

THE INITIAL OXIDATION OF NIOBIUM
AS STUDIED BY ELECTRON SPECTROSCOPY

by

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Submitted in fulfilment of the regulations
for Doctor of Philosophy

NOVEMBER 1982

To my mother and father.

A B S T R A C T

The initial oxidation of polycrystalline niobium has been studied by x-ray and ultra-violet photoelectron spectroscopy. The niobium was cleaned under ultra high vacuum conditions and the oxygen exposure carried out at low pressures and at room temperature. The results are interpreted as showing that the reaction of oxygen with clean niobium results in the formation of niobium monoxide, NbO , from the earliest stages. A 'chemisorbed' phase cannot be distinguished. The spectroscopic characteristics of the first NbO monolayer are similar to those of the oxygen containing layer produced by oxygen segregation, at high temperature, from the bulk. Further oxygen exposure leads to the formation of a second NbO layer, the mechanism for which may be place exchange with the underlying niobium. The reaction slows after completion of the second NbO layer.

Further oxygen adsorption results in the oxidation of the outer NbO layer to niobium pentoxide, Nb_2O_5 . No evidence for significant amounts of niobium dioxide was found. The resulting duplex $\text{NbO}/\text{Nb}_2\text{O}_5$ oxide film is stable to further oxygen exposure at low pressure. Gross exposure of this film to oxygen still produces only a very thin oxide layer.

Several aspects of the work shed light on the oxidation of metals in general. Firstly, it is suggested that for reactive metals oxygen incorporation into the first layer of metal atoms may be widespread. Secondly, low temperature oxidation can occur by place exchange, leading to a fall in the reaction rate after the completion of two oxide layers. Thirdly, the formation of duplex oxide structures may occur for metals other than niobium.

ACKNOWLEDGMENTS

The author would like to express his thanks to Dr. David Chadwick for his support and advice during the course of this work.

In addition this thesis could not have been completed without great understanding on the part of my wife, Amanda, to whom I am grateful. I also express my appreciation to Alec Christie for many useful discussions during the period of our studentships.

My thanks must also be expressed to Mrs. M.M. Iles for typing the manuscript.

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CHAPTER 1

INTRODUCTION

1.1 THE IMPORTANCE OF SURFACES

Many aspects of modern technology require a knowledge of thin film and surface phenomena for their successful operation. For products such as catalysts, solar cells and electronic devices, the chemistry of their surfaces determines, to a large extent, their effectiveness. Surface and thin film effects that are detrimental include tarnishing of noble metal alloys used for electrical contacts and gross corrosion of base metals and their alloys used in engineering. However, it is the formation of passivating thin oxide films on metals and their alloys that prevents them from being totally oxidised. It is evident that a good understanding of the surface chemistry of elements as well as their compounds, alloys, polymers and glasses is very important for their optimum exploitation.

Knowledge of the surface chemistry of niobium provides an example explaining both beneficial and detrimental surface effects particularly with regard to the formation of oxide films. On the merit side, a layer of insulating oxide is necessary for the fabrication of super-conducting Josephson junctions. In this application a thin film of oxide (Nb_2O_5) is sandwiched between metallic niobium and lead. This arrangement provides a very fast electronic switch which may soon be used in computer circuits operating at a

temperature of 4 K. One essential in the production of such devices is to ensure that there are no electrical short circuits in the oxide layer caused by the presence of lower oxides like the conducting form NbO (Grundner, M. and Halbritter, J. 1980). Similar surface related problems occur in the production of super-conducting radio frequency cavities (Hahn, H. and Halama, H.J. 1976).

1.2 LOW TEMPERATURE OXIDATION OF METALS

Low temperature oxidation is a chemical reaction occurring between atmospheres containing oxygen and a metal surface at temperatures up to about 300 K. It is manifested by the formation of a very thin corrosion layer that ultimately prevents further rapid oxidation and ultimate destruction of the bulk metal. The Al-O system is a classic example of this phenomenon.

Much experimental and theoretical work has been carried out with the aim of understanding the reaction mechanisms and kinetics. In particular, Mott and co-workers (Fehlner, F.P. and Mott, N.F., 1970 and Cabrera, N. and Mott, N.F., 1948) have presented a mechanistic framework upon which they have derived some successful theoretical rate equations.

The earlier publication dealt only with cationic transport through the oxide layer driven by the presence of oxygen ions at the oxide-atmosphere interface. The more recent work included those mechanisms where anion transport played a role and even dominated the reaction. Fehlner and Mott emphasized the importance of place exchange in ion transport, especially in the transition

from the 'chemisorption' stage to the formation of a thin oxide film.

Most of the data upon which these authors based their observations was obtained by gravimetric microbalance and metallographic techniques such as the optical examination of taper sections. The growth of surface analytical techniques, used to study the arrangement and chemistry of submonolayer and very thin films, occurred subsequent to the later publication. Studies of metals in the early stages of oxidation began to appear after 1970. These showed that for fairly unreactive metals such as nickel (Norton, P.R. et al 1977) and copper (Braithwaite, M.J. et al 1975) a chemisorption stage could be discerned, followed by, at higher exposures to oxygen, formation of a thin oxide film. By contrast, more reactive metals such as magnesium (Fuggle, J.C. 1977) and potassium (Peterson, L.G. and Karlson, S.E. 1977) formed oxide films even at the very lowest oxygen exposures. Many other metals have been studied e.g. aluminium (Flodstrom, S.A. 1976), iron (Brundle, C.R. 1977), chromium (Peruchetti, J.C. et al 1979), lead (Chadwick, D. and Christie, A.B. 1980), cerium and titanium (Platau, A. et al 1977), the rare earths (Padalia, B.D. et al 1979), molybdenum (Bauer, E. and Poppa, H. 1979), and tungsten (Barrie, A. and Bradshaw, A.M. 1975).

Although there are many studies that describe the extent of metal oxidation under low oxygen pressures, the mechanisms by which the reaction takes place are in general not discussed. For instance, many of the above studies

reported that oxidation terminated at a layer thickness of about 0.5 to 1.0 nm (or two to three oxide layers) but no mechanism was suggested for this result. The role and relevance of ideas like 'incorporation' (in which oxygen atoms penetrate the metal layers) and 'place exchange' (in which neighbouring atoms exchange their places in the lattice) have yet to be clarified. Owing to these, and other, unresolved aspects of the formation of thin oxide layers, the chemistry and physics of surfaces continue to be rapidly expanding areas of scientific research.

1.3 NIOBIUM

Niobium is a member of the second row transition elements. It has the atomic number, 41, with an electronic configuration of (Kr) d^5 . An understanding of the role of the oxide layer formed on niobium is important in several areas. Foremost amongst these is probably the application of niobium in Josephson junctions, where a niobium-niobium oxide - lead layered structure forms a very fast electronic switch at liquid helium temperatures. Other applications include certain zirconium based alloys containing niobium used in the nuclear industry and some stainless steels. An understanding of the nature of the oxide film formed on niobium in these various applications is necessary for its efficient use in industry.

The interaction of niobium and oxygen is characterised, on a bulk scale, by the formation of a range of Nb - O compounds. Nb_xO is formed at low oxygen pressures and high temperatures. The lowest, well

characterised oxide is NbO. This is a metallic conductor of similar conductivity to niobium itself. NbO₂ is a semiconductor at room temperature and transforms to a metallic conductor at temperatures above 1070 K, where a phase change occurs. Nb₂O₅ is a good insulator and the most stable oxide formed by niobium.

The crystal structure of niobium is body-centred cubic, in common with the other refractory metals W, Re, Mo and Ta, and its melting point is about 2740 K. The crystallography of the oxides is complex. NbO forms a defective NaCl based lattice; NbO₂ forms a rutile structure; and Nb₂O₅ exhibits polymorphism, with several structures formed from NbO₆ octahedra. A detailed description of the oxides is given by Terao, W. (1963).

1.4 SURFACE ANALYTICAL TECHNIQUES

A full description of a surface would include an analysis of the elements present; their distribution both laterally and in depth; their chemical state; the topography and morphology of the surface; and defect arrangements, such as grain boundaries, kinks and dislocations. No single technique could cover all of these requirements and so the method chosen should reflect the type of information sought. Most techniques of analysis require that a probe of photons, or electrons, or ions, is directed at the surface. The emissions from the surface, in the form of photons, or electrons, or ions are then measured. The various spectroscopies that may be used are presented below in Table 1.1 (based on a compilation by Werner, H.W. 1980).

EXCITING PARTICLES	EMITTED PARTICLES			
	PHOTONS		ELECTRONS	IONS
	PHOTONS	XRF	XPS, UPS X-AES	LAMMA
	ELECTRONS	EPMA APS	AES SEM EELS LEED	ESD
	IONS	PIXE GDOS	I-AES	RBS SIMS ISS

XRF	X-ray fluorescence
EPMA	Electron probe microanalysis
APS	Appearance potential spectroscopy
PIXE	Proton induced x-ray emission
GDOS	Glow discharge optical spectroscopy
XPS	X-ray photoelectron spectroscopy
UPS	Ultra-violet photoelectron spectroscopy
X-AES	X-ray induced Auger electron spectroscopy
SEM	Scanning electron microscopy
EELS	Electron energy loss spectroscopy
LEED	Low energy electron diffraction
AES	Auger electron spectroscopy
I-AES	Ion induced Auger electron spectroscopy
LAMMA	Laser microprobe mass analysis
ESD	Electron stimulated desorption
SIMS	Secondary ion mass spectroscopy
ISS	Ion scattering spectroscopy
RBS	Rutherford backscattering

Table 1.1 Surface analytical techniques arranged by exciting radiation and the resulting emitted particle or radiation.

As can be seen from the above compilation a substantial number of important techniques are based on the analysis of slow electrons (those with energies below about 2keV) emitted from surfaces. Of these, three techniques in particular, have been used to study metal oxidation. They are x-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The production of ultra high vacuum (UHV), capable of maintaining a prepared surface 'clean' while experimental measurements are taken, has made practical the above methods of surface analysis.

LEED relies upon the diffraction of electrons from a surface to provide a means of studying surface crystallography. The electron energy chosen is usually of the order of a few tens to a few hundred electron-volts. This range provides both surface sensitivity (Chapter 2) and an electron wavelength (0.2 - 0.05 nm.) convenient for diffraction through large, easily measured angles. Many chemisorptive systems have been studied, especially on unreactive substrates, where 'on top' adsorption takes place. A review of this area is given by May, J.W. (1970).

AES has developed very much in parallel with LEED in its application to surface physics since a typical LEED apparatus can be modified simply to perform Auger spectroscopy. The technique provides an elemental surface analysis by analysing the kinetic energies of electrons emitted from atoms that are relaxing after the production of a core hole, produced by the incident high energy electron beam. It has been described in detail by

Holloway, P.H. (1978). Until recently, most Auger analyses were being applied to the physics and chemistry of surfaces. In the last few years, the technique has emerged in the industrial sphere as a complementary tool to the EPMA providing information on the spatial distribution of elements heavier than Li. Although, in principle, chemical information is contained in Auger spectra, poor analyser resolution, beam effects, and the common differential mode of data collection have combined to preclude the widespread use of the technique for chemical state analysis. However, recently, there are hopeful signs that progress in this field is accelerating. For example, AES is increasingly being performed in combined XPS apparatus using analysers of potentially high resolution. Also the work of Yashonath, S. and Hegde, M.S. (1980) shows that the intensity of valence band Auger transitions depends upon the number of electrons in the valence band and information of this type is related to the chemical nature of the element examined.

While AES has been developed in UHV conditions at low resolution, XPS has followed a very different path. The early work of Seigbahn, K. and his group (1967), who pioneered the technique, was carried out in poor vacuum but at high resolution. Interest initially was in the use of the technique to determine the chemical state of an element by studying its atomic core levels. The surface sensitivity of the technique was at first not appreciated, and then considered a nuisance. When it was recognised that the technique was sensitive to the state of the top

few atomic layers of a material, instruments providing the UHV conditions to perform the XPS technique began to make their appearance commercially.

After a period of use solely for basic research, the major worldwide market for XPS equipment is now the industrial sphere. The major applications of XPS are in the study of catalysts, corrosion, thin films and adhesion as well as chemical state analysis of bulk materials. XPS is better suited than AES for chemical state analyses, since it is a 'one electron' process, whereas Auger electrons involve transitions between two or three electron levels. Since these two electron spectroscopies are essentially complementary, it is becoming common to find, commercially, one apparatus providing both types of spectroscopy by sharing a common analyser.

UPS is still essentially only used in basic research, since it does not, in general, provide an elemental analysis of a surface. Information is available regarding the valence electron arrangement of the surface atoms, and many studies have been performed upon clean, single crystal surfaces to investigate their band structure or surface electronic configuration e.g. dangling bonds on semiconductors (Rhodin, T. and Brucker, C. 1976). Other studies have examined the structure of adsorbate levels of small simple molecules on surfaces of catalytic interest. Another large field of interest has been, and continues to be, centred on the formation of thin oxide films on metals.

