XPS, AES AND LASER RAMAN SPECTROSCOPY: A FINGERPRINT FOR A MATERIALS SURFACE CHARACTERISATION

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ABSTRACT

This review briefly describes some of the techniques available for analysing surfaces and illustrates their usefulness with a few examples such as a metal and alloy. In particular, Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS) and laser Raman spectroscopy are all described as advanced surface analytical techniques. In analysing a surface, AES and XPS would normally be considered first, with AES being applied where high spatial resolution is required and XPS where chemical state information is needed. Laser Raman spectroscopy is useful for determining molecular bonding. A combination of XPS, AES and Laser Raman spectroscopy can give quantitative analysis from the top few atomic layers with a lateral spatial resolution of <10nm.

Keywords: AES, XPS, laser Raman microscopy, surface characterisation

INTRODUCTION

The surface of a metal may differ in properties from the bulk material and these differences may vary from surface free energy to differences in composition due to segregation or contamination. Techniques such as X-ray photoelectron spectroscopy (XPS), also called electron spectroscopy for chemical analysis (ESCA), can be used to quantify the chemical composition of surfaces. In this kind of analysis, a specimen is submitted to an X-ray beam and electrons from the valence layers are ejected giving rise to transitions of electrons from inner layers to occupy the generated vacancies. Peaks of binding energy corresponding to these transitions are detected and quantified, giving a “finger print” of the surface [Watt et al., 2003; Wild, 1995; Nordling et al., 1964; Kratos Analytical, 1985]. Auger Electron Spectroscopy (AES) is a powerful method of analysis of the atomic composition of the surface of the targets from which the Auger electrons issue [Lawrence et al., 1995; Madden, 1981]. It has been extensively used now and a number of instruments for surface and thin film studies. Laser Raman spectroscopy (LRS) can be used to obtain information about the vibrational spectrum of a material. This can lead to a better understanding of the chemical composition of the sample, as in many organic compounds, where different chemical bonds have very characteristic vibrational frequencies [Wild, 1995; Vickerman et al 2009]. It may also be possible to deduce the structure of a material; for example, in molecular systems, the juxtaposition of different chemical species leads to small modifications of the usual vibrational frequencies, so that longer-scale structure may be investigated [Vickerman et al., 2009].

Recently, a characterisation of the material surfaces can be performed using three surface analytical techniques, namely X-Ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES) and Laser Raman Spectroscopy (LRS). XPS and AES are well established analytical tools which are able to provide information about the chemical state and chemical composition of solid surfaces. LRS, on the
other hand, is used to study bonding structure in solids and is widely used in several research areas including physics and chemistry. The principles and applications of these techniques are described in the following sections.

**X-ray photoelectron pectroscopy (XPS)**

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), has become one of the most powerful tools for surface analysis. XPS is a quantitative spectroscopic technique that can measure the chemical and electronic state of the elements existing at the surface of a material, and can be used to define the empirical formula of the compounds which they make up. Photoelectron spectra are obtained by impacting a material with a beam of X-rays under ultra-high vacuum (UHV) while simultaneously measuring the number and kinetic energy (KE) of photoelectrons escaping from the uppermost 1 to 10 nm of the sample material [Kratos Analytical, 1985; Moulder et al., 1993; Siegbahn et al., 1967].

XPS analysis can be used to analyse the chemical state of the material surface in its "as received" state or after a designated surface treatment such as chemical etching, ion sputtering or gas exposure. Surface treatment can often be carried out under vacuum conditions within the XPS system. The technique of photoelectron spectroscopy works on the basis that when soft X-rays are used to irradiate a sample surface, electrons will be ejected from valence and core levels of both surface and near surface atoms. The kinetic energies of ejected photoelectrons are not only characteristic of the atoms from which they are emitted, but can also provide information on the chemical states of those atoms. Low energy X-rays from an aluminium or magnesium source (typically Mg-Kα or Al-Kα at 1253.6 and 1486.6 eV respectively) are commonly used [Moulder et al., 1993]. When soft X-rays strike a surface, electrons will be ‘knocked out’ of valence and core level electron shells. An electron will absorb the total energy of the individual X-ray and, given sufficient energy, will be ejected from the atom.

