Lecture

The Basis of Electron Spectroscopy for Surface Analysis

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(Received February 5, 1999)

Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) are the two commonly used electron spectroscopy methods for studying the compositions of solid surfaces. This paper will discuss the principles on which these techniques are based, and give some examples of their application to surface analysis.

1. Introduction

In surface analysis, we are concerned with the identification of the elements present in the few outermost atomic layers of a material. This is called a qualitative analysis. If the atomic concentrations of the elements can be determined, it is called a quantitative analysis. In many cases, the chemical bonding between elements detected at the surface can be determined, and this provides information about the surface chemistry. The distribution of elements across the surface is not always uniform, and these distributions can be measured and plotted as surface maps. Changes in composition with depth from the surface might also occur, and the measurement of this depth distribution of elements is called depth profiling.

Many processes occur at solid surfaces, such as catalysis, oxidation, corrosion, adhesion, diffusion, lubrication, and wear, and studies of surfaces are important to gain an understanding about their performance and properties. Coatings and thin films are also important and their compositions can be determined both at the surface and within using surface analysis techniques. The composition at the interface between a film and its substrate is also often of interest, as is the composition of surfaces produced on fracture of materials. The surface density of atoms is of the order of 10^{15} cm^{-2}.

The commonly used methods for determining the surface composition include Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), ion scattering spectroscopy (ISS), and secondary ion mass spectrometry (SIMS). XPS is also often referred to as electron spectroscopy for chemical analysis (ESCA), and these two names are often used interchangeably. Commercial equipment is available for these techniques, and is used for both basic research and to solve industrial problems. In AES and XPS, electrons from the surface are energy analyzed, whereas in ISS and SIMS, ions are analyzed.

This paper will discuss AES and XPS only. In AES, an electron beam is normally used as the probe, while in XPS a soft x-ray beam is used.

2. General References

There are many books dealing with AES and XPS, and some of them are listed here:

1. ESCA-Atomic, Molecular, and Solid State Structure Studied by Means of Electron Spectroscopy, K. Siegbahn et al. (Almqvist and Wiksells Boktryckeri AB, Uppsala, 1967).
2. Photoelectron and Auger Spectroscopy, T.A. Carlson (Plenum, New York, 1975).
3. The Theory of Auger Transitions, D. Chattarji (Academic, London, 1976).
4. Handbook of X-ray and Ultraviolet Photoelectron Spectroscopy, ed. by D. Briggs (Heyden, London, 1977).
5. Low Energy Electrons and Surface Chemistry, G. Ertl and J. Küppers (VCH, Weinheim, 2nd Edition, 1985).

6. Auger Electron Spectroscopy, M. Thompson, M.D. Baker, A. Christie, and J.F. Tyson (Wiley, New York, 1985).
7. Methods of Surface Analysis, ed. by J.M. Walls (Cambridge University Press, Cambridge, 1989).
8. Auger Microprobe Analysis, I.F. Ferguson (Adam Hilger, Bristol, 1989).
9. Practical Surface Analysis, 2nd Edition, Vol. 1, Auger and X-ray Photoelectron Spectroscopy, ed. by D. Briggs and M.P. Seah (Wiley, Chichester, 1990).
10. Surface Analysis Techniques, J.C. Rivière (Clarendon Press, London, 1990).
11. An Introduction to Surface Analysis by Electron Spectroscopy, J.F. Watts (Oxford University Press, Oxford, 1990).
12. Photoelectron Spectroscopy, S. Hüfner (Springer-Verlag, Heidelberg, 1994).
13. Introduction to Surface Physics, M. Prutton (Oxford University Press, Oxford, 1994).
14. Modern Techniques of Surface Science, D.P. Woodruff and T.A. Delchar (Cambridge University Press, Cambridge, 2nd Edition, 1994).
15. Surface Science Techniques, ed. by J.M. Walls and R. Smith (Pergamon, Oxford, 1994).
16. Surface Analysis: The Principal Techniques, ed. by J.C. Vickerman (Wiley, Chichester, 1997).

3. Handbooks

Handbooks of AES and XPS spectra are very useful to help identify peaks in spectra. Handbooks usually contain spectra of the pure elements, and sometimes contain spectra of compounds as well. Some of the handbooks currently available are:

AES:

1. Handbook of Auger Electron Spectroscopy, T. Sekine et al., published by JEOL, 1982.
2. Handbook of Auger Electron Spectroscopy, 3rd Edition, K.D. Childs et al. (Physical Electronics Inc., Eden Prairie, 1995).

XPS:

1. Handbook of X-ray Photoelectron Spectroscopy, N. Ideo et al., published by JEOL, 1991.
2. Handbook of X-Ray Photoelectron Spectroscopy, J.F. Moulder et al. Reprint. (Physical Electronics Inc., Eden Prairie, 1992).
3. High Resolution XPS of Organic Polymers - The Scienta ESCA 300 Database, G. Beamson and D. Briggs (Wiley, Chichester, 1992).
4. Handbooks of Monochromatic XPS Spectra, 5 volume series, B.V. Crist (XPS International, Kawasaki, 1997).

