</td>
<td>525.0</td>
<td>278.4</td>
<td>2199.7</td>
<td>77.2</td>
<td>2122.7</td>
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<td>933.1</td>
<td>849.1</td>
</tr>
<tr>
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<td>925.6</td>
<td>1850.3</td>
<td>523.6</td>
<td>276.9</td>
<td>2198.5</td>
<td>76.9</td>
<td>2122.6</td>
<td>8.1</td>
<td>932.8</td>
<td>848.8</td>
</tr>
<tr>
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<td>922.9</td>
<td>928.8</td>
<td>1851.7</td>
<td>521.0</td>
<td>274.6</td>
<td>2196.3</td>
<td>73.8</td>
<td>2122.5</td>
<td>10.3</td>
<td>933.2</td>
<td>849.1</td>
</tr>
</tbody>
</table>
using low voltage flood gun bias. Such changes in surface charge are due to the field penetration problem originating from the analyser entrance grids [3].

The differences in behaviour of the Au on Cu and Au on SiO₂ suggested an additional experiment involving both Au and Cu on SiO₂. Non-contacting
Table 2
Results for Au dot placed onto silica substrate

<table>
<thead>
<tr>
<th>Flood gun bias (V)</th>
<th>Si 1s</th>
<th>Si KLL</th>
<th>Si 2p</th>
<th>$A_{2p}^s$ (1s + KLL)</th>
<th>$A_{2p}^s$ (2p + KLL)</th>
<th>Si 1s-2p</th>
<th>O 1s</th>
<th>Au 3d$_{5/2}$</th>
<th>Au 4f$_{7/2}$</th>
<th>$\Delta$Au$_{shift}$ (84 - x)</th>
<th>Si 1s (ref. to Au 4f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1843.7</td>
<td>1609.0</td>
<td>108.1</td>
<td>3452.7</td>
<td>1717.1</td>
<td>1735.6</td>
<td>535.8</td>
<td>2205.0</td>
<td>90.2</td>
<td>2114.8</td>
<td>-6.2</td>
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<tr>
<td>2</td>
<td>1840.5</td>
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<td>3452.6</td>
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<td>1737.2</td>
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<td>2119.1</td>
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<tr>
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<td>1839.3</td>
<td>1614.3</td>
<td>99.1</td>
<td>3453.6</td>
<td>1713.4</td>
<td>1740.2</td>
<td>527.9</td>
<td>2202.5</td>
<td>79.8</td>
<td>2122.7</td>
<td>4.2</td>
</tr>
<tr>
<td>6</td>
<td>1837.7</td>
<td>1615.7</td>
<td>96.5</td>
<td>3453.4</td>
<td>1712.2</td>
<td>1741.2</td>
<td>525.7</td>
<td>2200.5</td>
<td>77.1</td>
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</tr>
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<td>1835.8</td>
<td>1617.3</td>
<td>94.8</td>
<td>3453.1</td>
<td>1712.1</td>
<td>1741.0</td>
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<td>75.1</td>
<td>2123.0</td>
<td>8.9</td>
</tr>
<tr>
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<td>93.2</td>
<td>3452.7</td>
<td>1712.4</td>
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<td>2196.3</td>
<td>73.9</td>
<td>2122.4</td>
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</tr>
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<td>91.3</td>
<td>3452.8</td>
<td>1712.3</td>
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<tr>
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<td>1712.4</td>
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<td>2192.2</td>
<td>70.1</td>
<td>2122.1</td>
<td>13.9</td>
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</table>
dots allowed both Si and Cu to be referenced to Au as an additional test of the biased referencing method. In addition, as there is no fundamental reason to choose Au for the reference, Si could be referenced to the Cu $2p_{3/2}$ line.
As found for the earlier results, Cu and Si peak positions vary rapidly with flood gun potential when referenced to Au until a stable region is obtained around 5 or 6 V (fig. 6 and table 3). A similar trend occurs for the Au 4f referenced to Cu (fig. 7), but not much change is observed when the Si 1s peak is referenced to Cu (fig. 7). This is probably due to the fact the Si 1s – Cu 2p peak separation is smaller than that for the Si 1s – Au 4f, allowing any field penetration effects present across the 3000 eV energy range to be seen more clearly. However, the Si 1s binding energy values obtained in the plateau region for the Cu and Au referencing are slightly different. If this difference were real it would support vacuum level alignment as opposed to Fermi level alignment (situation (2) rather than situation (3) in section 2.2).