In XPS, the kinetic energy of ejected photoelectrons is measured by an electron analyser. The recorded kinetic energy is translated into a binding energy for the specific atomic orbital of an electron using the following relationship [Watts et al., 2003; Nordling et al., 1964]:

\[
EB = h\nu - \phi - EK
\]  
(1)

Where:  
- \(EB\) = Electron binding energy /eV
- \(h\) = Planck's constant /eV.s
- \(\nu\) = Frequency of incident radiation /s\(^{-1}\)
- \(\phi\) = Surface work function /eV
- \(EK\) = Kinetic energy of emergent electron /eV

Since each element has a unique set of energy levels, each element also has a unique set of binding energies for electrons present in these levels. On this basis, each atom in a sample can be identified and information concerning to its chemical state can also be determined. The photoelectron process is shown schematically in Fig. 1, where an electron from the K-shell is ejected from an atom as a 1s photoelectron after ionization by incident X-rays [Watts et al., 2003].
The hole created by the ejected electron is filled up by an electron from an outer orbital and results in the rearrangement of electronic structure. The relationship between a recorded photoelectron spectrum and the electronic structure of the atoms from which it is generated is illustrated in Fig. 2. Excited photoelectrons that escape the sample surface without energy loss contribute to the characteristic peaks in the spectrum and those which undergo inelastic scattering and suffer energy loss contribute to the background of the spectrum.

In a solid specimen, the valence orbitals are usually delocalised but the core orbitals are centred primarily on the constituent atoms. As the electrons have quantised energies, the use of an X-ray source of known energy to bombard the sample will result in the emission of photoelectrons at fixed energies. Every element has a characteristic core photoelectron spectrum because it has a unique nuclear charge and unique core orbital energies. Bond formation between different elements will cause changes in the...
binding energies of core electrons. These changes are not so large that the spectrum can no longer be recognised as that of a particular element, but they are large enough to be correlated with the chemical environment and oxidation state of the element. This small but measurable change in the binding energy is known as the chemical shift and it is one of the most important aspects of XPS. The instrumental developments made by Kai Siegbahn and co-workers in the 1960s, allowed these small chemical shifts to be used from the outermost 2-4 nm of the surface layer [Moulder et al., 1993; Siegbahn et al.,]. An XPS system is typically composed of an X-ray source, an electron energy analyser and an ultra high vacuum chamber. All experiments were performed at ultrahigh vacuum (UHV) conditions, with a chamber base-pressure better than 2 x 10^{-10} Torr, obtained by a combination of turbomolecular, ion and titanium sublimation pumps.

A liquid nitrogen cold-trap was also used to enhance the efficiency of the ion pump. A photograph of the XPS system is illustrated in Fig. 3 [Zaidi Embong, 2007]. The XPS system was fitted with a sample stage-manipulator to allow the X-Y-Z position and rotation of samples to be modified relative to the detector. The analysis area on the sample surface was positioned with respect to the detection column using a laser spotter. The sample could also be rotated eucentrically from 0° to 360° in order to perform analysis at different angles. The method of acquiring photoelectron spectra at different sample rotations (or ‘tilts’) is known as Angle Resolved X-Ray Photoelectron Spectroscopy (ARXPS).

ARXPS has been most notably used for determination of the thickness and microstructure of thin films (<6 nm) on material surfaces [Jeurgens et al., 2006; Mack et al., 2006; Halbritter, 1989; Cumpson, 1995; Verpoort, 1995; Piyakis et al., 2003]. Hence, this method can be suitably applied to the study of thin oxide layers developing on most metals and alloys during progressive oxidation. In this case, ARXPS can provide detailed information on the chemical state and thickness of layers ranging from sub-monolayer to several nanometers thickness [Madden, 1981; Halbritter, 1989; Cumpson, 1995].
Furthermore, this method is also reliable for surface characterization of heterogeneous catalytic systems on metal or organic structures [Verpoort et al., 1995]. In ARXPS, the angle between the plane of the sample surface and the direction of the photoemission which goes directly to the detector is known as the photoelectron ‘take-off angle’. The ARXPS analysis can be performed at the take-off angle range of 0 - 60°. At a 0° take-off angle, the sample ‘normal’ direction lies parallel to the alignment direction of the photoelectron detection column. A schematic diagram illustrating the photoelectron take-off angle at 0° and 45° is illustrated in Fig. 4 [Zaidi Embong, 2007].