4. Databases

Some of the databases that are available for AES and XPS are:

1. NIST X-Ray Photoelectron Spectroscopy Database, Version 2.0, 1997. National Institute of Standards and Technology, Gaithersburg, Maryland 20899. Contains over 16,000 line positions, chemical shifts and splittings, from published literature through 1985, and selected data through 1991. (Contains no spectra).
2. Common Data Processing System for Surface Analysis, K. Yoshihara (Project Leader), National Research Institute for Metals, 1-2-1 Sengen, Tsukuba, Japan. Contains standard spectra, reference spectra, and data processing software (XPS and AES). Developed under VAMAS (Versailles Project on Advanced Materials and Standards).
3. Surface Science Spectra, a quarterly journal devoted to hard-copy distribution of surface spectroscopy data files. Spectra are also available online. Published by the American Vacuum Society.

5. Standards

There are several standards for AES and XPS that have been developed by national standards organizations. Other reference materials are available from industry. Standards for depth profiling are available from the National Institute of Standards and Technology (NIST), USA, and from the National Physical Laboratory (NPL), UK. Software for calibration of spectrometers in AES and XPS is available from NPL. Standard Terminology, Practices,

and Guides have been developed by the American Society for Testing and Materials (ASTM). Standards are also being developed by the International Standards Organization (ISO). Details are listed below:

NIST (Standard Reference Materials Program, Building 202, Room 204, Gaithersburg, MD 20899, USA; Tel: +1 301 975 6776; Fax: +1 301 948 3730; e-mail: srminfo@nist.gov; WWW: http://ts.nist.gov/ts/htdocs/230/232/232.htm):
SRM 2135c: nickel/chromium thin film depth profile standard.
SRM 2136: chromium/chromium oxide thin film depth profile standard. (Discontinued).
These two standards are for calibrating equipment used to measure sputtered depth and erosion rates in surface analysis.

NPL (Surfaces and Interfaces Section, CMMT, National Physical Laboratory, Queens Road, Teddington, Middlesex TW11 0LW, U.K.; Tel: +44 181 943 6620; Fax: +44 181 943 6453; e-mail: sjs@npl.co.uk; WWW: http://www.npl.co.uk/npl/cmmt/sis/refmat.html) :
CRM261: tantalum pentoxide depth profile reference materials, consisting of four 30nm thickness samples and four 100nm thickness samples of Ta_2O_5 on Ta, each approximately 10mm x 5mm in size.
SCAA87: copper, silver, and gold reference materials for intensity and energy calibration of Auger electron spectrometers.
SCAA90: copper, silver, and gold reference materials for intensity and energy calibration of x-ray photoelectron spectrometers.
Software: AES and XPS intensity calibration software used to calculate the intensity response (or transmission) function of the spectrometer. Also, PC138: Software to check that data files can be saved in compliance with the VAMAS (Versailles Project on Advanced Materials and Standards) Standard Data Transfer Format.

ASTM (American Society for Testing and Materials, 100 Barr Harbor Drive, West Conshohocken, PA 19428-2959, USA; Tel: +1 610 832 9500; Fax: +1 610 832 9555; e-mail: gcolling@astm.org; WWW: http://www.astm.org/COMMIT/e-42.htm):
Some of the most useful documents published by ASTM, that relate to AES and XPS are:
Terminology:
E 673 Relating to Surface Analysis
Standard Guides for:
E 983 Minimizing Unwanted Electron Beam Effects in AES
E 984 Identifying Chemical Effects and Matrix Effects in AES
E 995 Background Subtraction Techniques in AES and XPS
E 1016 Literature Describing Properties of Electrostatic Electron Spectrometers
E 1078 A Specimen Preparation, Mounting and Analysis in AES, XPS and SIMS
E 1127 Depth Profiling in AES
E 1523 Charge Control and Referencing Techniques in XPS
E 1577 Reporting of Ion Beam Parameters used in Surface Analysis
E 1634 Performing Sputter Crater measurements
E 1829 Handling and Preparation of Specimens Prior to Surface Analysis
Standard Practices for:
E 684 Approximate Determination of Current Density of Large Diameter Ion Beams for Sputter Depth Profiling of Solid Surfaces
E 827 Elemental Identification by AES
E 902 Checking the Operating Characteristics of X-ray Photoelectron Spectrometers
E 996 Reporting Data in XPS and AES
E 1217 Determination of the Specimen Area Contributing to the Detected Signal in XPS and AES
E 1636 Analytically Describing Sputter-Depth-Profile Interface Data by an Extended Logistic Function.

6. Internet Resources

Some internet resources have been included in the section on Standards above.

Other useful internet resources include:

The Surface Analysis Society of Japan: http://sekimori.nrim.go.jp/
This site has access to a Common Data Processing System that can be downloaded, and to AES and XPS spectra from many of the elements in the periodic table. The spectra can be viewed on line, and members of the Society can download files. Membership information is available online.
The American Vacuum Society is the main professional society for those working in AES and XPS in the USA. It has links to its scientific journals, scientific meetings, a buyers guide, and to the International Union for Vacuum Science, Technique, and Applications (IUVSTA). http://www.vacuum.org/
A surface science mailing list for users in AES and XPS has been set up by Surface Science Western at the University of Western Ontario, Canada, and information about the mailing list can be accessed from their home page at http://www.uwo.ca/ssw/ An archive of messages is also kept.
Scientific journals can also be accessed on line, and downloaded, usually for a fee. Members of professional societies can sometimes access journals published by their societies, and download articles for their own use at no charge. Where an employer subscribes to online journals (for example, through their library), employees can usually access the journals and download articles from their office. Some useful addresses for journals are:
American Institute of Physics:
http://www.aip.org/tips/jall.html
Institute of Physics:
http://www.ioppublishing.com/EJ/welcome
Wiley/Interscience:
http://www.interscience.wiley.com/index.html
Elsevier/Pergamon:
http://www.sciencedirect.com/
Many publishers allow tables of contents and abstracts to be viewed at no charge. A useful, no-cost, search engine for scientific articles by author, key words, or journal is UnCoverWeb (articles can be faxed for a fee): http://uncweb.carl.org/