In order to clearly determine if the observed difference was due to vacuum level alignment or Fermi level alignment, a pair of metals with greater differences in work functions were chosen. According to the Handbook of Chemistry and Physics, the work function difference for Pt and Cu should be...
Table 3
Results for Au and Cu dots placed onto silica substrate

<table>
<thead>
<tr>
<th>Flood gun bias (V)</th>
<th>Si 1s</th>
<th>Si 2p</th>
<th>Si 1s–2p</th>
<th>Au 3d_{5/2} (x)</th>
<th>Au 4f_{7/2} (y)</th>
<th>Cu 2p_{3/2} (932.7 – y)</th>
<th>Au 3d–4f (ref. to Au 4f)</th>
<th>Si 1s (ref. to Cu 2p)</th>
<th>Cu 2p – Au 4f</th>
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<td>0</td>
<td>1843.2</td>
<td>106.2</td>
<td>1737.0</td>
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<td>72.2</td>
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<td>920.5</td>
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<td>70.2</td>
<td>13.8</td>
<td>918.5</td>
<td>14.2</td>
<td>2122.1</td>
</tr>
</tbody>
</table>

*Reference value.*
approximately 1 eV as compared to 0.5 eV for Au and Cu, since the work function values for Cu, Au and Pt are 4.65, 5.10 and 5.65 respectively.

Consequently, three types of conditions were created corresponding to the three situations proposed in section 2.2. One specimen was copper with Au and Pt dots deposited. The second specimen was SiO₂ deposited with isolated Pt and Cu dots, while the third was SiO₂ with connected Pt and Cu dots. The results shown in table 4 reflect earlier predictions, with the Au and Pt dots on copper connected to the spectrometer producing a Cu 2p – Pt 4f peak separation (861.7 eV) essentially identical to that measured for Pt and Cu dots in contact on SiO₂ (861.6 eV), whereas the Cu 2p – Pt 4f value (860.6 eV) for the Pt and Cu dots isolated on SiO₂ differs from the others by approximately 1 eV. Similarly, when monitoring the Cu 2p – Pt 3d peak separation a similar discrepancy is apparent.

It is interesting to note that when the reference metal dots are separated, the referenced position of the Si 1s is 1843.7 eV when referenced to copper and 1842.8 eV when referenced to platinum, as would be predicted by work
function differences of the two metals. However, when the reference dots are in contact, the Si 1s referenced to copper becomes 1843.0 eV whilst that referenced to platinum becomes 1843.1 eV. Thus their values are approximately equal, as would be expected, though the drift of the “corrected value” to 1843.1 eV reflects a greater movement in that referenced to copper than for platinum in the separated condition, since the Si 1s drifts towards 1842.8 eV rather than 1843.7 eV. This might be due to the ability of the copper 3s electrons to be able to enter the vacant orbitals present in the Pt 4f levels, which is behaving as a transition metal.

The use of the biased referencing technique for vitreous SiO₂ with respect to metal deposits of Cu, Au and Pt enables a quantitative measure to be applied to the possible energy position of the Si 1s peak in this material/chemical environment, since the spectrometer work function is known to be set to 4.5 eV, and we appear to be measuring binding energies with respect to the vacuum level. Thus its position can be accurately defined as that referenced to the vacuum level, plus Δw, when Δw is the change in work function between the reference metal and the spectrometer itself: i.e.

when referenced to Au 4f₇/₂:

\[ \text{Si 1s} = 1843.6 + (5.10 - 4.5) = 1844.2 \text{ eV}, \]
### Table 4
Results for the Pt-based experiments

(1) Pt and Au on Cu

<table>
<thead>
<tr>
<th></th>
<th>Au 3d&lt;sub&gt;3/2&lt;/sub&gt;</th>
<th>Au 4f&lt;sub&gt;1/2&lt;/sub&gt;</th>
<th>Au 3d&lt;sub&gt;5/2&lt;/sub&gt;</th>
<th>Pt 3d&lt;sub&gt;3/2&lt;/sub&gt;</th>
<th>Pt 4f&lt;sub&gt;1/2&lt;/sub&gt;</th>
<th>Pt 3d&lt;sub&gt;5/2&lt;/sub&gt;</th>
<th>Cu2p – Pt4f</th>
<th>Cu2p – Pt3d</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu2p&lt;sub&gt;3/2&lt;/sub&gt;</td>
<td>932.9</td>
<td>2207.2</td>
<td>84.1</td>
<td>2123.1</td>
<td>2122.1</td>
<td>71.2</td>
<td>2050.9</td>
<td>861.7</td>
</tr>
</tbody>
</table>