![Diagram of photoelectron detector](image)

**Fig. 4:** A diagram depicting ‘take-off angle’ for (a) $\theta = 0^\circ$ and (b) $\theta = 45^\circ$ [Zaidi Embong, 2007]

In general, the electron analyzer in XPS instrumentation uses a double focusing principle. An electrostatic field extracts the electrons. As the field is varied, electrons of an appropriate kinetic energy are focused into the detector. The X-ray photoelectron spectrometer used in this study was fitted with a hemispherical sector analyzer (HSA) with a total mean deflection of 180° (Fig. 5) [Allen, 1985]. It consists of a pair of hemispherical surfaces of fixed radii positioned concentrically. A mu-metal shield placed around the analyzer reduces the effect of any stray magnetic field or local fields (e.g. Earth’s) on the photoelectron analysis. Both the hemispheres are electrically isolated and potentials +V and -V applied to the inner and outer spheres. The lenses provide the mechanism for selecting and scanning the particular photoelectron energy of interest. Only electrons with the energies within the pass energy range of the instrument are able to enter the analyzer.
The so-called ‘chemical shift’ in XPS is the most important feature of the method and certainly accounts for its popularity as a surface technique. The changes in binding energy of core electrons arise from different chemical environments and oxidation states of atoms in compounds [Watts, 2003; Moulder, 1993]. Changes in electron density alter the effective nuclear attraction experienced by core electrons and, as a result, changes in the binding energies occur. It is possible to determine the change in core binding energies for elements in a solid, based on the oxidation state of the element, its molecular environment and its lattice, by considering the effect of these factors on the nuclear attraction experienced by the core electrons. The main strength of XPS as an analytical tool lies in the fact that chemical shifts are observed for every element in the periodic table except hydrogen and helium [Moulder, 1993].

The determination of the relative concentration of the atomic constituents present in the sample is an important part of XPS analysis. Atomic sensitivity factors (S) and the photoelectron peak areas are used. For a homogeneous sample of infinite thickness, the number of electrons per second (I) in a specific peak is given by:

\[ I = nF\sigma\theta\lambda AT \]  
\[ \text{or} \quad n = I/F\sigma\theta\lambda AT \]

Where:
- \( n \): Atomic concentration of the element per cm\(^3\) of the sample
- \( F \): X-ray flux (photon cm\(^{-2}\)S\(^{-1}\))
- \( \sigma \): Photoelectric cross-section for the atomic orbital of interest (cm\(^2\))
- \( \theta \): Angular efficiency (related to the angle between the X-ray beam and the detected electrons)
- \( \chi \): Photoelectric efficiency factor
- \( \lambda \): Mean free path of the photoelectron emerges from the sample (cm)
- \( A \): Sample area from where the photoelectron detected (cm\(^2\))
- \( T \): Detection efficiency from the electrons emitted from the sample
Equation 4 can be rearranged to give

\[ n = \frac{I}{S} \]  \hspace{1cm} (5)

where \( S \) is known as the atomic sensitivity factor. For two elements, their atomic concentrations are given by the following equation:

\[ \frac{n_1}{n_2} = \frac{(I_1/S_1)}{(I_2/S_2)} \]  \hspace{1cm} (6)

Equation (6) may be used for all homogeneous samples if the ratio \( S_1/S_2 \) is matrix independent for all elements of interest.

**Auger Electron Spectroscopy (AES)**

When an atom is impacted by an incident X-ray (as in XPS) or electron of sufficient energy, an electron can be removed or ‘knocked out’ from a core level, leaving a core hole. This hole can then be filled by an outer shell electron from the same atom, in which case the electron moves to a lower energy state, and the energy associated with the transition is the difference in orbital energies. This is known as the Auger effect [Lawrence et al., 1995; Madden, 1981; Auger, 1941] This transition energy must be released in some fashion and may either appear as a photon, or as kinetic energy given to another higher bound electron, which is then ejected from the atom. Of these two competing processes, photon emission dominates only when the initial core hole is deeper than about 10 keV. Indeed, this is the physical process used in a conventional laboratory X-ray generator. The alternative release of energy as electron kinetic energy is the Auger effect, named after one of its discoverers, Pierre Auger in the 1920s. Figure 6 shows a schematic of the two processes. In the case of photon emission, we have (ignoring relaxation, etc) [Auger, 1941]:

![Energy level diagram](image)

**Fig. 6:** Energy level diagram showing the filling of a core hole, giving rise to (X-ray) photon emission on the left, or Auger emission on the right.
\[ h\nu = E_x - E_y \]  