7. Auger Electron Spectroscopy

7.1 The Auger Process

In the most commonly used form of AES, a sample is bombarded with electrons having an energy between 3 and 30 keV, resulting in the ejection of core level electrons from atoms in the sample. The resulting core vacancy can be filled by an outer level electron, with the excess energy being used to emit another electron from the atom. This emitted electron is called an Auger electron and is named after Pierre Auger who first observed such events in a cloud chamber in the 1920s. An example of the Auger process is shown in Figure 1. In this example,

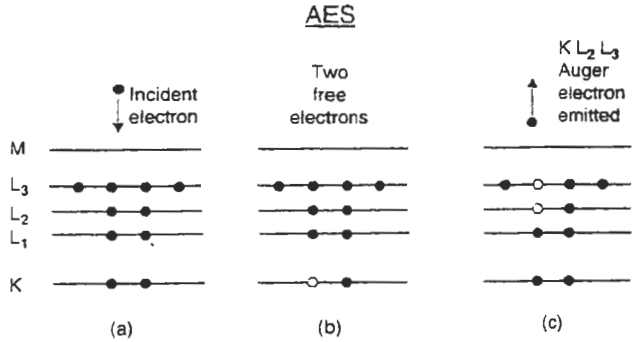

Figure 1. Illustration of the production mechanism for KL_2L_3 Auger electrons, (a) initial state with K, L, and M levels occupied, (b) K level ionized by incident electron, and (c) K level filled by an L level electron, with energy produced used to remove another electron from the L level.

the K and L levels in the atom are shown to be fully occupied by electrons, Figure 1(a), and the initial ionization occurs in the K level, Figure 1(b). Following relaxation and the emission of an Auger electron, the atom has two vacancies in outer levels, the L_2 and the L_3 levels in this example, Figure 1(c). This process can be thought of as (i) an electron drops down from the L_2 level to fill the K level vacancy, (ii) energy equal to the difference in binding energies between the K and the L_2 levels is released, and (iii) this energy is sufficient to remove an electron from the L_3 level of the atom, with the excess energy going into the

kinetic energy of the Auger electron. Alternatively, an x-ray can be emitted when the atom relaxes following its ionization, and the measurement of these x-ray energies forms the basis for electron microprobe analysis. The probability for relaxation by Auger emission is much higher than for x-ray emission for the energies usually measured in AES.

The three atomic levels involved in Auger electron production are used to designate the Auger transition. The first letter designates the shell containing the initial vacancy and the last two letters designate the shells containing electron vacancies created by Auger emission. The Auger electron produced in the example shown in Figure 1 is therefore referred to as a KL_2L_3 Auger electron. When a bonding electron is involved, the letter V is sometimes used, e.g. KVV and LMV. After the initial Auger electron is produced, further Auger transitions can occur to fill these electron vacancies, resulting in a cascade of Auger electron emissions as vacancies are filled by outer electrons.

Some of these Auger electrons will escape from the specimen without losing energy, and be measured as peaks in a spectrometer. These Auger peaks will be superimposed on a continuous background of secondary and backscattered electrons. Secondary electrons are usually defined as the background below 50 eV, and backscattered electrons are those from 50 eV up to the incident beam energy. Electrons ejected from the initial ionization, Figure 1(b), can also appear in the measured spectrum, where the excess energy of the incoming electron following ionization is shared by that electron and the emitted electron.

The energy of the Auger electron depends on the binding energies, B.E., of the levels involved and not on the energy of the incident beam. In its simplest form, the kinetic energy, K.E., of the Auger electron KL_2L_3 (Figure 1) is given approximately by:

$$\text{K.E.}\ (KL_2L_3) \approx \text{B.E.}\ (K) - \text{B.E.}\ (L_2) - \text{B.E.}\ (L_3)$$

(This equation neglects contributions from the interaction energy between the holes in the L_2 and L_3 levels, as well as intra-atomic and extra-atomic relaxation.)

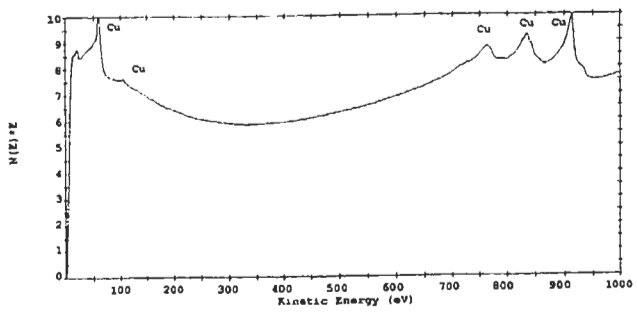

Figure 2. AES spectrum of Cu in direct mode, taken from a sputtered Cu gasket, using a 40 nA, 5 keV electron beam. The spectrum was acquired in 100 s.