(2) Pt and Cu on SiO<sub>2</sub> (separated)

<table>
<thead>
<tr>
<th>Flood gun bias (V)</th>
<th>Si 1s</th>
<th>SiKLL</th>
<th>( A'_{\text{Si}} )</th>
<th>Cu2p&lt;sub&gt;3/2&lt;/sub&gt;</th>
<th>Pt3d&lt;sub&gt;3/2&lt;/sub&gt;</th>
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(3) Pt and Cu on SiO<sub>2</sub> (connected)

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<sup>a)</sup> Average.
<sup>b)</sup> Average.
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when referenced to Cu 2p$_{3/2}$:

\[ \text{Si} 1s = 1844.0 + (4.65 - 4.5) = 1844.15 \text{ eV}, \]

when referenced to Pt 4f$_{7/2}$:

\[ \text{Si} 1s = 1843.0 + (5.65 - 4.5) = 1844.15 \text{ eV}. \]

Thus the binding energy of the vitreosil SiO$_2$ can be accurately defined to be 1844.2 eV.

As a further test of the gold dot biased referencing technique, an NaY-type zeolite was investigated. Zeolite materials are notorious for their handling difficulty and general sensitivity, due to the possession of such large surface areas as to make them suitable for use as catalysts in the petrochemical industry. The zeolite powder was imbedded into indium foil prior to Au dot evaporation.

The results for the NaY zeolite are listed in table 5, whilst fig. 8 shows how the Si 1s peak position rises before reaching an apparently stable plateau region at 1843.5 ± 0.1 eV once a level of 8 V applied bias has been reached.

5. Discussion

Two overall observations can be made from the data presented in this paper. First, there is strong evidence that the surface charge or potential of an insulating specimen may change during the course of the XPS analysis, if conditions are not stabilised by some external control such as an electron flood gun. Second, for the conditions used in this experiment, there is no evidence of Fermi level alignment as suggested by Stephenson and Binkowski [10] (eq. (7)). Rather vacuum level alignment, as described by eq. (5), would seem to occur.

An earlier paper [3] has already shown that for Auger parameter data, operation of an electron flood gun at 6 V or greater usually produces stable and reliable data. One reason for this is due to the variation of current arriving at the specimen as the spectrometer retard potential changes during a scan. It appears that the appropriate use of a flood gun can stabilise the surface potential so that reproducible XPS and/or Auger parameter measurements can be made. The desirable conditions are likely to vary with X-ray source, specimen, spectrometer and flood gun geometry. Variations in flood gun emission current with time will potentially cause a significant problem with surface charge present and is a major concern for low intensity X-ray sources such as the one used in this experiment [19]. The observed difference in Pt and Cu binding energies when the Pt and Cu were in contact and when isolated indicates another major source of uncertainty involved in the careful analysis of insulating materials. If a completely insulating specimen, such as a mineral,
contained small amounts of two or more metallic components, the binding energies measured would vary depending upon whether the metals were in contact with each other or electrically isolated.

The lack of Fermi level alignment for Pt and Cu isolated dots on SiO₂ (both within the X-ray beam) indicates that XPS measurements on insulators are fundamentally different from similar measurements on metals. However, the combined use of a metal reference dot and an electron flood gun is a highly reproducible way of obtaining reliable measurements of binding energies from insulators. The measurements are referenced in a different way, but they are nonetheless very useful and important.

The original data of Stephenson and Binkowski [10] used to support Fermi level alignment could be explained in terms of changing specimen charge and potential as described above, if the Hewlett-Packard spectrometer behaves in a manner similar to the ESCA3. However, that explanation and the current results contain an important warning: if the specimen potential changes during the measurements, that change will affect a supposedly charge independent parameter such as the Auger parameter. The extent and importance of such change will vary with the instrument and nature of the experiment.

6. Conclusions

Biased referencing, which involves the use of a metal dot and an electron flood gun, can allow reproducible binding energy measurements, accurate to ±0.1 eV, to be made on insulating and isolated specimens. However, the binding energy obtained is not independent of the work function of the measured materials. For some spectrometers and geometries, use of an electron flood gun is necessary to stabilise the surface potential of the specimen. Because of the differences between vacuum level alignment and Fermi level alignment, the measured binding energies of metals on or in insulating materials will depend on whether the metals are in contact with each other or isolated.

Acknowledgement

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References