(7)

and in the case of Auger electron emission, we have:

\[ EAuger = E_x - E_y - E_z - \phi \]  

(8)

Where:

- \( E_x \): the energy of the core orbital electron knocked out by the incident electron
- \( E_y \): the energy of the original orbital of the electron that fills the core vacancy
- \( E_z \): the energy of the orbital from where the third Auger electron is ejected
- \( \phi \): surface work function

Auger transitions are named after the principle quantum number of the electronic shells involved with the letters K, L, M, N, etc, corresponding to the principle quantum numbers \( n = 1, 2, 3, \) etc [Watts et al., 2003]. For example, a \( KLL \) Auger transition means that a \( K \)-level (1s) electron undergoes the initial ionisation. An \( L \)-level (2s) electron moves to fill the \( K \)-level vacancy and, at the same time, gives up the energy of that transition (\( L \) to \( K \)) to another \( L \)-level (2p) electron, which then becomes the ejected Auger electron. Electrons are emitted from a heated tungsten filament or LaB6 crystal. The filament is heated by passing current through it, emitting heat and light, but also forms an electron cloud around the filament. The filament has a high negative potential, typically between 10 and 20 kV [Lawrence et al., 1995]. Without disruption, electrons remain in the cloud and are reabsorbed into the filament when the current is removed. When a positive electrical potential is applied to a neighboring anode plate, the electron cloud is strongly attracted to the anode plate. The anode plate has a small hole in it and a fraction of the electrons produced travel through the hole and accelerate down into the electron column and towards the sample surface. Electromagnetic lenses are used to collimate and focus the beam while electrostatic plates are used to deflect the beam across the surface of the sample. The gun configuration ensures that electrons striking the sample have similar energies and are emitted from a nearly perfect point source.

The energy distribution of the Auger electrons emitted from the target area on the sample surface is measured by varying the voltage applied to the cylindrical mirror analyzer (CMA), or a hemispherical analyzer. As electrons pass through the analyzer, they are detected using a photomultiplier tube and then recorded as spectra. A second photomultiplier tube is used to detect the secondary electrons emitted from the target which are exploited for sample imaging. As the beam is rastered across the surface, a high-resolution secondary electron micrograph of the surface can be produced. The secondary electron image represents the variation of the electron emission from the surface, which approximates to a topographic image. A brighter area on the image indicates an area of high secondary electron emission. The degree of image resolution is affected by the ability of the electron source to produce a monochromatic beam and the ability of the electron optics to focus that beam to a spot.

During the discussion of photoelectron peak intensities in the XPS technique, it was recognized that two of the main contributions to peak intensity were the ionization cross-section and inelastic mean free path of the photoelectron. The intensities of Auger lines also depend upon these factors. These are included in the following expression, where the Auger electron intensity \( dI \) from a layer of thickness \( dx \) and the distance \( x \) into the solid, is given by the following [Madden, 1981]:
\[ dl = k \sigma D I p B e^{-(x/\lambda)} dx \] (9)

where:
- \( k \): the proportionality constant
- \( \sigma \): the ionization cross-section of the electron ionized initially
- \( D \): the density of the atoms of interest
- \( I p \): the primary electron beam current
- \( B \): the backscattering factor
- \( \Omega \): the Auger transition probability
- \( \lambda \): the Auger electron inelastic mean free path

The energy of an Auger electron is dependent upon the energy difference of the three electronic states involved in the transition. The transitions in each core-ionized element have unique energies and therefore the presence of a peak at a particular energy indicates the presence of a particular element. When chemical bonding occurs, the energy of the electronic states is changed and a chemical shift occurs. Changes in chemical bonding are often seen, but in general, the chemical shift effect is more complicated in AES than XPS due to the three energy levels involved in the process.

In AES, it is possible to detect 1% of a monolayer of almost any elemental species. One of the greatest strengths of AES, however, particularly in comparison with XPS, is the fact that the stimulating beam is an electron beam of intermediate energy that can readily be focused and moved or scanned across a surface by electrostatic or magnetic fields [Watts et al., 2003]. This means that it is easy to produce high spatial resolution and perform surface composition imaging. AES elemental imaging, particularly combined with ion sputtering to produce depth profile images into a sample, has proved of great value in this study. Recording spectra from the oxide layer of as-received and electropolished stainless steel samples at various depths achieved this. These profiles were obtained by alternately sputtering the sample surface with argon ions followed by AES analysis.