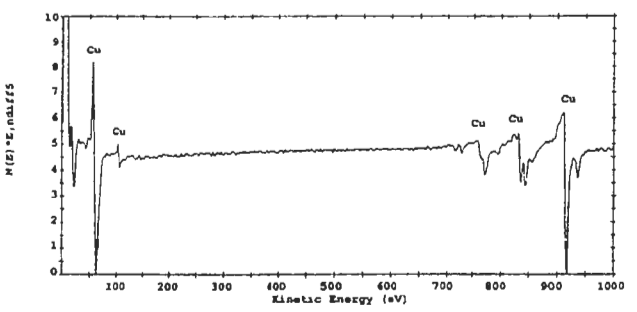

Figure 3. AES spectrum of Cu in derivative mode, by numerical differentiation of direct spectrum in Figure 1.

The Auger electron kinetic energies are characteristic of the material, and the measurement of their kinetic energies is used to identify the elements that produce these Auger electrons. An Auger spectrum from a clean Cu surface is shown in Figure 2, where the number of electrons detected is plotted against their kinetic energy. The high energy peaks are from the LMM (including LMV and LVV) transitions, while the low energy peaks are from MVV transitions. This spectrum is called a "direct spectrum". A derivative of this Cu spectrum is shown in Figure 3, and this type of display is that normally used for further analysis. Note that the Auger features are enhanced in the derivative, but the signal-to-noise has decreased. A direct spectrum of a contaminated Cu surface is shown in Figure 4, and its derivative in Figure 5. Note the presence of Cl, C, N and O on the contaminated surface. The concentrations of elements detected can be determined from the intensities of the Auger

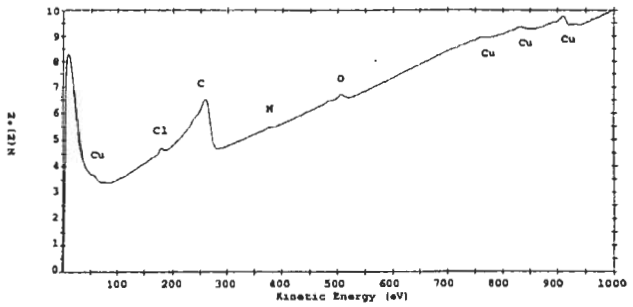

Figure 4. AES spectrum in direct mode, taken from a used Cu gasket, using a 40 nA, 5 keV electron beam. The spectrum was acquired in 100 s.

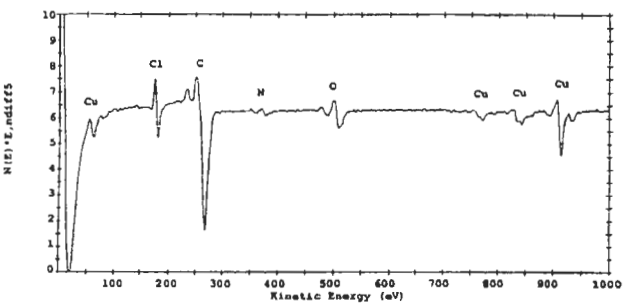

Figure 5. AES spectrum of used Cu gasket in derivative mode, by numerical differentiation of direct spectrum in Figure 4.

peaks. Typical detection limits are in the range of 0.1 to 1 atomic percent.

7.2 Surface Sensitivity of AES

AES is a surface sensitive technique due to the strong inelastic scattering of electrons in specimens. Auger electrons from only the outermost few atomic layers are emitted from the specimen without energy loss, and contribute to the peaks in a spectrum. Auger electrons that have lost energy in escaping from the specimen will appear as an additional background signal at lower kinetic energies, superimposed on the backscattered and secondary electron background.

Obviously, hydrogen and helium cannot be detected as three electrons are needed for the Auger process.

7.3 Chemical Effects in AES

Besides identifying the elements present at surfaces, AES can often provide useful information about the chemical environment of surface atoms. Such chemical effects can affect the measured Auger spectrum in a number of ways, e.g. the kinetic energy at which an Auger peak occurs can change, the energy distribution of the Auger electrons can change, or the loss structure associated with Auger peaks can change.

Energy shifts are expected to occur whenever there is charge transfer from one atom to another. Thus, changes in composition of metallic components in metal alloys would not be expected to produce measurable changes in the Auger energies (for core levels) of the components. However, oxygen adsorbed on clean metal surfaces can produce measurable changes in the metal Auger peaks, the shift increasing with coverage. Changes in the lineshape of Auger spectra can also occur due to changes in bonding, particularly when one or two valence electrons are involved in the relaxation process. Changes in lineshape of transitions involving valence electrons are usually accompanied by significant shifts in Auger energies as well.

Examples of changes in the carbon KVV Auger lineshape for different chemical states of carbon are shown in Figure 6.