1.5 THE PRESENT WORK

As discussed above, electron spectroscopy in its various forms is widely accepted as a powerful technique for application to the study of thin layers on surfaces. In particular, the general area of gas-metal interactions has received considerable attention with the view to understanding the corrosion and tarnishing of metal and alloy surfaces. In the present study, the formation of thin oxide layers on niobium, after exposure to low pressures of oxygen, has been studied by XPS, UPS and X-AES. Full use is made of all the features in the photoelectron spectrum.

The layout of this thesis is as follows: chapter 2 introduces those theoretical aspects of electron spectroscopy that are relevant; chapter 3 reviews previous work by other investigators on the adsorption of oxygen on niobium; chapter 4 discusses the experimental arrangement and methods; chapter 5 presents the spectroscopic results; chapter 6 is concerned with spectral processing and measurement; chapter 7 interprets the raw data in terms of oxide layer thickness, composition and general chemistry; chapter 8 presents and discusses the UPS spectra; chapter 9 brings the XPS, UPS and X-AES work together to present a reaction scheme for the adsorption of oxygen on niobium. An Appendix tabulates the data on peak intensities, binding and kinetic energies, peak asymmetry and width.

CHAPTER 2

SURFACE SCIENCE AND PHOTOELECTRON SPECTROSCOPY

2.1 SURFACE STUDIES IN ULTRA HIGH VACUUM

The study of very thin structures formed by the interaction of gaseous (and liquid) phases with solid surfaces has become possible on a wide scale owing to development of ultra high vacuum techniques during the 1960's. These improvements ultimately led to the emergence of commercial instruments. The requirement for ultra high vacuum (UHV), i.e. pressures below 1×10^{-9} Torr, can be seen by examining the rate at which gas molecules strike a surface.

The frequency of collisions with a surface, N , is given by the kinetic theory of gases, as

$$N = 3.5 \times 10^{26} \times \frac{p}{MT} \quad \text{m}^{-2}\text{s}^{-1}$$

where p is the pressure in Torr,

M is the molecular weight of the gas molecule

and T is the temperature (K).

This gives for oxygen at room temperature, a collision rate of $3.62 \times 10^{18} \text{ m}^{-2}\text{s}^{-1}$ at a pressure of 1×10^{-6} Torr and $3.6 \times 10^{15} \text{ m}^{-2}\text{s}^{-1}$ at 1×10^{-9} Torr. As solids have about 1×10^{19} atoms per square metre, it can be seen that a pressure of less than 1×10^{-9} Torr is required in order to prevent significant surface contamination in an experimentally convenient period of time, e.g. 1000 sec.

Fuggle, J.C. (1977) has described in detail the means by which ultra high vacuums are achieved and surface science experiments performed. The usual features of an UHV chamber are: stainless steel construction with copper gaskets and an absence of high vapour pressure materials; high speed pumping using either ion pumps, turbomolecular pumps, or diffusion pumps charged with low vapour pressure oil; and facilities for raising the temperature of the apparatus to above about 150°C.

Having achieved suitable vacuum conditions, several groups of techniques have emerged to examine surfaces in UHV. These include electron and ion spectroscopies as well as non-spectroscopic methods such as work function measurements. In the present study an UHV electron spectrometer was used to perform x-ray and uv photo-electron spectroscopy as well as Auger electron spectroscopy. The equipment and its use are described in Chapter 4.

2.2 PHOTOELECTRON SPECTROSCOPY

When a photon of sufficient energy interacts with an atom, an electron from that atom may be ejected with a kinetic energy given by

$$KE = h\nu - BE$$

where KE is the kinetic energy of the electron

$h\nu$ the energy of the incident photon

BE the binding energy of the level from

which the electron was emitted

If the energy of the photon is sufficiently high,

then atomic core levels will be excited. Since these levels are characteristic of the atomic number of the atom being excited, the technique may be used to identify the atoms present in a material. The photons required for this purpose lie in the soft x-ray region, and consequently this type of experiment is known as x-ray photoelectron spectroscopy (XPS). When ultra violet radiation is used, the electrons are excited from the valence band region of the specimen, and information concerning the bonding levels is obtained. Ultra violet photoelectron spectroscopy (UPS) has been particularly and extensively applied to gas phase studies of small molecules (Turner, D.W. et al 1970), and to the band structures of elements and compounds (Williams, P.M. 1977).

2.3 FUNDAMENTALS OF PHOTOELECTRON SPECTROSCOPY

The photo electron current (R, E, h) excited in a crystal in a particular direction $\underline{R}$ by incident photons of energy h may be described, following Feuerbacher, B. and Willis, R.F. (1976), by:

$$(R, E, h) = \frac{2 e \pi}{h} \cdot \left(\frac{e}{mc} \right)^2 \sum |M_{fi}|^2 \delta(E - E_i - h\nu) \quad \dots 2.1$$

where E is a particular kinetic energy

E_i an occupied initial state

M_{fi} the matrix element between the final and initial states, f and i respectively

e the electronic charge

m the electronic mass

The delta function selects those transitions which satisfy the energy selection rule. The matrix element

connecting the allowed transitions between initial and final states is:

$$M_{fi} = \langle f | \underline{A} \cdot \underline{p} + \underline{p} \cdot \underline{A} | i \rangle \quad \dots 2.2$$

where $\underline{A}$ is the vector potential of the incident photons and $\underline{p}$ is the momentum operator for the system. After a suitable transformation, Feuerbacher, B. and Willis, R.F. (1976), separated equation 2.1 into three terms:

$$M_{fi} = \left(\frac{-i}{\nu} \right) \left(\langle f | \underline{A} \cdot \nabla V_b | i \rangle + \langle f | \underline{A} \cdot \nabla V_s | i \rangle \right) - i\hbar \langle f | \partial \underline{A} / \partial z | i \rangle \dots 2.3$$

where V_b is the effective bulk potential term
 V_s the surface potential term
 ν the frequency of the radiation
 $\partial \underline{A} / \partial z$ the rate of change of the vector potential.

The first term refers to bulk effects, and the second two terms are concerned with the contribution to the photocurrent produced directly by the surface. These two terms may be particularly important at low photon energies (e.g. in UPS), but may be ignored at high energies (i.e. for XPS).

X-ray photoelectron spectroscopy

Only the first term in equation 2.3 need be considered at XPS energies since x-rays are not refracted significantly by solids and the contribution by the term containing V_s will be small compared to that containing V_b . For XPS the matrix elements, M_{fi} , are encountered experimentally in the form of photoelectron cross-

sections. These cross-sections indicate the intensities of photoelectrons to be expected from particular levels within atoms. Relative cross-sections can be measured experimentally (Evans, S. et al 1978) or determined theoretically (Scofield, J.H. 1976).

In XPS the energy selection rule is relaxed completely as for electrons of >100 eV kinetic energy the available final states merge to form a continuum. Thus for XPS the measured spectrum mirrors the distribution of initial states E_i .

Ultra-violet photoelectron spectroscopy

In the regime of ultra-violet photoelectron spectroscopy (UPS) all three terms in equation 2.3 may be of some importance. The first term, covering bulk photoemission, is generally assumed to account for most of the photoelectrons and many experimental results are interpreted along such lines. However, this assumption may not be entirely valid as the second term and to some unknown extent the third term in equation 2.3, could produce significant yields of photoelectrons under certain conditions. The third term, involving $\partial A / \partial z$, may be important as uv photons can undergo refraction at a surface - producing non-zero values for this differential. Photoemission, through these two surface effects, ought to be very surface sensitive and need not satisfy the bulk energy selection rules (the δ function in equation 2.1), since the final state would be a continuum into the vacuum.

As a result of these three contributing terms, a

particular UPS spectrum probably consists of a mixture of bulk and surface effects, making the interpretation of UPS spectra from solids a complicated procedure. A simple discussion of the spectra obtained in this work is given in Chapter 8, based upon the separation of the observed features into either oxygen 2p or niobium 4d bands.

2.4 INELASTIC SCATTERING

In the above sections the photoelectron current excited by photons has been described. However it is very important that the region in the sample from which the detected electrons emerge is known. In the energy range commonly used in XPS the incident soft x-rays penetrate about 10 microns into the solid. Photoelectrons are generated throughout this depth, but experiments have shown that only those electrons excited within ten nanometers of the surface have a reasonable probability of escaping. This is because an electron, as a charged particle, interacts more strongly with matter than x-rays.

The mean distance that an electron of a given energy will travel before losing energy to the solid is called the inelastic mean free path (imfp) or simply the mean free path (mfp). For electrons with energies of about 1keV, the mfp in many materials has a value of about one to two nanometers. The diagram below, Fig. 2.1, taken from Feuerbacher, B. and Willis, R.F. (1976) shows the behaviour of mfp as a function of electron kinetic energy. A minimum value, at energies of around 10 - 100 eV,

represents the region of high electron-material interaction. Towards both lower and higher energies the interactions become less likely and the mfp increases.

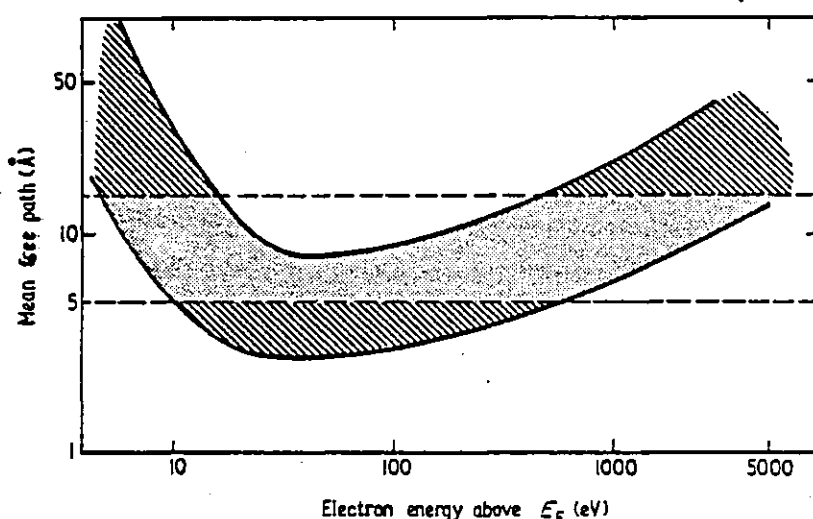


Fig. 2.1 The behaviour of the inelastic mean free path for electrons in the range of energies encountered in photoelectron spectroscopy.

The rate at which the mfp increases with energy, for energies greater than 100eV, is generally considered to follow the form given in the relationship:

$$\text{mfp} = kE^n \quad \text{where } n \text{ is } 0.5 - 0.7$$

The most thorough recent survey of experimental data in this area has been carried out by Seah, M.P. and Dench, W.A. (1979). Their conclusions were that the best fit to all reported data was achieved by the

following equations:

$$\lambda_m = 538/E^2 + 0.41(aE)^{\frac{1}{2}} \quad \dots 2.4$$

for elemental solids, and

$$\lambda_m = 2170/E^2 + 0.72(aE)^{\frac{1}{2}} \quad \dots 2.5$$

for compounds.

In these equations, λ_m is the mean free path, E is the electron kinetic energy (eV), and a is the monolayer thickness (nm). Experimental data on mfp are difficult to obtain. The usual approach is to use 'overlayer' experiments, in which thin layers of one element are evaporated onto a substrate of another element. The decrease in the substrate signal with increasing overlayer thickness yields information on the mfp of the electron. The experiment relies upon even, layer by layer, growth of the evaporated element. This assumption is difficult to verify completely in practice, and Evans, S. et al (1977) have called into question experiments using gold, since this element tends to sinter on surfaces very readily.

The values of mfp for niobium have been inferred from the work of Evans, S. et al (1977). These authors studied the mfp of 1200eV kinetic energy electrons in the first row transition elements and their conclusions are listed below, (taken from their Table 4).

Element and photoelectron	mean free path (nm)
V 3p	1.4
Cr 3p	1.4
Fe 3p	1.4
Co 3p	1.4
Ni 3p	1.4
Cu 3p	1.7
Zn 3p	1.5

Table 2.1 Inelastic mean free paths for electrons of about 1200eV kinetic energy in first row transition elements (Evans, S. et al 1977).

The valence band density of vanadium is the same as for niobium, d^5 , such that an extrapolation to 1150eV electrons in Nb is reasonable resulting in an estimated mfp of 1.3nm. This figure is well within the universal band of Feuerbacher, B. and Willis, R.F. (1976), shown in Fig. 2.1.

2.5 QUANTITATIVE X-RAY PHOTOELECTRON SPECTROSCOPY

The intensity ratio between two photoelectron lines from elements A and B in a compound A_nB_m is given by:

$$\frac{I_A}{I_B} = \frac{\sigma_A}{\sigma_B} \cdot \frac{T_A(E)}{T_B(E)} \cdot \frac{n}{m} \cdot \frac{E_A}{E_B}^{\frac{1}{2}}$$

where $I_{A,B}$ are the intensities, by peak area,
for the two lines

$\sigma_{A,B}$ are the relevant photoelectron cross-
sections including the asymmetry
factor

$E_{A,B}$ are the kinetic energies for the two
photoelectrons

$T_{A,B}$ are the transmission functions of the
analyser at the kinetic energies
of the photoelectron lines.