![Auger Electron Spectrometer, JEOL JAMP 30](image)

**Fig. 7:** A photograph of Auger Electron Spectrometer, JEOL JAMP 30 [Zaidi Embong, 2007]

A JEOL JAMP 30 model, operated with primary electron beam energy of 10 keV, was used in this study. The photograph of this system is illustrated in Fig. 7. A base-vacuum of better than or equal to 5x10^{-9} mbar was maintained for sample analysis [Zaidi Embong, 2007]. Samples were mounted for
analysis on aluminum or stainless steel stubs. Samples were admitted to the JEOL AES system via an entry lock evacuated by a turbo molecular pump. When the vacuum in the entry chamber was sufficient, the sample could be transferred into the main chamber for analysis. PISCES software was used to control the energy analyzer and record Auger spectra. Typically data were accumulated over a number of scans in order to reduce the background signal generated by secondary electron generation [Lawrence et al., 1995].

**Laser Raman Spectroscopy (LSR)**

Laser spectroscopy is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a chemical system [Vickerman et al., 2009; Laserna, 1996]. It relies on inelastic scattering, or Raman scattering of monochromatic light, usually from a laser in the visible, near infrared or near ultraviolet range. The laser light interacts with phonons or other excitations in the system, resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system, essentially providing information about the types of bonding present in a sample material. Raman spectra are generally complementary to those obtained by infra-red spectroscopy (IR) since, for a molecule with a centre of symmetry, those molecular vibrations which are infra-red active are Raman inactive, and vice versa. A vibration is Raman active if it is capable of inducing a change in polarisability of a molecule. The Raman effect was first observed by Indian physicist C. V. Raman in 1928, having been predicted by Smekal five years earlier [Laserna, 1996]. It can be described as inelastic scattering of light, manifested by a small change in the frequency of the emitted beam following interaction with a molecule or crystal. The inelastic scattering of light is a much less likely process than elastic, or Rayleigh, scattering. Typically only one interaction in every 103-105 will result in inelastic scattering.

When a photon strikes a surface, two situations may arise. Firstly, molecules in the vibrational ground state may absorb some of the photon energy, giving rise to scattered photons with lower energy. These photons give rise to bands in the spectra called Stokes lines. Secondly, photons may interact with vibrationally excited molecules giving rise to scattered photons with higher energy. These photons give rise to bands in the spectra called anti-Stokes lines. Both Stokes and anti-Stokes lines appear around the central laser frequency. Stokes lines are usually used to perform chemical analysis [Palletier, 1999; Manner et al., 1999]. These are more intense because, under usual circumstances, most molecules are initially in the lowest vibrational energy level. Since the Raman effect is generated by the use of a concentrated beam of light, it is possible to use an optical microscope to focus the beam down to a small spot size, and the wavelength of the light used to impact the sample can be limited by the use of filters.

This allows for small area analysis, and can also reduce problems with stray light interference. A related benefit is that images of the sample surface may be obtained either using white light, laser light, or light at one particular Raman-scattered wavelength. This enables distribution maps of a particular component, represented by a specific Stokes line, to be determined over discrete areas of a sample surface [Laserna, 1996; Palletier, 1999; Manner et al., 1999].

In a typical Raman spectrometer, the incident laser light is focused onto the sample using an ordinary glass objective lens and the scattered light collected through the same lens. A beam splitter allows the two components to be separated. The Raman scattered light is then focused onto the slit of the spectrometer and the energy spectrum recorded. Although this set-up allows samples to be analyzed with a spatial resolution of a few microns, the overall collection efficiency of Raman scattered light is low, due to the use of a beam splitter in the optical path, the use of a pin hole as a spatial filter and the
use of double and sometimes triple monochromators. The Raman microscope used in this study was a Renishaw System 2000 Imaging Raman Microscope, illustrated in Fig. 8. It is fitted with a 20 mW He-Ne laser excitation source, which gives an excitation line at 632.8 nm. The attached Olympus microscope allowed samples to be magnified up to 1000 times. The laser beam is focused down the lens of the microscope into a spot on the sample surface. The reflected light travels back up the microscope lens and is focused onto an entrance slit of the spectrometer. The spectrometer consists of a motorized grating, which splits the light according to wavelength. The light is detected by a charged coupled device (CCD), which is essentially a two dimensional array of detectors. A schematic diagram of the Renishaw instrument is shown in Fig. 9. The emitted light is incident upon the CCD and recorded spectra are displayed as the intensity of detected light against the calculated difference between the incident photon energy and emitted photon energy plotted in cm$^{-1}$, with peaks corresponding to the energies of vibrational transitions. The instrument was calibrated using a spectrum with known wave number shift, for example a silicon wafer.