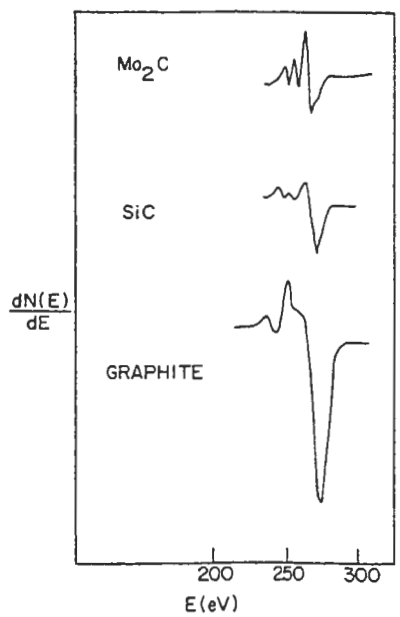

Figure 6. Derivative C KVV Auger spectra taken from Mo_2C, SiC, and graphite, illustrating different Auger lineshapes.

7.4 Line Scans and Maps in AES

Electron beams can be focussed to small diameters, thereby allowing the composition of small areas (~50 nm and below) on a surface to be determined. This is called point analysis. The specimen itself is imaged in the SEM mode, and the analysis point is then selected on this image. The electron beam can also be rastered over small areas to reduce possible electron beam damage where this might be a problem. Analysis can be performed at pre-selected points or areas on the specimen.

The electron beam can be scanned in a straight line across part of the specimen surface and Auger data can be acquired as a function of beam position, resulting in what is called an Auger line scan. An example of an Auger line scan is shown in Figure 7.

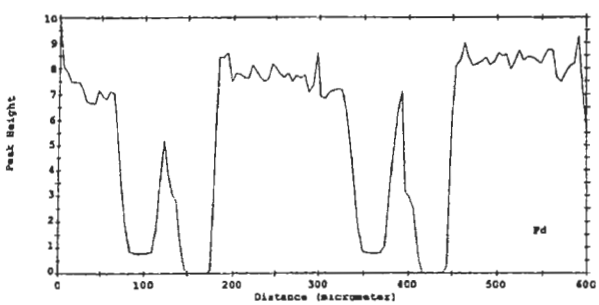

Figure 7. Pd MNN Auger linescan taken from a Pd foil with a Cu mesh positioned slightly above it. There are two dips in the Pd signal in the region of the mesh, one when the Pd signal is masked from the energy analyzer by the Cu mesh, the other when the electron beam is on the Cu mesh. The line scan was taken in about 6 min using a 40 nA, 5 keV electron beam.

With Auger maps, Auger data are acquired as a function of position within a defined area on the specimen. The maximum dimensions of the area that can be mapped depend on the acceptance area of the analyzer, and the deflection capability of the electron gun. Auger maps show the variation in elemental composition (and concentration) across a region of the surface, and is referred to as scanning Auger microscopy (SAM). Auger maps of Cu and Pd from a Cu grid placed slightly above a Pd substrate are shown in Figure 8. Auger maps can be displayed in different ways, such as a selected number of gray levels, on a thermal scale, in pseudocolor, or in a selected color for comparing with a map of a different element in the same map area.

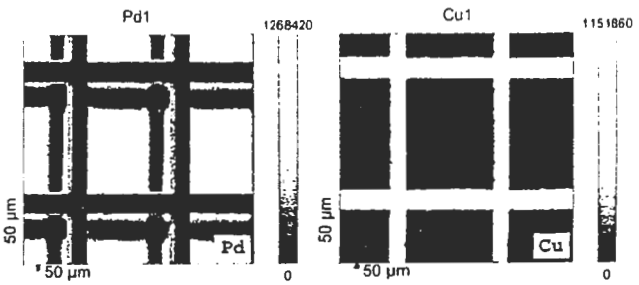

Figure 8. Auger maps of Pd (left) and Cu (right) taken from a Cu mesh positioned slightly above a Pd foil. The second set of mesh-lines in the Pd map is from shadowing of the Pd signal by the Cu mesh. Maps were taken with 128 x 128 pixels, and an acquisition time of 50 ms per pixel.

7.5 Depth Profiling in AES

Variations in composition with depth can be determined by depth profiling, which is usually accomplished by continuously removing atomic layers by sputtering with inert gas ions while monitoring the Auger signals from the newly created surfaces. Ion bombardment is also referred to as sputtering. Auger measurements are made continuously while sputtering, or sequentially with cycles of sputtering and analysis. Ar or Xe ions at an energy of a few keV are usually used for sputtering. Typical sputter rates are of the order of 10 nm/min. It is important that the ion beam is correctly aligned to the analysis area on the specimen, and the ion beam is often rastered over a small area of the specimen to ensure that the electron beam used for Auger analysis strikes the flat bottomed crater formed by the rastering.