The individual terms in this relationship are now
discussed.

Cross-sections

The cross-sections $\sigma_{A,B}$ are related to the M_{fi}
matrix elements involved in equation 2.1 and are
composed of two terms. The first is a cross-section
describing the probability that photoexcitation will
take place. Those atoms having a high cross-section
at a particular photon energy have a greater chance of
being ionised by that photon than an atomic orbital
with a low cross-section. The second term describes the
probability that an excited electron will be emitted
in a particular direction, with respect to the incident
photon.

The basic cross-sections for Mg $K\alpha$ radiation for
the atomic core levels in question in this study are
taken from the experimental study of Evans, S. et al
(1978). The niobium 3d cross-section was not determined
from niobium containing compounds but was obtained by

interpolation from other neighbouring elements which were studied.

The angular asymmetry term, $L(\gamma)$, is given by:

$$L(\gamma) = 1 + \frac{1}{2}\beta(1.5 \sin^2\gamma - 1) \quad \dots 2.7$$

where β is the asymmetry term (varying with each core level)

γ is the angle between the incident photon and the emitted electron.

For s levels β is always 2, but for the other core levels it is a function of atomic number and core level and may vary between -1 and 2, (Reilman, R.F. et al 1976). This asymmetry factor has an important influence ($\pm 20\%$) upon the relative cross-sections between two elements.

Transmission function

The influence of the analyser has been assumed to follow a E^{-1} behaviour expected for a constant pass energy system (Seah, M.P. 1980) at least in the kinetic energy range greater than 500 eV (Chapter 4). This includes the important Nb 3d and O 1s photoelectrons (Mg $K\alpha$). At lower kinetic energies the transmission function may become constant with kinetic energy, but this regime is not of quantitative importance for the present work, although Auger electrons are studied in this region.

Energy dependence of mean free path

The term $E_A/E_B^{\frac{1}{2}}$ accounts for the behaviour of the mean free path with kinetic energy (E_A , E_B). A

complete survey of mean free paths reported in the literature has recently been published by Seah, M.P. and Dench, W.A. (1979). The authors show that the best fit to the data is obtained using relationships with the exponent of the electron kinetic energy being 0.5. (Section 2.3).

Intensity measurement

The exercise of measuring the intensities I_A and I_B is not straightforward. Firstly, the peak area must be measured as chemical environment or multiple chemical states influences the peak width and hence the peak height. However, as Evans, S. et al (1976) have argued it is possible that the total photocurrent associated with a particular emission may not be entirely within the peak area normally considered. An extreme example of this situation is the well known case of satellite structure on the 2p emission from paramagnetic transition metal salts e.g. Co^{2+} . In such a manner, the proper peak intensity of a spectral feature may be missed owing to its inclusion as a contribution to a featureless "background" to lower kinetic energy.

In the solid state such losses may occur owing to excitation of plasmons or shake up phenomena. Plasmons (Section 2.9) are collective excitations of the valence band electrons and may be excited during the photo-excitation event. As a result a certain fraction of the emitted electrons have kinetic energies lower than that of the main, no energy loss, peak by an amount corresponding to the energy of the plasmon (about 10-20eV).

Shake-up events result in similar spectra to plasmons, but the excitation in this case involves transfer of an electron from the valence band to some part of the conduction band. The best known examples of this phenomena occur during photoemission from the 2p core levels in paramagnetic salts of the first row transition elements. Fig. 2.2 below shows the 2p spectra from a series of Co salts demonstrating shake-up phenomena.

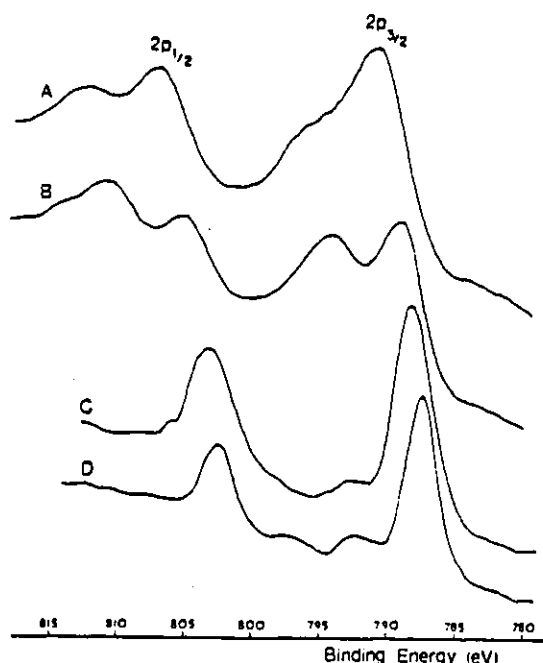


Fig. 2.2 Photoelectron spectra showing shake-up phenomena in paramagnetic Co compounds.
 (A) CoF_2 , (B) CoCl_2 , (C) $\text{K}_3\text{Co}(\text{CN})_6$,
 (D) $\text{Co}(\text{en})_3 \text{Cl}_3$.

2.6 RELATIVE INTENSITIES FROM THIN OVERLAYERS ON SUBSTRATES

The discussion in Section 2.4 considered the intensity ratio to be expected for an homogenous material $A_n B_m$. A more relevant situation in the present work arises when an oxide overlayer of thickness d is formed upon a semi-infinite elemental substrate.

The diagram below illustrates the model, Fig.2.3.

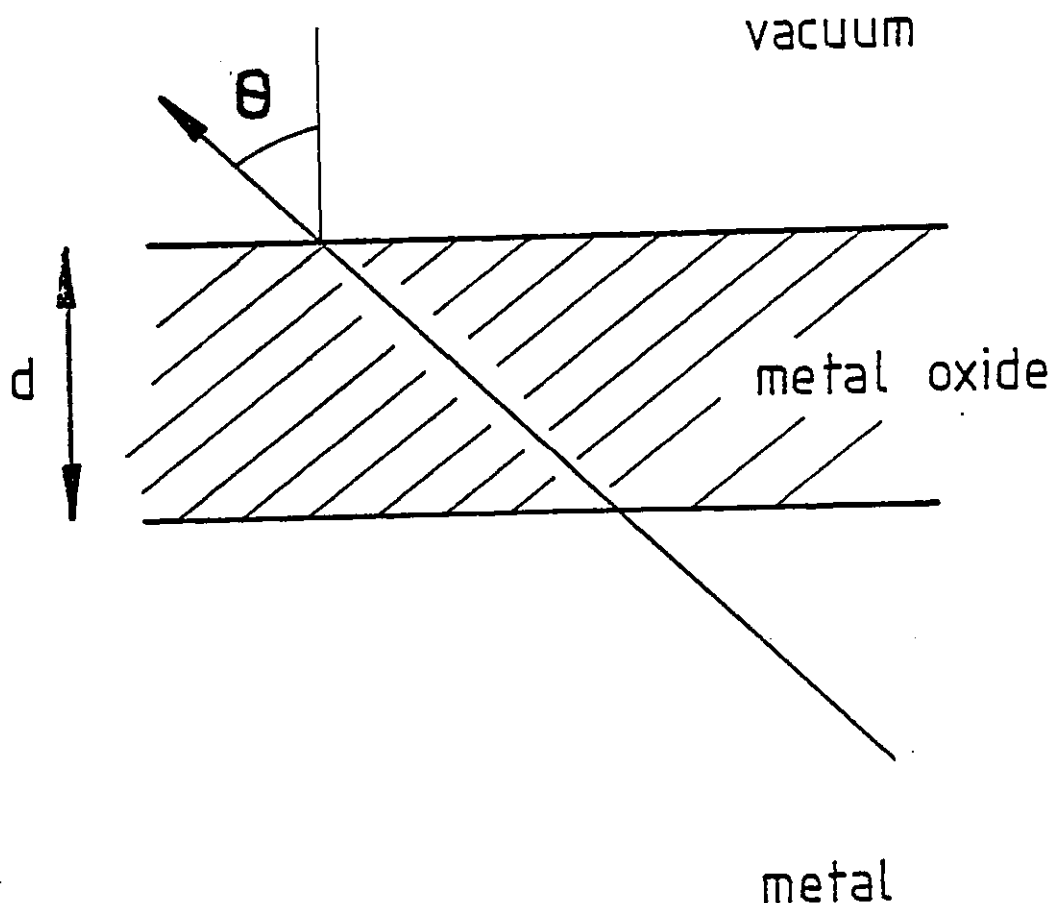


Fig. 2.3 The model describing the emission of photoelectrons from a metal with an oxide layer of thickness d . The emission angle is .

The overlayer is composed of an oxide M_xO_y with a characteristic mean free path, for photoelectrons generated from a particular level of atom i , of $\lambda_{i,o}$. The substrate may be considered as the elemental form of M with another characteristic mean free path, for photoelectrons generated from atoms i , of $\lambda_{i,sub}$. The electron emission angle is Θ with respect to the surface normal.

The intensity from a small element dz , at a depth z in a solid, may be written:

$$dI_i(z) = n_i \sigma_i \exp(-z/\lambda_i \cos \Theta) dz \quad \dots 2.7$$

where I_i is the intensity of a particular photoelectron emission from atom i
 n_i is the number density of atoms i in the solid
 σ_i is the cross-section for the core level being examined in atom i
 λ_i is the mean free path for the photoelectrons from atom i .

The total intensity, I_i , from the solid, of electrons excited from an atom i , is:

$$dI_i(z) = n_i \sigma_i \int_0^{\infty} \exp(-z/\lambda_i \cos \Theta) dz \quad \dots 2.8$$

$$= n_i \sigma_i \lambda_i \cos \Theta \quad \dots 2.9$$

The intensity expected from an overlayer as in Fig. 2.3 may be obtained in a similar manner to equation 2.9. In the case of an overlayer the total

intensity, $I_{i,o}$, is:

$$dI_{i,o}(z) = n_{i,o} \epsilon_i \int_0^d \exp(-(z/\lambda_{i,o} \cos \theta)) dz$$

$$I_{i,o} = n_{i,o} \epsilon_i \lambda_{i,o} (1 - \exp(-(d/\lambda_{i,o} \cos \theta))) \quad \dots 2.10$$

The fraction $F_{sb}(d)$ of the intensity from the substrate sb which passes through the overlayer of thickness d is:

$$F_{sb} = \exp(-(d/\lambda_{i,o} \cos \theta)) \quad \dots 2.11$$

Therefore, the intensity $I_{i,sb}$ observed from the substrate through the overlayer of thickness d is, from equation 2.11 and 2.9:

$$I_{i,sb} = n_{i,sb} \epsilon_i \lambda_{i,sb} \cdot \exp(-(d/\lambda_{i,o} \cos \theta))$$

The ratio of overlayer intensity to substrate intensity is then:

$$\frac{I_o}{I_{sb}} = \frac{n_{i,o} \epsilon_i \lambda_{i,o} (1 - \exp(-(d/\lambda_{i,o} \cos \theta)))}{n_{i,sb} \epsilon_i \lambda_{i,sb} \exp(-(d/\lambda_{i,o} \cos \theta))} \quad \dots 2.12$$

The attenuation A may be defined as I_{sb}^o/I_{sb}^∞ where I_{sb}^o is the substrate intensity with an overlayer present and I_{sb}^∞ is the intensity from a clean substrate. The following relationship then holds for the attenuation A :

$$A = \frac{n_{i,sb} \epsilon_i \lambda_{i,sb} \cos \theta \exp(-(d/\lambda_{i,o} \cos \theta))}{n_{i,sb} \epsilon_i \lambda_{i,sb} \cos \theta}$$

which reduces to

$$\ln A = \frac{d}{\lambda_{i,o} \cos \theta}$$

and hence to

$$d = \ln A \lambda_{i,o} \cos \theta \quad \dots\dots 2.13$$

This particular relationship provides a method of obtaining the thickness of an overlayer without a knowledge of its composition, assuming a mean free path value $\lambda_{i,o}$.

In a situation where adsorption takes place in the form of a monolayer of adsorbed atoms the following relationships hold.

$$I_{ad} = \sigma_{ad} C T_{ad}$$

$$\text{and } I_{sub} = \sigma_{sb} n_{sb} T_{sb} \lambda_{sb} \cos \theta$$

where I_{ad} , I_{sb} are the measured intensities for the adsorbed atoms and the substrate atoms respectively

σ_{ad} , σ_{sb} are the cross-sections for the adsorbed and substrate core levels

T_{ad} , T_{sb} are the transmission functions for the adsorbed atoms and substrate atoms photoelectrons

C is the concentration of adsorbed atoms

λ_{sb} is the mean free path in the substrate

n_{sb} is the number density of the substrate

where $n_{sb} = \frac{\rho \cdot N}{M}$

ρ is the substrate density

N is Avogadro's number

and M is the atomic weight of the substrate.