Fig. 8: A photograph of a Renishaw System 2000 Imaging Raman Spectrometer

Fig. 9: A diagram of the Renishaw Raman spectrometer [Laserna, 1996]
XPS, AES and Laser Raman applications: The study of the oxidation of uranium and its alloy U-6Nb

XPS analysis:

One of the typical research areas that related to this surface analysis technique is the study of the oxidation state of metal such as pure uranium and its alloy, U-6Nb. Of particular interest are the initial stages of oxidation and corrosion of these materials when induced by oxidative or corrosive species. Knowledge of these initial stages is important for a clear understanding of the changes in the surface chemical and physical properties, which reflect the corrosion behavior of the metal on long exposure to either atmospheric or storage environments. Characterization and determination of the type of oxide and stoichiometry of the exposed products on both pure uranium and its alloy, U-6Nb was performed using a combination of AES, XPS and Laser Raman Spectroscopy. In this case, the establishment of appropriate oxidation models for uranium and U-6Nb supported by evidence from the AES and Laser Raman analyses.

The superimposition of a series of uranium, U4f and oxygen, O1s narrow scan using ARXPS recorded from a clean surface at various positions of take-off angle (0°, 15°, 30°, 45° and 60°) under UHV conditions is shown in Fig. 10 (a)-(b) [Zaidi Embong, 2007]. The U 4f_{5/2} and U 4f_{7/2} photoelectron signals for uranium metal at 387.7 eV and 377.0 eV were prominent. Both U 4f_{5/2} and U 4f_{7/2} peaks were quasi-symmetrical and narrow with a 10.89 eV gap between them. A very small hump or shoulder was observed at the high binding energy side, indicative of the presence of an oxide film that developed with acquisition time at 0°. Since acquisition of the entire spectrum [ U 4f (250 sec), O 1s (45 sec) and C 1s (40 sec)] was about 335 sec, the three runs made for analysis at each takeoff angle requiring roughly 1005 sec to be completed. The total duration of the measurements between the initial state at 0° and final state at 60° take-off angle was 5025 sec. Thus the shoulder between the two uranium metal peaks exhibited a progressive increase in intensity between the initial and final acquisition state.

The shape of the uranium peak observed at 0° was similar to that observed in other studies [Allen et al., 1973; Fu et al., 2003; Grundner et al., 1980] and was mainly for the uranium metal. When the sample surface was tilted to 15° with respect to the detector, a marked change was observed in the spectrum.
The signals originating from U 4f\(_{5/2}\) and U 4f\(_{7/2}\) photoelectron were found to change from sharp-narrow peaks to a broad doublet produced by an increasing contribution from a signal from uranium oxide collected from a region close to the uranium metal surface. The most significant feature of the spectrum was the elevation of a broad oxide peak next to the uranium metal signal of intensity only slightly lower than that from the metal. It was also observed that while the uranium oxide started to grow, at the same time the uranium metal intensity decreased to nearly half of its original value recorded at 0°. This also indicated that tilting the sample surface to 15° permitted the acquisition of oxide signal from the surface.

Further tilting of the sample surface to 30° also increased the changes in the shape of the narrow scan spectrum to the point where both U 4f\(_{5/2}\) and U 4f\(_{7/2}\) photoelectron peaks became nearly symmetrical. The shape and the intensity of both U 4f\(_{5/2}\) and U 4f\(_{7/2}\) photoelectron peaks continued to broaden as the take off angle was increased from 45° to 60° to a point at which the uranium metal signal became very weak and almost disappeared at the latter. The formation, distribution and the incremental change in the uranium spectrum during the ARXPS were reflected in changes in the O1 s photoelectron peaks. The recorded O1 s spectra from 0° to 60° are shown in Fig. 10 (b). As the take off angle changed from 0° to 60°, the O1 s intensity became increasingly strong and symmetrical in shape from 15° to 30° followed by the development of a small shoulder to the high binding energy side of the main peak at 531.0 eV for take-off angles of 45° and 60°. This shoulder at 532.9 eV was characteristic of hydroxide formation, arising from H2O contamination [Allen, 1985]. To distinguish the O 1s binding energy value for different metals in oxygen or water vapour, two ranges of O 1s binding energy values for oxides and hydroxides were considered, between 530.4 – 531.0 eV and 532.6 – 533.5 eV respectively. For water, either in the condensed form or in the form of ice, the O1 s binding energy values were between 535.1 – 536.6 eV. Allen et al. also assigned O1 s binding energy values for hydrated UO3 associated with water at 535.7 eV [Allen, 1984].