Auger survey scans could be taken in depth profiling, but a technique called multiplexing is normally used instead. With multiplexing, several energy analysis windows are pre-selected with each one encompassing an Auger peak of the element of interest This procedure

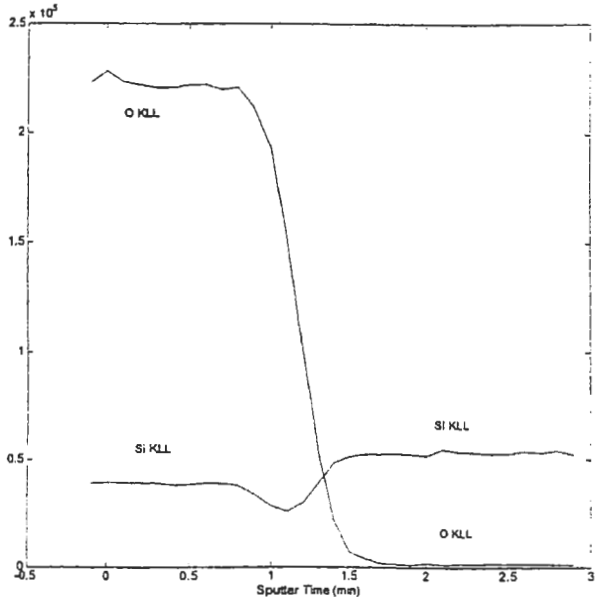

Figure 9. Auger sputter depth profile of SiO_2 on Si, using the peak-to-peak heights in derivative spectra. The apparent decrease in Si near the interface is an artifact due to chemical effects on the Si KLL spectrum.

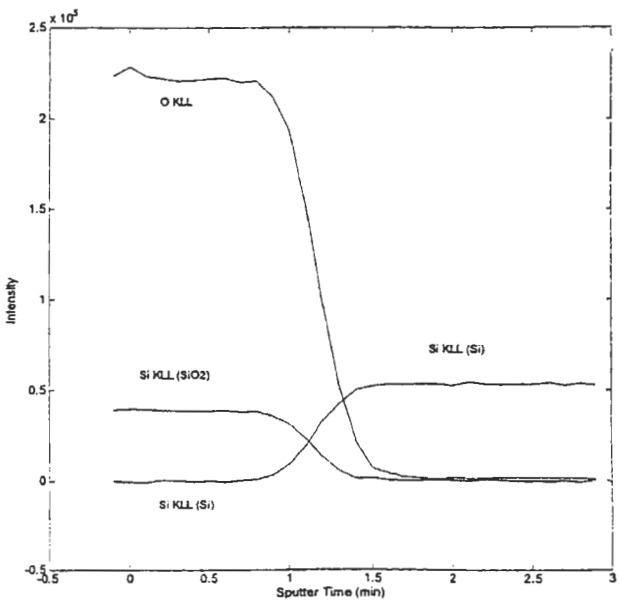

Figure 10. Auger sputter depth profile of SiO_2 on Si, using the peak-to-peak heights in derivative spectra, after the application of linear least squares fitting to the data used in Figure 9. Note the separation of the Si KLL peak into its two chemical states, and the absence of the artifact near the interface in Figure 9.

saves time, as only energy regions of interest are scanned. This will also provide a higher density of data points in the depth profile, but means that other elements that might be present below the original surface could go undetected.

An Auger sputter depth profile of SiO_2 on Si is shown in Figure 9, using O KLL, and Si KLL Auger transitions. The dip in the Si KLL signal at the SiO_2 / Si interface is an artifact due to the chemical shift of the Si KLL Auger peak in going from SiO_2 to Si. Such artifacts can be removed by numerical methods, such as linear least squares fitting or factor analysis. The application of linear least squares fitting of the data is shown in Figure 10, where the artifact has been removed and the Si has also been separated into its two chemical components, SiO_2 and Si.

Depth resolution can be improved by using lower energy ions, and by rotating the sample during sputtering.

8. X-ray Photoelectron Spectroscopy

8.1 The Photoionization process

In XPS, the sample is bombarded with soft x-rays, resulting in the ejection of electrons from electron orbitals of the atoms in the material. Soft x-rays are those that have an energy of the order of 1 keV. The photoelectron process is illustrated in Figure 11, where an electron is removed from the 1s shell. The ejected electron is called a 1s photoelectron, since it was ejected from the 1s shell by a photon (x-ray). In XPS, the spectroscopic notation for energy levels (1s, 2s, 2p, 3s, 3p, 3d, 4s, etc.) is used instead of the x-ray notation (K, L_1, L_2, L_3, M_1, M_2, M_3, M_4, M_5, N_1, etc.) that is used in AES. Of course, there is a direct one-to-one correspondence between these different notations. Ideally, the x-rays used in the beam are monoenergetic, that is, having just one energy. Such monoenergetic sources are often used in XPS, and typically use part of the Al

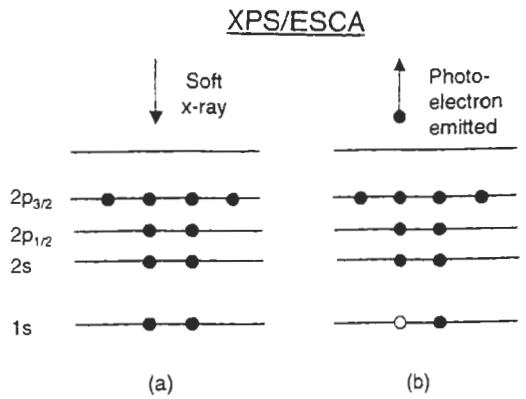

Figure 11. Illustration of the production mechanism for a 1s photoelectron, (a) initial state with 1s, 2s, and 2p levels occupied, (b) a 1s level vacancy produced by incident photon, with the corresponding emission of the 1s electron.

$K\alpha_{1,2}$ radiation having an energy of 1486.6 eV. (XPS is also performed at synchrotrons, where the energy of the monochromatic x-ray beam can be selected).