Therefore the following equation may be written:

$$\frac{I_{ad}}{I_{sb}} = \frac{G_{ad} \cdot C \cdot T_{ad} \cdot M}{N \cdot G_{sb} \cdot T_{sb} \cdot \cos\theta \cdot \lambda_{sb}}$$

or

$$C = \frac{G_{sb} \cdot \lambda_{sb} \cdot \cos\theta \cdot N}{G_{ad} \cdot M} \cdot \frac{T_{sb} \cdot I_{ad}}{T_{ad} \cdot I_{sb}}$$

For oxygen adsorbed onto niobium this reduces to:

$$C_o = \frac{I_o}{I_{Nb}} \cdot 8.75 \times 10^{19} \text{ oxygen atoms. m}^{-2} \dots\dots\dots 2.14$$

and for carbon on niobium to:

$$C_c = \frac{I_c}{I_{Nb}} \cdot 26 \times 10^{19} \text{ carbon atoms. m}^{-2} \dots\dots\dots 2.15$$

2.7 CHEMICAL SHIFTS

In Section 2.1 it was shown that XPS measured the distribution of initial states E_i . The most important factors influencing the value E_i for a particular atomic core level are the spatial distribution of the orbital about the effective nuclear charge of the atom. Thus the binding energies of the 1s levels depend upon Z^2 , the atomic number of the atom, as predicted for H like atoms by Bohr and demonstrated experimentally by Moseley using the $K\alpha$ x-ray lines of the elements.

A second order influence upon the binding energy of core levels occurs through the chemical state of the atom involved. In the charge-potential model introduced by Siegbahn, K. et al (1969), in an atom A the binding energy of a core level may be written as:

$$BE(i_A) = K_i^A q_A + eV_A \quad \dots\dots\dots 2.16$$

where q_A is the partial charge on the atom A

K_i^A is an adjustable parameter, and

V_A is the potential due to neighbouring atoms B. V_A is approximately:

$$V_A = \sum_{B \neq A} \frac{q_B}{4\pi \epsilon_0 d_{AB}} \quad \dots\dots\dots 2.17$$

where d_{AB} are interatomic distances.

The BE of a core level is sensitive to variations in the charge on an atom through changes in chemical bonding. The local chemical environment also influences the binding energy through V_A , the Madelung potential. Both of these factors will change owing to differing chemical environments.

Approaches such as the charge potential model described above do not take into account the relaxation around an atom during photoexcitation. Relaxation stabilises the charge left on the excited atom in the final state ion as shown schematically below, Fig. 2.4, for the case of a metal.

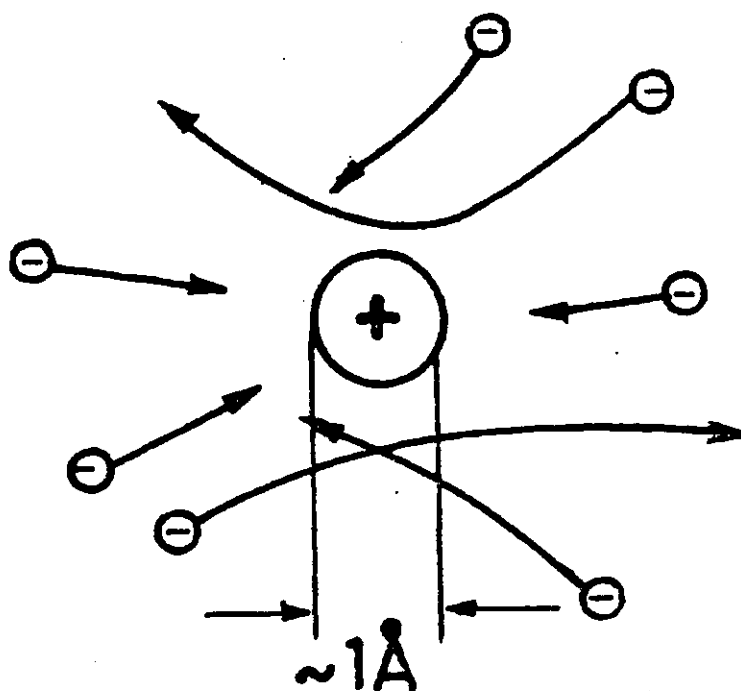


Fig. 2.4 The response of electrons in the vicinity of a suddenly created core hole relaxes the final state energy.

Although the magnitude of relaxation may be considerable it is usually taken as being sufficiently constant, between chemical states, not to significantly alter the validity of approximations such as Eq. 2.16.

The figure below, Figure 2.5, presents the XPS spectrum of ethyl trifluoroacetate.

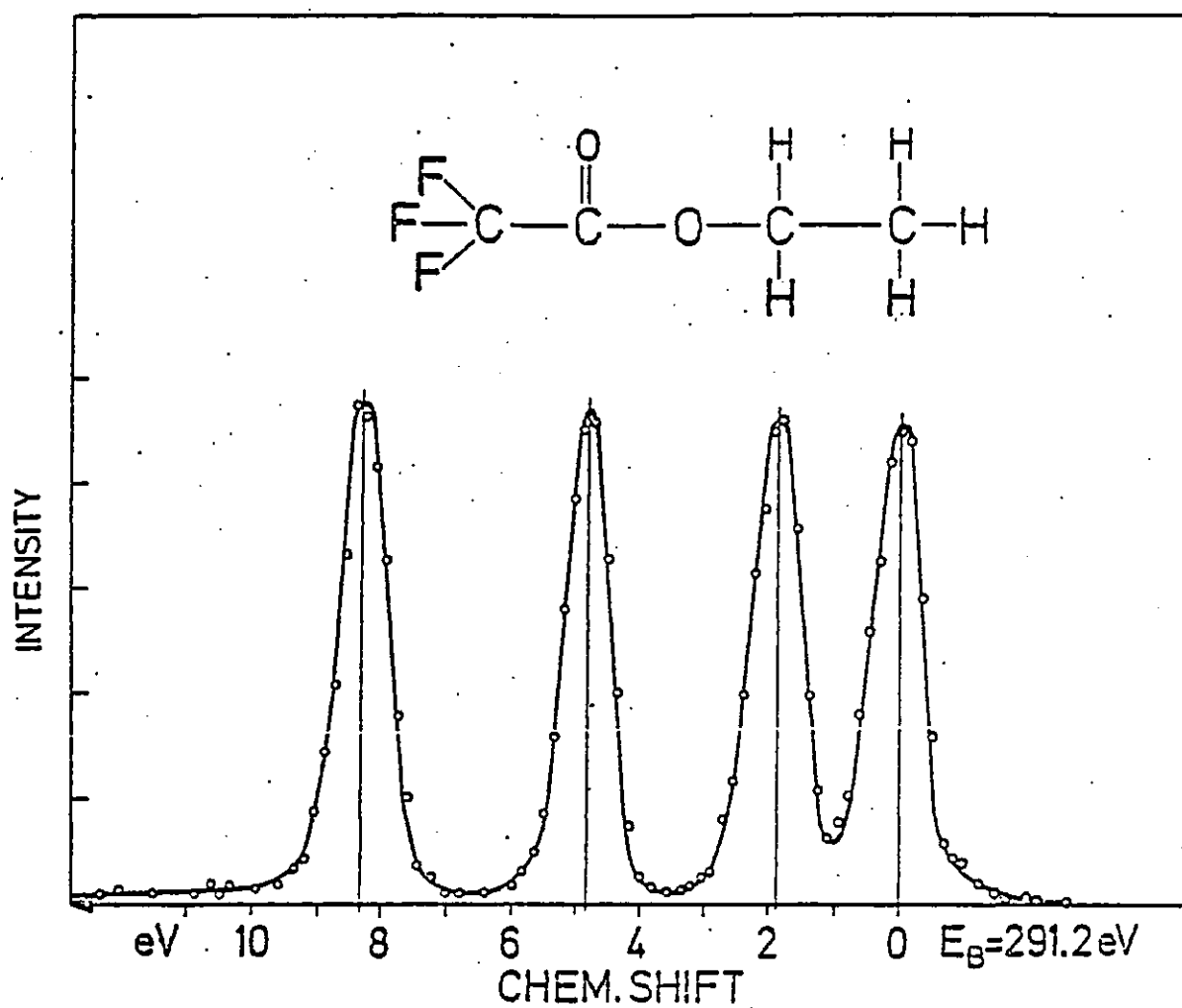


Fig. 2.5 The XPS spectrum of ethyl trifluoroacetate showing the influence of chemical environment upon the binding energy of the four carbon atoms.

The four separate peaks are associated with the increasingly positively charged carbon atoms. This assignment may be made as the effective nuclear charge is higher for positively charged atoms than for neutral atoms.

A shift towards higher binding energy is usually seen in a particular element for the transition from

metal to oxide. Smaller shifts are also observed for the O 1s level in different chemical environments e.g. oxides, silicates and organic groups etc. (Wagner, C.D. 1980). For niobium, there are several reports of chemical shifts between metal and the oxides, and these are reviewed in Chapter 3. It is only because of the chemical shift effect that the distinction between I_{metal} and I_{oxide} can be made, and the relationships in Section 2.6 actually used.

A description in some detail of the chemical shift is given by Carlson, T.A. (1972) and also by Orchard, A.F. (1977).

2.8 THE AUGER PROCESS

When a core hole is created in an atom by a photon or electron one of two events may occur. The first is x-ray fluorescence in which a high energy photon is released as an electron from a lower binding energy level occupies the hole. This process is the basis of x-ray analysis in electron microscopes, microprobes and x-ray fluorescence instruments.

The alternative process occurs when a high energy electron is emitted from a low binding energy level as the deep core hole is filled. These two schemes are shown diagrammatically below in Fig. 2.6. This alternative relaxation method was first described by Auger, M.P. (1925), who was concerned with some studies of radioactive elements.

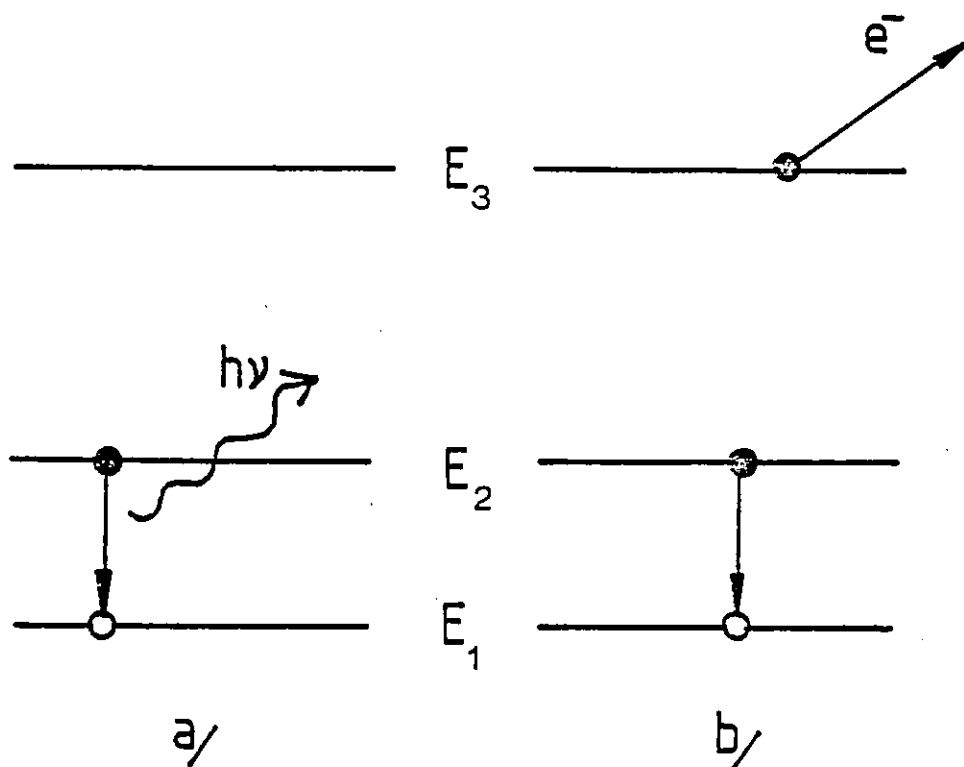


Fig. 2.6 Schematic representation of the emission of an x-ray photon (a) or an Auger electron (b).

Auger electrons are the predominant route for an atom when a core level of less than 10keV has been ionised. At greater energies the x-ray emission mode becomes dominant. Thus for the light elements up to fluorine 99% of ionised 1s levels are relaxed by Auger emission.

In the spectra to be examined in the body of this work 0 Auger peaks derived from a 1s ionisation will be shown, together with Nb Auger spectra from the $M_{4,5}(3d)$ level. These two transitions involve upper levels (E_3 in the diagram) which are in the valence band. As a result, the peak positions and shapes reflect changing chemical environments. The chemical effect in Auger

spectroscopy is now widely appreciated as discussed by Haas, T.W. et al (1972).