An example of a curve fitting of the recorded uranium spectra at take-off angles 45° is illustrated in Fig. 11 [Zaidi Embong, 2007]. Using a curve fitting software, CasaXPS an appropriate Shirley background model was chosen and eight peak-positions were selected, consisting of the two metal peaks, two oxide peaks and four shake-up satellite peaks for both metal and oxide. The binding energies of the peaks for the uranium metal (U 4f\(_{5/2}\) and U 4f\(_{7/2}\)), uranium oxide (U 4f\(_{5/2}\) and U 4f\(_{7/2}\)) and the satellite peaks U 4f\(_{5/2}\) and U 4f\(_{7/2}\) are listed in Table 1 [Allen et al., 1973; Fu et al., 2003; Pireaux et al., 1977]. At the initial state of the first ARXPS analysis recorded at 0° take off angle, the position of uranium metal (U 4f\(_{5/2}\) and U 4f\(_{7/2}\)) and uranium oxide (U 4f\(_{5/2}\) and U 4f\(_{7/2}\)) binding energies are in good agreement with those reported previously: 377.6 eV (U 4f\(_{7/2}\)), 388.4 eV (U 4f\(_{5/2}\)) and 380.3 eV (U 4f\(_{7/2}\)), 391.2 eV (U 4f\(_{5/2}\)) respectively [Allen et al., 1973; Fu et al., 2003; Pireaux et al., 1977]. In addition, a single small shoulder was observed in association with both uranium metal and uranium oxide peaks 6.55 eV to the high energy side of the main photoelectron peak assigned to a ‘shake up satellite’ peak [Winer et al., 1987]. The variation of this gap may be due to the different species of uranium oxide layer observed during the depth profiling by ARXPS. From other research works, the difference between the main 4f\(_{7/2}\) photoelectron peak and its satellite peak for UO2 was observed to be 6.8 eV [Pireaux et al., 1977, Winer et al., 1987] and 6.9 eV on oxygen exposure [Allen et al., 1973]. The comparison between the present measurements and those in previous studies is given in Table 2 indicating good agreement.
Fig. 11: The curve fitting of uranium 4f_{5/2} and 4f_{7/2} photoelectron peaks for the uranium surface at 45° take-off angle

Table 1: The binding energy values of uranium metal, uranium oxide and the corresponding satellites for U 4f_{5/2} and U 4f_{7/2} photoelectron peaks

<table>
<thead>
<tr>
<th>Photoelectron line</th>
<th>U 4f_{7/2} (eV)</th>
<th>U 4f_{5/2} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium metal</td>
<td>377.4±0.1</td>
<td>388.3±0.1</td>
</tr>
<tr>
<td>Uranium dioxide (UO₂ₐ)</td>
<td>380.9±0.1</td>
<td>391.7±0.1</td>
</tr>
<tr>
<td>Satellite</td>
<td>387.6±0.1</td>
<td>398.0±0.1</td>
</tr>
</tbody>
</table>

Table 2: Satellite energies (measured from U 4f peaks) of selected uranium compound (sources taken from [Pireaux et al., 1977; Winer et al., 1987])

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reference</th>
<th>Satellite energies (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[Fung et al., 1989]</td>
<td>[Fung et al., 1988]</td>
</tr>
<tr>
<td>UO₂</td>
<td>8.2</td>
<td>6.9</td>
</tr>
<tr>
<td>UO₃</td>
<td>3.7</td>
<td>-</td>
</tr>
<tr>
<td>U₃O₈</td>
<td>8.0</td>
<td>7.8</td>
</tr>
</tbody>
</table>