Electrons can be ejected from any of the electron orbitals in atoms in the material, up to electron binding energies equal to the energy of the incident x-rays. In this process, the x-ray is annihilated, with the excess energy going into the kinetic energy of the photoelectron. In its simplest form, the kinetic energy (K.E.) of the photoelectron is given by:

K.E. = x-ray energy – B.E. ,

where B.E. is the binding energy of the electron in the shell from which it was ejected. XPS spectra are usually plotted as the number of electrons detected against their binding energy. (The electron kinetic energies are actually measured in the energy analyzer, and the above equation is used to convert the horizontal axis to binding energy). An XPS spectrum obtained from a sputter-cleaned Cu gasket (as used to seal stainless steel vacuum flanges) with monochromatic Al Kα x-rays is shown in Figure 12. Besides the photoelectron peaks, Auger peaks are also seen, since Auger electrons can be produced by electronic relaxation of the atom after photoionization. Also note that the Auger peaks are identified using x-ray notation. The peaks in the spectrum

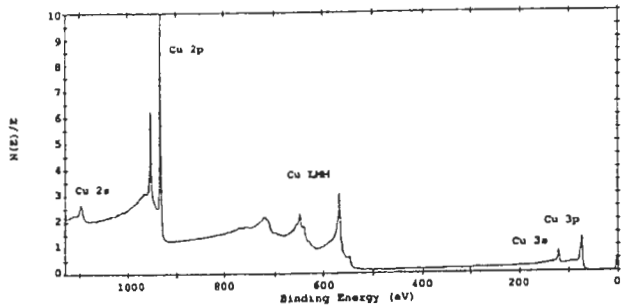

Figure 12. XPS spectrum from sputter cleaned Cu gasket taken with monochromatic Al Kα x-rays. The acquisition time was 5 minutes.

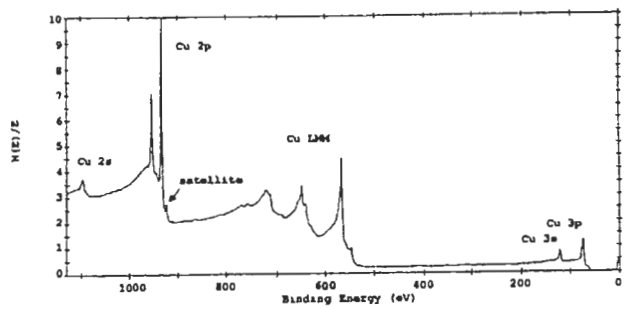

Figure 13. XPS spectrum from sputter cleaned Cu gasket taken with non-monochromatic Al Kα x-rays. The acquisition time was 5 minutes.

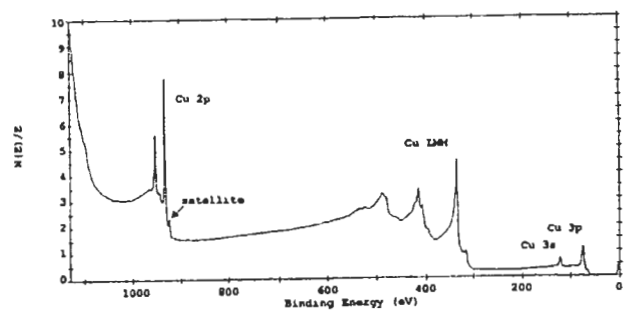

Figure 14. XPS spectrum from sputter cleaned Cu gasket taken with Mg Kα x-rays. The acquisition time was 5 minutes.

are from electrons that have been ejected from the outermost atomic layers of the sample. The x-rays will penetrate deeply into the sample and produce photoelectrons (and Auger electrons) at great depths, but if they travel to the surface and are measured they will have lost kinetic energy and will appear in the increased background on the low binding energy side of each peak, as seen in Figure 12. Sometimes, XPS spectra are

plotted with the binding energy increasing to the right, rather than to the left.

Non-monochromatic x-ray sources are also used in XPS. The most commonly used non-monochromatic sources are Al Kα and Mg Kα, where the most intense photoelectron peaks will occur from the $K\alpha_{1,2}$ x-rays, but peaks at about 10% intensity will also be detected from the $K\alpha_{3,4}$ x-rays at about 10 eV higher binding energy. This is illustrated in Figure 13, for the Cu XPS spectrum taken with a non-monochromatic Al x-ray source. Note that only photoelectron peaks will have such satellite peaks, as the kinetic energy of the Auger peaks is independent of the incident beam energy. The x-ray satellites will add to the intensity of the Auger electrons measured, however. The Auger intensity is also increased by the bremsstrahlung produced in non-monochromatic sources. (Compare the intensities of the Auger peaks to the photoelectron peaks in Figures 12 and 13). The bremsstrahlung is a continuous distribution of x-rays up to an energy corresponding to the high voltage used in the x-ray source, typically 10 to 15 keV. The bremsstrahlung will also increase the background across the entire spectrum and will even produce electrons at negative binding energies (these are electrons that will have a kinetic energy greater than the $K\alpha_{1,2}$ x-ray energy used to convert K.E. to B.E. in the above equation).