The influence of the chemical environment may be apparent in two ways. The first involves shifts in the kinetic energy of the Auger emission usually towards lower kinetic energy upon compound formation, the magnitude of which is sometimes considerably larger than the equivalent shift in the XPS binding energy measurement (Wagner, C.D. 1977). Unfortunately although the size of the effect is large the inherent width of Auger emission peaks is quite large and these shifts are usually more difficult to use.

The second effect of the chemical environment has only recently been pointed out (Yashonath, S. and Hegde, M.S., 1980). If the upper levels involve valence electrons then the availability of electrons to take part in the process becomes important, and the yield of Auger electrons in that transition is effected. This can be easily seen in the L derived Auger peaks from the first row transition elements (Allen G.C., et al 1977). These transitions are characterised by three emission lines the two most energetic of which involve the valence band. At the beginning of the series e.g. V or Cr these two peaks are very weak relative to the low energy peak. At the end of the transition series, e.g. Cu or Ni where the valence band is full (d^{10}), the high energy, valence band Auger peaks become the strongest in the whole L group. Sarma, D.D. et al (1980) have shown that this effect is also apparent in the spectra

of the oxides and sulphides of these elements and that the effect can be used for chemical state identification. As the Nb Auger peak is concerned with the valence band, this effect must be taken into account when chemical state data is being sought in the peak shape.

In particular, the equations derived in Section 2.6 cannot be used to estimate overlayer thicknesses as the 'cross-section' for the metal and oxide environments cannot be assumed to be the same.

2.9 PLASMONS

Plasmons are collective oscillations of the valence band electrons in a metal. They may be observed in the XPS spectra from metals and alloys as a series of low intensity peaks towards lower kinetic energy from an elastic photoelectron peak. Oscillations of the valence band electrons may be excited by a high energy electron travelling through the solid. Alternatively, it is possible that a plasmon may be created simultaneously with the ejection of a photoelectron from an atom. In the former case the event is termed extrinsic, and in the second, intrinsic, to the photoexcitation process. If it is extrinsic then the plasmon excitation is part of the electron scattering that contributes to the short mean free path in solids. In the second case, the intensity associated with the plasmon ought to be included in the photoelectron peak intensity for the purposes of quantification (in the same way as satellite structure is part of the true peak intensity).

The energy associated with a plasmon is given by

the following relationship (Kittel, C., 1971)

$$\omega_p = \left(\frac{4\pi N e^2}{m} \right)^{\frac{1}{2}}$$

where e is the electronic charge

m is the electron mass

N is the number of electrons per
unit volume

This relationship gives a volume plasmon energy of around 20eV for niobium, assuming that the s and d electrons in the valence band are free-electron like. A characteristic plasmon associated with the surface of metal also occurs. Its energy is approximately $E_p/\sqrt{2}$ or about 14eV for niobium. As XPS is a surface probe the intensity associated with the surface plasmon is expected to be significant. The surface plasmon may be identified by its sensitivity to surface contamination.

Both volume and surface plasmons are identified in the spectra presented in Chapter 5, and discussed in subsequent chapters.

CHAPTER 3

PREVIOUS STUDIES OF THE INITIAL OXIDATION OF NIOBIUM

3.1 INTRODUCTION

Early studies of the oxidation of niobium were performed at elevated temperatures and pressures producing relatively thick oxide layers. The composition of these layers appears to vary depending upon temperature, pressure and exposure time, but all three oxides (NbO , NbO_2 and Nb_2O_5) have been detected.

The availability of ultra high vacuum over the last decade and of suitable analytical techniques have allowed reliable measurements of thin surface layers to be made. All of the studies to be described below fall into this group. Studies have been made using some combination of the following techniques: LEED; AES; surface potential measurements; SIMS; XPS and UPS.

3.2 PANTEL, R., BUJOR, M. and BARDOLLE, J. (1977).

Following previous publications by this group (Simon, D. et al 1971, 1974) on the formation of thick oxide layers, these authors used a combination of LEED, AES and surface potential measurements to investigate the initial oxidation of (100), (110) and (111) Nb crystal faces.

To illustrate their work the results which deal with the Nb(110) face will be described. Fig 3.1 shows change in surface potential of a clean niobium surface upon exposure to oxygen.

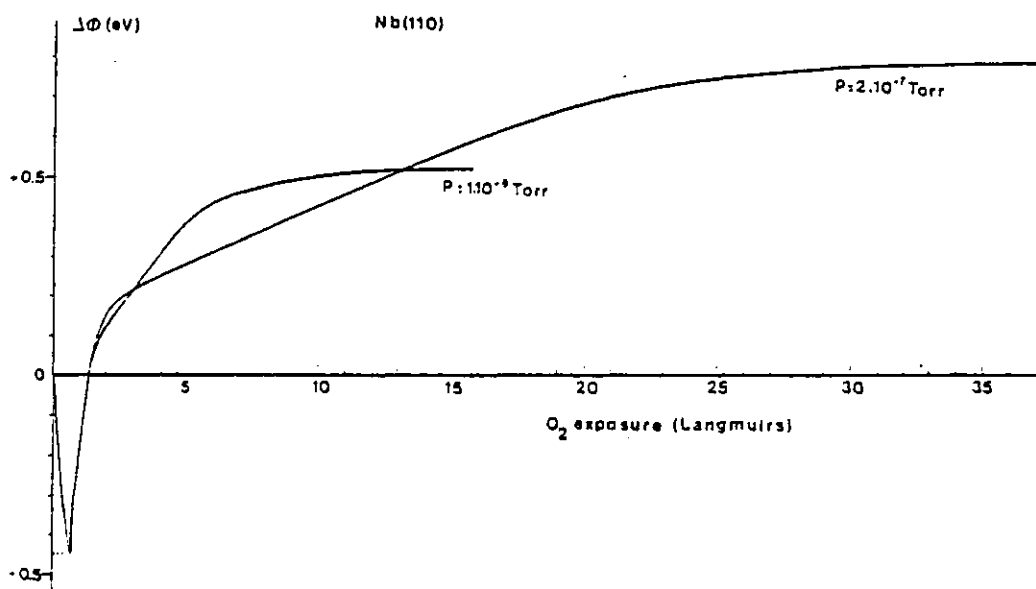


Fig. 3.1 Surface potential variations of a Nb(110) crystal place upon exposure to oxygen at room temperature.

The surface potential was measured using a mirror electron microscope, an instrument in which high energy electrons are reflected from a single crystal surface. The energy of the reflected electrons provide information on the surface potential.

Fig. 3.1 shows that the surface dipole initially decreases followed by an increase back to the original clean metal value. A linear rise then occurs up to exposures of about 5 L O_2 (3.6×10^{19} $O.m^{-2}$). Following this exposure the surface potential increases more slowly and approaches a saturation value. This

saturation value depends upon the partial pressure of oxygen. Pantel, R. et al interpreted these four regions in the following manner.

3.2.1 The initial decrease of surface potential.

The initial decrease is caused by oxygen incorporation under the first layer of niobium. The minimum in the surface dipole corresponds to a one third occupation of available sites on the Nb(110) surface. The LEED pattern at this stage is interpreted as a NbO(110) type plane on a Nb(110) substrate. The accuracy of the fit would be within 4% of the bulk NbO lattice dimensions.

3.2.2 The fast rise in surface potential.

The rise in surface potential resulting in a return to the original clean surface value occurs and the LEED pattern indicates a doubling of the oxygen periodicity in one direction on the surface. Again the authors conclude that a NbO layer, this time compact, is formed on the Nb(110) substrate.

3.2.3. Linear increase in surface potential.

The third stage, a linear increase up to exposures of 5 L O_2 ($3.6 \times 10^{19} \text{ O.m}^{-2}$), was interpreted as chemisorption of oxygen on the previously formed NbO layer. The authors noted that the formation of the 'chemisorbed' layer was independent of pressure (in the range $5 \times 10^{-9} - 5 \times 10^{-8} \text{ Torr}$) and required five minutes exposure to complete.

The authors suggested that the rate determining step was the dissociation of oxygen molecules at an

active site followed by diffusion of oxygen atoms across the surface. An alternative suggestion claimed that suitable sites for oxygen chemisorption were constantly created and so determining the overall reaction rate.

3.2.4 Approach to a limiting surface potential.

During the final stage the surface potential approached a saturation value. Higher pressures of oxygen produced higher saturation values for the surface potential. Physically adsorbed oxygen molecules were thought to be responsible for this behaviour, since if the oxygen flow was cut off then the surface potential immediately fell. On this evidence the adsorption was considered to be reversible.

Basically similar results were obtained on the Nb(100) and Nb(110) surfaces. These authors therefore suggested that initially a monolayer of NbO forms an niobium crystal surface. This structure then chemisorbs another oxygen layer followed, in turn, by some physical adsorption of oxygen. The formation of higher oxides was not postulated to take part in the reaction.

3.3. RIEDER, K.H. (1980).

In this recent report the author is concerned with the nature of oxygen adsorption upon Nb(110) and Nb(750) crystal planes. The techniques of LEED, AES and SIMS were utilised. A major part of the study was concerned with oxygen segregation from the bulk at elevated temperatures, although room temperature adsorption was examined.

The adsorption of oxygen at room temperature was

studied in the pressure range from 5×10^{-10} to 5×10^{-8} Torr. The oxygen $KL_{2,3}L_{2,5}$ Auger peak to peak height signal increased rapidly up to exposures of 5 L O_2 (3.6×10^{19} $O.m^{-2}$) followed by a plateau regime where the signal intensity increased more slowly. The Nb $M_{4,5}N_{2,3}V$ Auger signal at a kinetic energy of 167 eV fell rapidly in intensity and a second peak, shifted by 5 eV, appeared towards lower kinetic energy, as shown in Fig. 3.2.

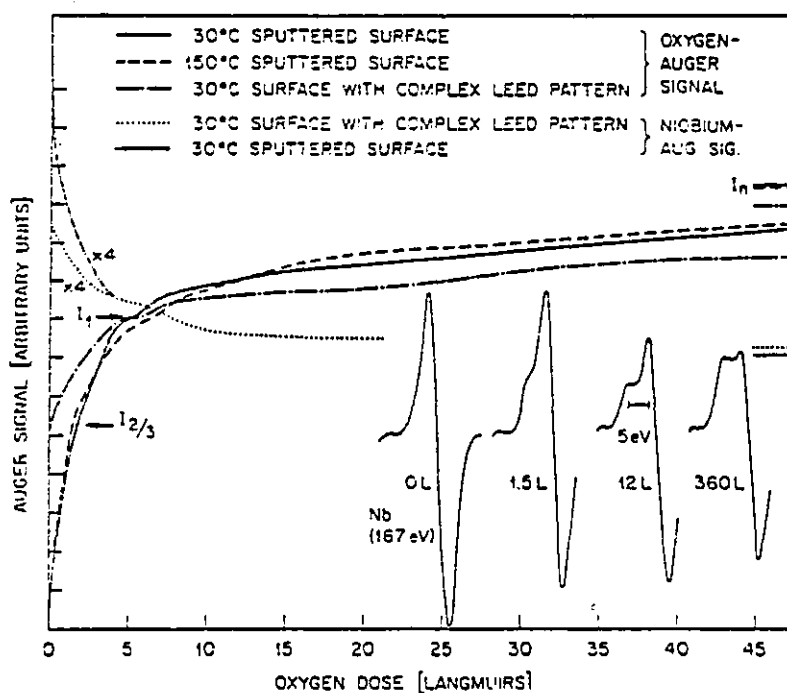


Fig. 3.2. Oxygen and niobium Auger peak intensities as a function of exposure to oxygen. The insert shows the Nb $M_{4,5}N_{2,3}V$ Auger peak lineshape.

Steady values for the Auger peak to peak heights were achieved at an exposure of 300 L O₂ (216×10^{19} O.m⁻²). At this stage the complex LEED patterns characteristic of lower exposures faded to give a featureless background which the author interpreted as evidence for an amorphous surface.

Rieder associated the appearance of a shifted Nb Auger peak with the formation of niobium pentoxide, Nb₂O₅, on the surface. At oxygen exposures lower than that required to produce this peak the author considered that oxygen chemisorption was taking place.

The SIMS work, carried out under conditions such that negligible damage to the sample surface took place, are relevant. The author noted that the SIMS spectrum from an oxygen saturated surface was very similar to that obtained from a bulk Nb₂O₅ sample. This suggested to the author that the outer surface layer was arranged in a manner related to Nb₂O₅.

By considering the escape depths and relative oxygen intensities from a saturated oxygen surface and bulk Nb₂O₅ specimen, Rieder obtained an overlayer thickness of 0.5 - 0.6 nm. This was interpreted as showing that, at the most, only two structural units of NbO₆ octahedra were formed. The author did not take into account the possible presence of lower oxides in considering the thickness of the oxide layer and its composition.

To summarise this work, Rieder proposed two regimes of adsorption. The first, up to exposures of

1.7 L O₂ (1.22×10^{19} O.m⁻²), results in oxygen adsorption onto the niobium surface. The second stage continues the rapid reaction up to exposures of 5 L O₂ (3.6×10^{19} O.m⁻²) by the formation of NbO₆ octahedra giving an overall surface stoichiometry equivalent to Nb₂O₅. Saturation of the surface occurred at exposures of about 300 L O₂ (216×10^{19} O.m⁻²), giving an amorphous oxide layer with a thickness of 0.5 - 0.6 nm.