AES analysis

Fig. 12 (a-c) shows typical differentiated Auger electron spectra obtained from the sputter-cleaned surfaces of uranium, niobium and U-6Nb and following their exposure to the UHV environment for different lengths of time ranging from 3 to 130 minutes (4-180 L) [Zaidi Embong, 2007]. Analysis and assignment of the peaks in the spectra recorded allowed the elements U and O to be identified in pure uranium (Fig. 12 (a)); Nb, O and C in pure niobium (Fig. 12 (b)); and U, Nb and O in U-6Nb alloy (Fig. 12 (c)). The position and shape of the peaks exhibited in the bottom traces of Figure 12 (a-b) are similar to those seen previously for clean uranium and niobium devoid of oxygen [Fu et al., 2003; Franchy et al., 1996; Allen, 1987]. The bottom trace of Fig. 12 (c) is representative of a clean surface of alloy U-
6Nb also devoid of oxygen. In all three cases, the oxygen signal was not detected until the exposure reached approximately 15 L.

Fig. 13 shows the concentrations of uranium, niobium and oxygen at the U- 6Nb alloy surface as a function of increasing exposure [Zaidi Embong, 2007]. The initial concentration of niobium was calculated to be 14.2 ± 0.4 %, which is quite close to the nominal concentration in the bulk (14.1 at. %). This indicated that there was no surface segregation of niobium species induced by the ion etching process. With increasing exposure, however, the concentration of uranium and niobium decreased and that of oxygen increased due to increased surface coverage with the UHV gaseous species and subsequent formation of the oxide. The concentration trend indicates that saturation exposure was reached at ~160 L. Beyond this point there was little change in the overall atomic concentration of uranium and oxygen. The O/U ratios determined at the saturation points (160 - 200 L) were in the range
of 1.94 - 2.03, suggesting that after exposure for more than 160 L the oxide that formed on the alloy surface consisted of the UO$_{2.0}$ phase.

![Graph showing concentration of uranium, niobium, and oxygen](image)

**Figure 13:** Atomic concentration of uranium, niobium and oxygen on the surface of U-6Nb alloy as a function of increasing UHV exposure.

### Laser Raman analysis

Raman analysis on the exposed surface of pure uranium and U-6Nb was carried out in order to confirm the molecular structure defined from AES and XPS analysis. The spectrum for an exposed surface of pure uranium is illustrated in Fig. 14 together with the image of the analysis surface area [Zaidi Embong, 2007]. From the image of the surface area, it appeared as a mixture of gold and brownish colour affected by the exposure. The image indicates that the exposure has induced a transformation on the morphology after the initial state of corrosion. From the spectrum deconvolution it is revealed that the spectrum contains uranium peaks at 448.76 cm$^{-1}$, 574.25 cm$^{-1}$ and 621.83 cm$^{-1}$. There were no observations of uranium peaks at more than 650 cm$^{-1}$ [Brooker, 1992], indicating that the molecular structure of this surface is not U$_3$O$_8$, but instead a fluorite structure of UO$_2$. The position of the extra peak is confirmed at 1015.32 cm$^{-1}$, which agreed with the sulphur peak at 1020.5 cm$^{-1}$ [McKeown et al., 2001; Fung et al., 1988; Fung et al., 1989; Tafi et al., 1991; Ray et al., 2005; Younes et al., 2007]. The Raman analysis has given extra support evidence on the AES and XPS analysis, which confirmed that UO$_2$ structure formation occurred during wet SO$_2$ + NO$_x$ exposure. The appearance of the sulphur signal from this analysis also supports the formation of UO$_x$ (SO$_4$)$_y$ which had been determined from AES and XPS analysis.
CONCLUSIONS

There are many surface analytical techniques available commercially, the most important being AES, XPS and laser Raman. AES can give a quantitative analysis from the top few atomic layers with a lateral spatial resolution of <10 nm, but care must be exercised to ensure that there is no beam damage and the technique is not suitable for insulating specimens. XPS can also give a quantitative analysis from the top few atomic layers as well as providing chemical state information; however, it has poor lateral spatial resolution, with the best instruments giving a resolution of 1 μm. Laser Raman
spectroscopy can be used to obtain information concerning the bonding of atoms and molecules but needs to be used in conjunction with one or more of the other techniques such as XPS or AES.

REFERENCES


Kratos Analytical, Manchester, XSAM 800 Operator Handbook. (1985): Section 1 - Section 18


Palletier, M.J. (1999), Analytical Applications of Raman spectroscopy, Blackwell Science Ltd.


Watts, F. and Wolstenholme, J. (2003), An Introduction to Surface Analysis by XPS and AES. John Wiley and Sons,