The Cu XPS spectrum taken with a non-monochromatic Mg x-ray source is shown in Figure 14. Again, note that the photoelectron peaks have satellites. The Mg $K\alpha_{1,2}$ x-rays have an energy of 1253.6 eV, so the Auger peaks will appear at a different "binding energy" in this spectrum compared with an Al source, since the Auger kinetic energies are unchanged. In many instruments both non-monochromatic Al and Mg x-ray sources are made into what is called a dual anode, and either Al or Mg x-rays can be selected. This can be helpful in identifying peaks, because Auger peaks will shift in the XPS spectrum when the source is changed, but the photoelectron peaks will not.

8.2 Surface Sensitivity in XPS

As mentioned above, the x-rays will penetrate deeply into the sample and produce photoelectrons (and Auger electrons) to great depths, but they must travel to the surface and escape to be measured. Only those photoelectrons produced near the surface will have a high probability of escaping without losing energy and appear in the peaks. Those produced at greater depths will have lost kinetic energy in travelling to the surface and will appear as the increased background on the low binding energy side of each peak, as seen in Figures 12 – 14.

Hydrogen and helium are not detected in XPS spectra from solids as their peak intensities are too low.

8.3 Chemical Effects in XPS

Besides identifying the elements present at solid surfaces, XPS can provide valuable information about the surface chemistry. This is usually manifested as shifts in the binding energies of photoelectron peaks with changes in chemistry. Chemical shifts in XPS are easier to interpret than in AES as only one energy level is involved, and the peaks are sharper. However, chemical shifts in AES will be bigger than in XPS due to larger relaxation effects. Other manifestations of chemical effects are the presence or absence of plasmon peaks, shake-up peaks, or multiplet splitting. Plasmon peaks are due to discrete energy losses suffered by electrons as they pass through the free electron "gas" in conductors, and will appear as equally spaced peaks but of decreasing intensity on the high binding energy side of photoelectron and Auger peaks. Shake-up occurs during the photoelectron process, where an outer electron is shaken-up into a higher unoccupied energy level. This effect can be seen in graphite and aromatic compounds due to a π - π^* transition. Multiplet splitting occurs due to an electron spin interaction between the photoelectron and unpaired electrons in the valence levels. An example of chemical shifts is shown in Figure 15, where W 4f photoelectron spectra are shown for clean W, an anodized W surface, and a W sample showing both chemistries.

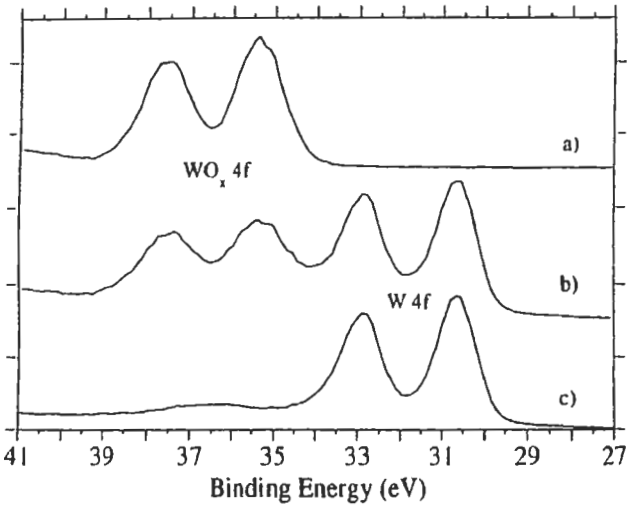

Figure 15. W 4f XPS spectra from (a) anodized tungsten (WO_x), (b) a W foil taken from storage, and (c) a sputter cleaned W foil, obtained with monochromatic Al Kα x-rays.

8.4 Line Scans and Maps in XPS

Unlike electrons, x-rays cannot be focussed to very small areas. X-rays are usually focussed with the curved crystals used in monochromators, and the limit today in commercial XPS instruments is about 5 μm. (AES measurements can be made on dimensions of ~ 50 nm and below). At synchrotrons, XPS measurements have been made on dimensions below 0.5 μm using zone plates. Some XPS instruments limit the analyzed area with the input lens (and its apertures).

As in AES, line scans and maps can also be obtained in XPS, but as mentioned above, at much poorer spatial resolution. Line scans and maps are often obtained by scanning a focussed x-ray beam across the sample, or by using sets of electrostatic deflector plates within the input lens to the energy analyzer. One manufacturer can image regions on a surface to a spatial resolution of a few μm using a non-monochromatic source coupled with special imaging optics. In some cases, line scans and maps have been obtained by scanning the sample on its manipulator under computer control (this is also the method used with zone plates at synchrotrons).

8.5 Depth Profiling in XPS

As in AES, depth profiles are often obtained by sputtering with inert gas. With XPS, larger areas are usually analyzed and the ion beam is therefore usually rastered over a region of the surface to form a flat-bottomed crater for good depth resolution. Unlike AES, sputtering and analysis are usually done consecutively in XPS depth profiling, as the electrons produced from the impact of the ion beam on the surface can produce a large background signal in the XPS spectrum, particularly at higher binding energies (lower kinetic energies). As in AES, depth resolution can also be improved by using lower energy ions, and by rotating the sample during sputtering.

9. Summary

This paper has attempted to address some of the basic principles of AES and XPS. Obviously, it cannot cover all aspects of surface analysis using these techniques, and the reader is referred to the General References in Section 2 for more details.