3.4 USAMI, S., TOMINAGA, N. and NAKAJIMA, T. (1978)

These authors used LEED and AES to study the adsorption of oxygen on the Nb(100) crystal face. After noting that high temperature (2300K) treatment was the most effective method of surface cleaning, the authors studied oxygen adsorption, in the range up to exposures of 100 L O₂ (72×10^{19} O.m⁻²), at room temperatures. Although no structural model was proposed several interesting features were noted.

The Nb Auger transition at a kinetic energy of 26eV was completely suppressed after an oxygen exposure of only 10 L O₂ (7.2×10^{19} O.m⁻²). The work function remained constant up to an exposure of about 1 L O₂ (0.72×10^{19} O.m⁻²) before rising by 2eV to the saturation value. The LEED pattern at an exposure of 1 L O₂ (0.72×10^{19} O.m⁻²) was a sharp c(2x2) pattern, which faded completely by 4 L O₂ (2.9×10^{19} O.m⁻²) to leave the original (1x1) pattern. By an exposure of 20 L O₂ (14.4×10^{19} O.m⁻²) this pattern had been replaced by a featureless bright background.

The lack of a periodic structure when studied by

LEED, for a well exposed surface, agrees with Rieder, K.H. (1980) and therefore supports the suggestion that an amorphous surface is formed. However, these authors did not report any chemically shifted peaks in the Auger spectrum. They also failed to detect the fall in the work function with very small oxygen exposures as reported by Pantel, R. et al (1977).

3.5 LINDAU, I. and SPICER, W.E. (1974a, 1974b).

These authors studied the adsorption of oxygen on electron beam evaporated niobium by ultra violet photoelectron spectroscopy, UPS, using photons of energy up to 11.8 eV. Two reports appeared, one concerned primarily with the oxidation of niobium (1974a) and the other being concerned with the valence band structure of niobium as studied by UPS (1974b).

The latter report studied the valence band structure of clean niobium films over a range of photon energies from 7.6 to 11.8 eV. The authors compared their experimental results with available theoretical band structures (Matheiss, L.F. 1970). Lindau and Spicer postulated the presence of contributions in the UPS spectra from surface states.

In the oxidation report the results of exposing niobium films to oxygen in the range up to 10^5 L O₂ (7.2×10^{23} O.m⁻²), and at temperatures between 20 and 700°C, were reported. A typical set of spectra are shown below in Fig. 3.3

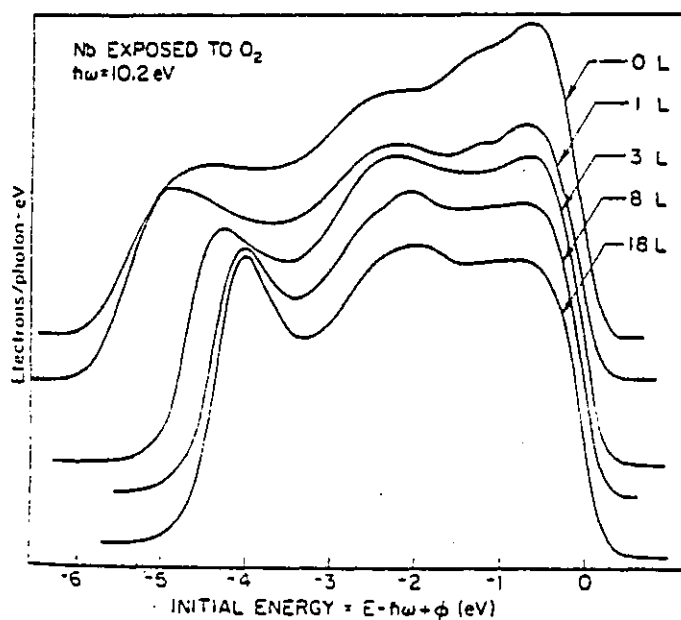


Fig. 3.3 The UPS spectra from a clean and oxygen exposed niobium surface ($h\nu = 10.2$ eV).

These authors noted the reduction of emission close to the Fermi level (E_F) for small oxygen exposures and the appearance of substantial emission around 4–5 eV binding energy (BE). For very large oxygen exposures ($4000 \text{ L O}_2 : 2.9 \times 10^{22} \text{ O.m}^{-2}$) emission from levels with a BE of less than 3 eV is reduced, and the major feature in the spectrum has a BE of about 4 eV. In these studies with relatively low energy photons the work function cut off occurs at a BE of

about 5 eV and therefore photoelectrons from the O 2p levels are not available for analysis.

Despite these limitations Lindau and Spicer came to the following conclusions:

- a) A protective oxide layer, possibly NbO, covers the surface.
- b) Above 500°C, and certainly at 700°C, a new oxide phase is formed, possibly NbO₂.
- c) When exposed to the atmosphere a thick insulator-like overlayer is formed that is most probably Nb₂O₅.

The authors suggested that further studies using higher energy u.v. sources, possibly in combination with x-ray photoelectron and/or Auger electron spectroscopy, would be useful.

3.6 MILLER, J.N., LINDAU, I. and SPICER, W.E. (1978)

Following the previously described study using low energy u.v. radiation, a further study by UPS has been reported, using HeI and HeII radiation, of the initial oxidation of niobium. By using the higher energy radiation, studies of the O 2p levels become possible. Based upon an analysis of these levels the authors suggested the following scheme for the initial oxidation of niobium.

- a) For small oxygen exposures a bonding arrangement of only one oxygen per niobium atom occurs.
- b) In the second stage above 10 L O₂ (7.2×10^{19} O.m⁻²), the formation of NbO_x, where

x is likely to be 2, takes place.

- c) In the final stage Nb_2O_5 is produced giving, at exposures of 1000 L O_2 ($720 \times 10^{19} \text{ O.m}^{-2}$), an oxide layer consisting of both NbO_2 and Nb_2O_5 is formed to a thickness greater than the UPS sampling depth.

3.7 THE BINDING ENERGY FOR THE Nb $3d_{5/2}$ LEVEL IN THE OXIDES NbO, NbO_2 AND Nb_2O_5 :

There are two reports in this area. The first is by Simon, D. et al (1976). These authors used XPS to study thick, thermally grown films of NbO and NbO_2 on Nb substrates. The composition of the films was determined by x-ray diffraction. A thick film of Nb_2O_5 , grown by electrochemical means, was also studied. The binding energies for the oxides (and niobium metal) are tabulated below.

	Binding Energy (eV)	Chemical Shift (eV)
Nb	201.7	0
NbO	203.0	1.3
NbO_2	205.4	3.7
Nb_2O_5	207.4	5.7

Table 3.1 The binding energies and chemical shifts for niobium and the three major oxides according to Simon, D. et al (1976).

The other report, by Karulkar, P.C. and Nordman, J.E. (1980), presents the following data for the same materials as Simon, D. et al. The authors used the B.E. of the

C 1s peak as a reference.

	Binding Energy (eV)	Chemical Shift (eV)
Nb	202.2	0
NbO	204.0	1.8
NbO ₂	206.0	3.8
Nb ₂ O ₅	207.3	5.1

Table 3.2 The binding energy and chemical shifts for niobium and the three major oxides according to Karulkar, P.C. and Nordman, J.E. (1980)

The agreement between these two sources is only fair. Karulkar and Nordman report higher chemical shifts for the two lower oxides, and a lower chemical shift for Nb₂O₅ than Simon, D. et al. This lower figure for Nb₂O₅ (5.1 ± 0.2 eV) is in good agreement with another brief report (Grundner, M. and Halbritter, J. (1980)). The error in the work of Simon, D. et al may lie in their assumption that charging of an electrochemically grown Nb₂O₅ layer would be negligible. As Nb₂O₅ is an excellent insulator it may have charged up by the 0.5 eV required to account for the discrepancy. However their measurements of the BE's of the lower oxides may be more accurate than Karulkar and Nordmann as in the spectra reported by Simon, D. et al, metallic Nb is present in both spectra.

Some uncertainty must remain in these reported values due to the problems of charge correction and the production of representative oxide structures within

the very thin XPS sampling depth.

3.8 SUMMARY OF PREVIOUS WORK.

Surface potential measurements on single crystal surfaces suggest that four stages in the oxidation can be observed. Simultaneous LEED results indicate that in the low exposure regime ordered overlayers are formed. These layers appear to be based upon an NbO lattice. At higher exposures an amorphous surface structure appears together with chemically shifted peaks in the Auger spectrum. Also at this stage the SIMS spectrum is similar to that obtained from bulk Nb₂O₅ powder. An oxide overlayer thickness of 0.5 - 0.6 nm has been estimated. Studies by UPS show that changes in the Nb 4d and O 2p bands take place. XPS studies of the oxidation of niobium prepared under ultra high vacuum conditions are not available.

CHAPTER 4

EXPERIMENTAL

This chapter describes the apparatus and techniques that were used to obtain the spectra in this thesis.

4.1 THE ULTRA HIGH VACUUM ELECTRON SPECTROMETER

4.1.1 Vacuum system

All the results in the present work were gathered using a Vacuum Generators ESCA 3 Mk 1 ultra high vacuum photoelectron spectrometer. The basic arrangement of the instrument is shown in Fig. 4.1, and a more detailed description has been given by Brundle, C.R. et al (1974).

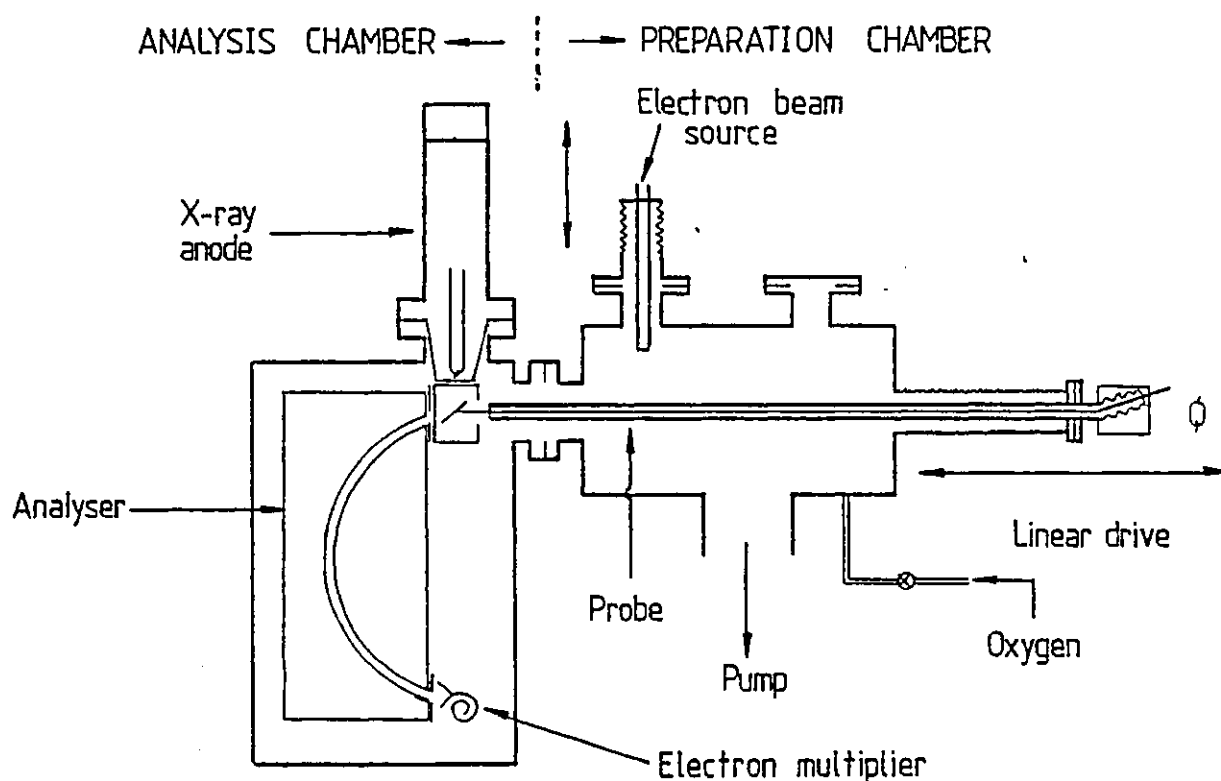


Fig. 4.1 Schematic arrangement of ESCA 3 Mk 1 spectrometer.

In order to obtain a sufficiently good vacuum to facilitate surface studies on clean materials, the system is constructed of stainless steel and uses copper gaskets. This combination allows the instrument to be baked to about 180°C in order to remove the more stubborn lower vapour pressure contaminants from the inner walls of the system. Two Edwards diffusion pumps, charged with Santovac 5 oil, and backed by two rotary pumps provide the pumping system. Both are connected to their respective chambers via liquid nitrogen cooled cold traps. These traps, to some extent, act as cryogenic pumps, but their main purpose is to reduce the vapour pressure of residuals in the region near the top of the pumps. These regions cannot be properly baked owing to the presence of indium seals, which would melt in the process. Two ion gauges (VG 20), located next to the cold traps, measure the pressure in the system. Their readings are usually lower than those found in the two experimental chambers themselves, because they are so close to the liquid nitrogen traps. Ultra high vacuum is routinely obtained following an overnight bake at $150\text{--}180^{\circ}\text{C}$. The pressure measured on the analyser side is usually 2×10^{-10} Torr, and on the preparation side about 3×10^{-10} Torr.

The heart of the instrument is an almost hemispherical, 150° electrostatic analyser, with a radius of 100 mm, housed in a mu-metal chamber. A Faraday cage source volume lies next to one set of slits and a channel electron multiplier lies at the

other. A more detailed description of the analyser's characteristics is given in Section 4.2. Immediately above the Faraday cage is an x-ray source with an aluminium and magnesium twin anode. This allows rapid switching from one radiation source to the other. At right angles to the x-ray source lies a windowless, noble gas, discharge lamp that provides ultra violet radiation from the noble gases Ar, Ne and He. These are all more fully described in Section 4.3.

The preparation chamber consists of a 3" diameter stainless steel cylinder with its major axis in the horizontal plane. It supports two sets of ports perpendicular to its axis. The preparation chamber is fitted at one end with a gate valve that isolates it from the analyser chamber. The specimen is introduced at the other end on a carrier fixed to a long worm drive. In this study the specimen carrier, often referred to as 'the probe', is aligned under either set of ports and rotated to face the preparative treatment arranged at that port. A VG AG 2 ion source is located at the line of ports immediately adjacent to the analyser chamber. This source provides a wide beam of argon ions and atoms with energies up to 10 keV and at currents of about 50 uA cm^{-2} for sputter etching specimens. On this same line of ports is sited a specially constructed, thoria-coated tungsten filament that provides a source of electrons at currents of up to 100 mA. These electrons can be accelerated by a 4-5 kV potential and when directed onto the rear face

of a specimen foil are capable of inducing sufficient heat to melt it. Other ports are occupied by a mass spectrometer (VG Q8), an evaporator for low melting point solids, a titanium sublimation pump (not used during these studies), a viewing window or left blanked. The preparation chamber is served by an Edwards EO2 diffusion pump via a UHV valve and 2" diameter steel tubing, a combination that considerably reduces the pumping speed of the chamber.

An independently pumped, gas handling system is available for use with the instrument. It consists of an Edwards EO2 air cooled diffusion pump suitably backed and bakeable stainless steel pipe work, with provision for six separate connections to bottles of high purity gases. The system can be connected quite simply to the ESCA 3, via a leak valve and a flexible stainless steel bellows.

4.1.2 Electronics

There are two basic requirements for data acquisition during electron spectroscopy experiments. First, a method is required of generating the necessary potential to scan the spectrum, followed, secondly, by a means of measuring the electron current at the exit slit of the analyser. A diagram of the arrangement that fulfilled these requirements during the course of this study is shown in Fig. 4.2.

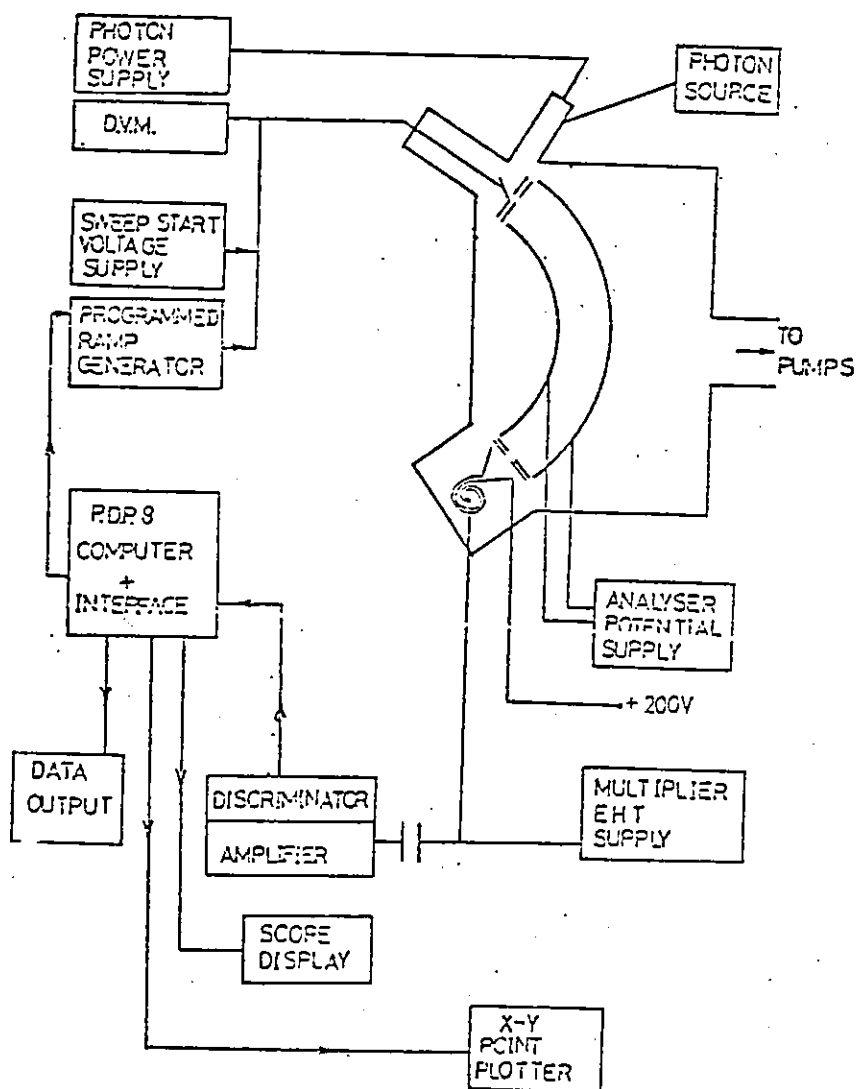


Fig. 4.2 The electronic arrangement fitted to the ESCA during the course of these studies.

The analyser on this instrument operates on the constant pass energy or fixed analyser transmission (FAT) mode. The latter phrase is commonly used although the analyser transmission is not fixed. 'Fixed' in fact only refers to the kinetic energy of the transmitted electrons. The first description, that of constant pass energy, avoids ambiguity and is probably the more suitable. In this mode fixed potentials are applied to the hemispheres and a retarding potential is ramped by a control unit to the specimen and the Faraday cage. The measured kinetic energy is the sum of the retard potential, the pass energy selected, and the analyser work function. A detailed description of the behaviour of the analyser is contained in Section 4.2.

An unconventional technique is required to measure the electron current at the exit slit of the analyser since it is small, of the order of $10^{-13} - 10^{-16}$ A. A channel electron multiplier is used to amplify this current. Individual electrons striking the inner wall of the multiplier produce a cascade of three or four electrons per collision. This electron shower increases in amplitude as it passes down the high voltage gradient in the multiplier. At the end of the sequence, a pulse of about ten nanoseconds duration and containing around 10^8 electrons is produced. This is fed through a discriminator and converted into a NIM standard pulse of 500 nanoseconds duration before being introduced to the counting circuit.

4.1.3 Data acquisition

A PDP 8f minicomputer is utilised to drive the instrument and perform the counting operations required to record a spectrum. An associated interface coordinates the electronic requirements of the computer and the instrument. The computer provides digitally coded information, representing a position along a spectrum that is then converted to an analog voltage by a digital to analog converter. This voltage drives a ramp generator in the control unit. The pulses from the detection equipment are counted for a particular dwell time (usually 40 ms) and the total number of counts stored in a channel in a memory array. The number of individual channels is 1024 (2^{10}). A spectrum thus consists of a fine histogram with the number of counts at a particular kinetic energy and dwell time displayed as the ordinate.

Once stored in the array the spectrum may be manipulated by various simple routines. These include smoothing techniques and subtraction of one memory half from the other. Raw and processed data can be stored on cassette tape, paper tape or plotted on graph paper using an X-Y recorder. The computer commands are entered and controlled from a ASR teletype.

4.2 THE ANALYSER AND ITS PROPERTIES

The analyser installed in the ESCA 3 instrument is of the 'hemispherical' type (actually 150°) of 100 mm radius. It is a high band pass-filter transmitting only those electrons in a certain kinetic energy band.

The diagram below illustrates the arrangement for dispersing electrons according to their kinetic energy.

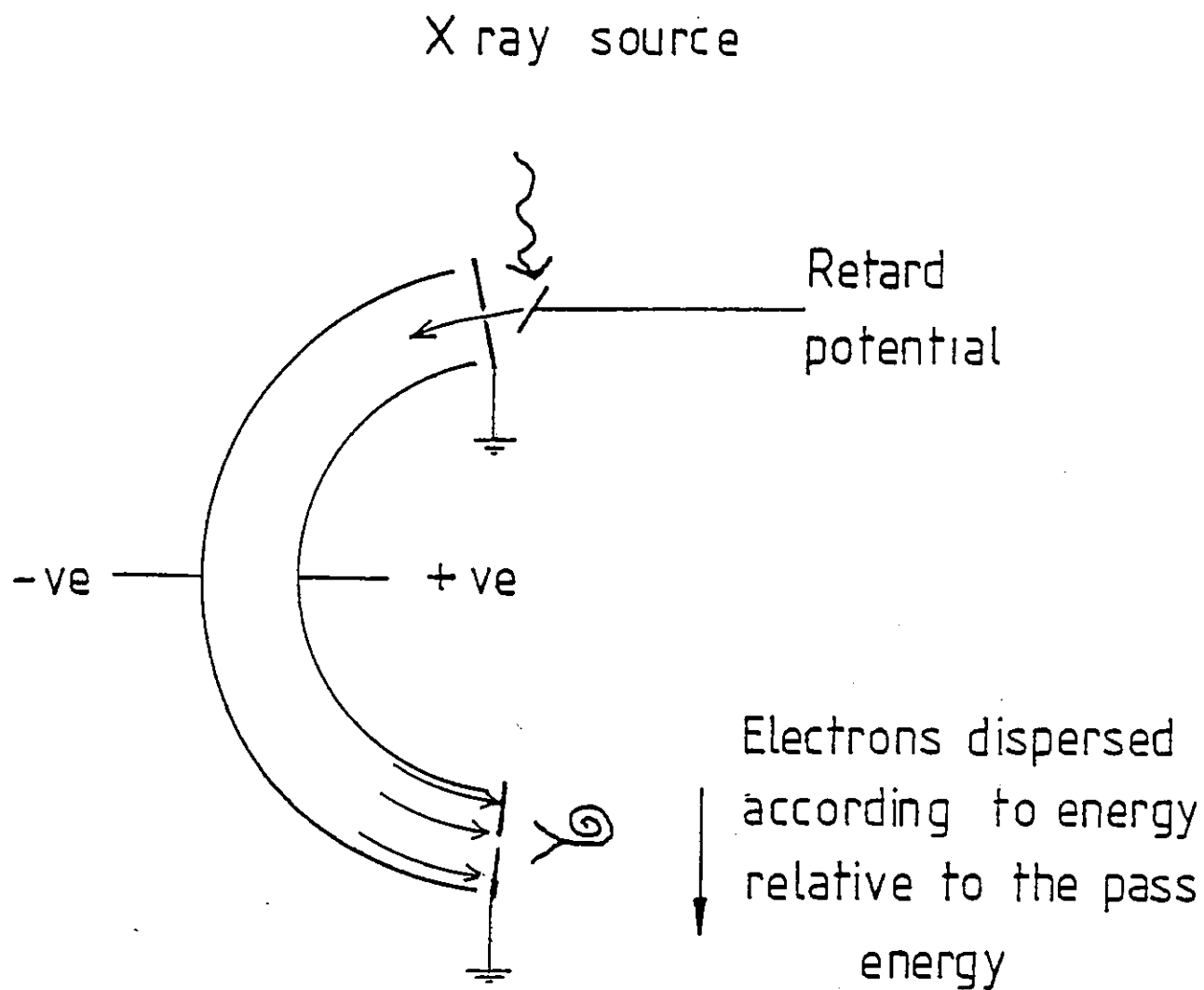


Fig. 4.3 Analyser arrangement

Electrons leaving the field-free region of the source volume pass through the earthed slits and enter the spherically symmetrical electric field of the hemispheres. Those electrons with kinetic energies close to the pass energy are dispersed along a focal plane at the exit slit. A small section of the dispersed electrons are transmitted by the slits and are collected by the electron multiplier. Those electrons with energies far from the pass energy will collide with the walls of the analyser and may contribute to the background level.

4.2.1 Resolution

The relationship between pass energy, analyser broadening and slit width is:

$$\frac{\Delta E}{E} = \frac{S}{2r} = \frac{S}{200}$$

where ΔE is the analyser broadening

E is the pass energy

S is the slit width

and r is the radius of the electron orbit

It can be seen that increasing the slit width, or increasing the pass energy, decreases the resolution, although the sensitivity is increased. The typical operating parameters in this study were $E = 50\text{eV}$ and $S = 2\text{ mm}$ giving an analyser broadening of about 0.5eV . Since the line width of the Mg $K\alpha$ radiation is 0.8eV , this degree of analyser broadening represents an acceptable compromise between resolution and sensitivity.

4.2.2 Transmission function

The transmission function of the analyser determines the relative sensitivity of different sections of the kinetic energy spectrum. The graph below in Fig. 4.4 shows various suggested transmission functions for a hemispherical analyser, operated in the fixed pass energy mode. Line a) shows the theoretical behaviour described by Brundle C.R. et al (1974) in the paper describing the ESCA 3 prototype. The transmission function is said to be inversely proportional to kinetic energy.

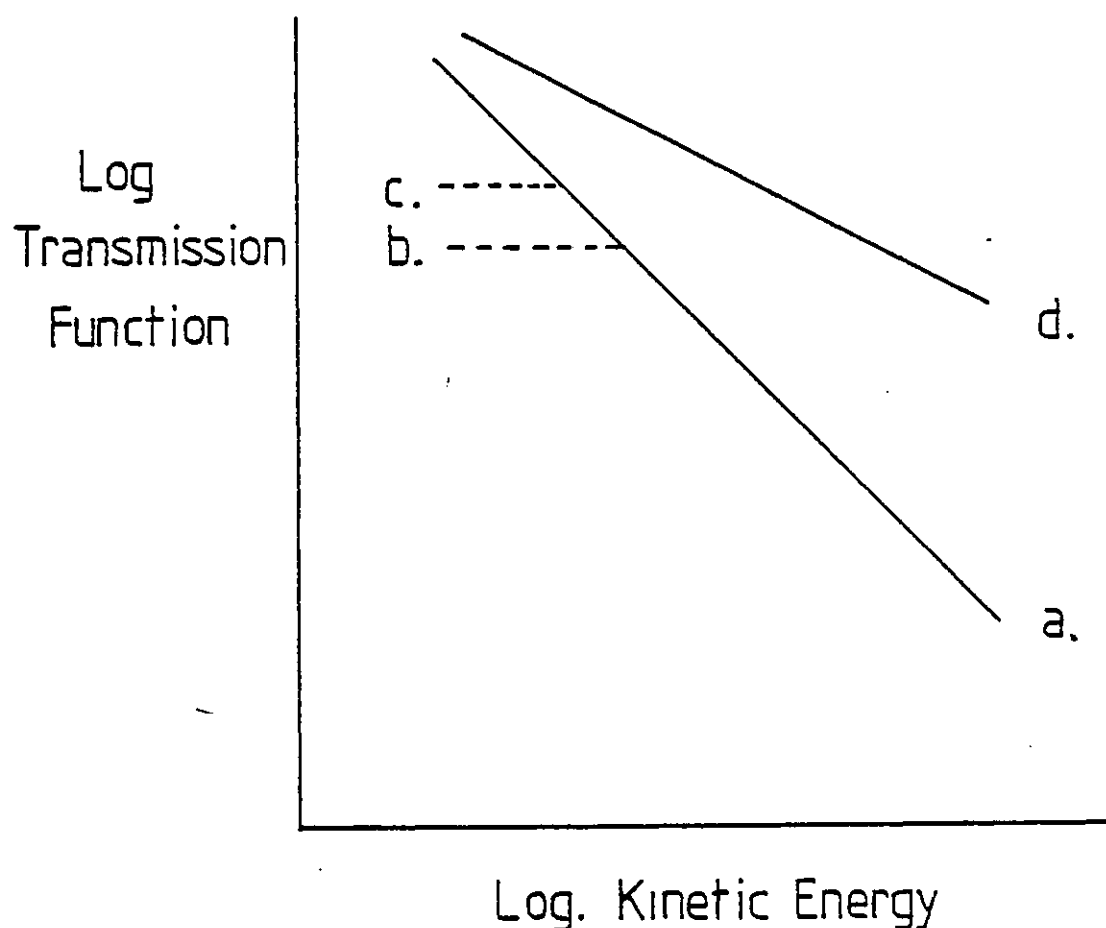


Fig. 4.4 Transmission functions of hemispherical analysers according to several authors, see text.

Lines b) and c) are intended to show the effect of 'the filling of apertures', which occurs when an area on the specimen, acting as a source of electrons, becomes limited by the slit dimensions (Seah, M.P. 1979). In these examples line b) represents a larger pass energy than line c). Line d) has been suggested recently by Castle J. (1979), based upon an examination of cross sections using a Si $K\alpha$ x-ray source. The relationship is $Tr \propto KE^{-\frac{1}{2}}$ rather than $Tr \propto KE^{-1}$ that is usually supposed.

Unfortunately, the actual behaviour of these analysers is not known. The kinetic energy at which 'the filling of apertures' becomes effective is thought to be below 500eV for the usual range of pass energies. The O 1s and Nb 3d photoelectrons will probably therefore fall on the KE^{-1} section of the function. However, some uncertainty does remain and this presents a problem when providing quantitative analysis by electron spectroscopy.

4.2.3 Take off angle from the specimen surface

The arrangement of the specimen and analyser is shown above in Fig. 4.3. It can be seen that as the electrons are only deflected by 150° during their dispersion, analysed electrons are not those emitted from the sample along the axis of the probe but at some angle from it. The angle is 15° and as a result for a flat specimen mounted at an angle of 45° with respect to the probe axis, analysed electrons are those emitted at an angle of around 60° with respect to the surface normal. This is shown in more detail in Fig. 4.5 below.

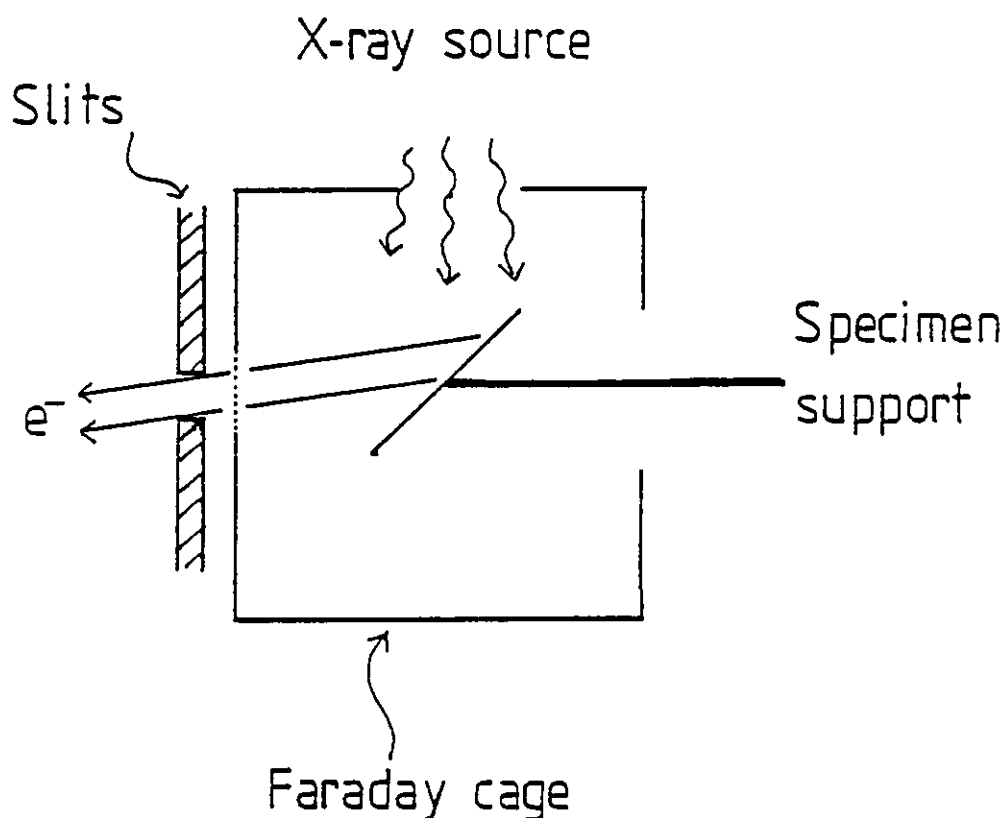


Fig. 4.5 The geometric arrangement for emitted electrons that enter the analyser from a specimen inclined at 45° to the probe axis.

4.3 RADIATION SOURCES

The ESCA 3 instrument is fitted with a twin anode x-ray source and a noble gas discharge lamp. The probe axis, x-ray source and discharge lamp are mutually orthogonal.

4.3.1 The X-ray source

The x-ray source consists of a water cooled twin anode, separately pumped by a small ion pump, with

aluminium and magnesium films supported on a copper block. Separate filaments supply electrons to the two coatings. The geometric arrangement is such that the filaments and Al and Mg films are not in line of sight. This minimises contamination from an outgassing or subliming filament. Either source can be selected without breaking the vacuum. The maximum power dissipation is 1000 W (15kV : 66mA) for the Al film and 500 W (12kV : 40mA) for the Mg film. In practice, however, these ratings lead to gross outgassing of the anode and boiling of the cooling water. In this study the Mg film was run at 12kV : 20mA.

The radiation produced by the x-ray tube is principally the $K\alpha_{1,2}$ line, superimposed upon a continuous Bremsstrahlung background, and it has the following characteristics for Al and Mg:

	$h\nu(\text{eV})$	Width at half maximum (eV)
Al	1486.6	0.85
Mg	1253.6	0.7

The transition responsible for the x-ray line is $2p \rightarrow 1s$ in the neutral atom. It is in fact the superimposition of two narrow lines originating in the spin orbit splitting of the 2p level ($2p_{3/2}$ and $2p_{1/2}$). In addition to this line there are also satellites at higher energies formed from charged atoms undergoing the same transition. For example $K\alpha_{3,4}$ arises from a singly charged atom; the $K\alpha_{5,6}$ from a doubly charged atom; etc. Another line inherent in the radiation is

the $K\beta$ line, a broad emission resulting from a $3s \rightarrow 1s$ 'forbidden' transition. It has 50eV (70eV) more energy than the $MgK\alpha_{1,2}$ ($AlK\alpha_{1,2}$) lines.

The relative intensities from the Al and Mg K lines are tabulated below in Table 4.1, taken from "Handbook of X-ray Photoelectron Spectroscopy", ed. Briggs, D. (1977).

Radiation may also be present originating from electron 'overflow' onto the other film (which is also at high voltage), and also Cu $L\alpha$ radiation from the backing material. Cu $L\alpha$ has an energy at about 930eV and is quite broad.

X-ray line	Separation from $K\alpha_{1,2}$ (eV) and relative intensity ($K\alpha_{1,2}=100$)	
	Mg	Al
$K\alpha_3$	8.4 (9.2)	9.6 (7.8)
$K\alpha_4$	10.0 (5.1)	11.5 (3.3)
$K\alpha_5$	17.3 (0.8)	19.8 (0.4)
$K\alpha_6$	20.5 (0.5)	23.4 (0.3)
$K\beta$	48.0 (2.0)	70.0 (2.0)

Table 4.1 X-ray emissions from Mg and Al sources

A calculation by Barrie, A. (1977) suggests that a Mg anode operating at a power dissipation of 600W provides an x-ray flux of 3×10^{12} photons s^{-1} onto a typical specimen.

4.3.2 The UV source

The radiation source for ultra violet photoelectron spectroscopy (UPS) is a differentially pumped, windowless, noble gas DC discharge lamp. Helium is the most common gas to be used in the source although neon and argon do provide some useful lines.

These ultra violet radiations are produced from the relaxation of excited atoms, both neutral and ionised. The atoms are excited during a continuous DC discharge at about 800 V and more than 50 mA in a gas cell. A capillary tube leads the radiation through a differentially pumped section and into the source volume. For He I and He II radiations at 21.2eV and 40.8eV, the atomic transition involved is $2p \rightarrow 1s$ in a neutral and ionised atom respectively. The transition involved is the same as that which produces the X-radiation from Al and Mg atoms.

Neon and argon can also be used, although their radiations are not as well separated or monochromatic as the He lines. The table below lists these characteristic lines.

He I	21.2eV
He II	40.8eV
Ne I	16.8eV
Ne II	26.9eV
Ar I	11.8eV

Table 4.2 Characteristic uv emission lines

With relatively high gas pressures (0.1 Torr) in the cell the predominant radiation is the He I line, but as the pressure approaches 5×10^{-1} Torr the population of ionised atoms increases in the discharge and He II radiation appears. Even so, under the most favourable conditions the He I to He II ratio will only be about 3. The overall intensity is much lower than when optimised for the He I line.

4.4 SPECIMEN PREPARATION

The specification for the Goodfellow Metals foil niobium used in this study was as follows:

Element	Analysis (ppm)
Fe	200
Ta	2000
Ti	30
C	50.
H	5
N	50
O	100

It was found that a satisfactory support could be fabricated from 0.5 mm tungsten wire to the following design:

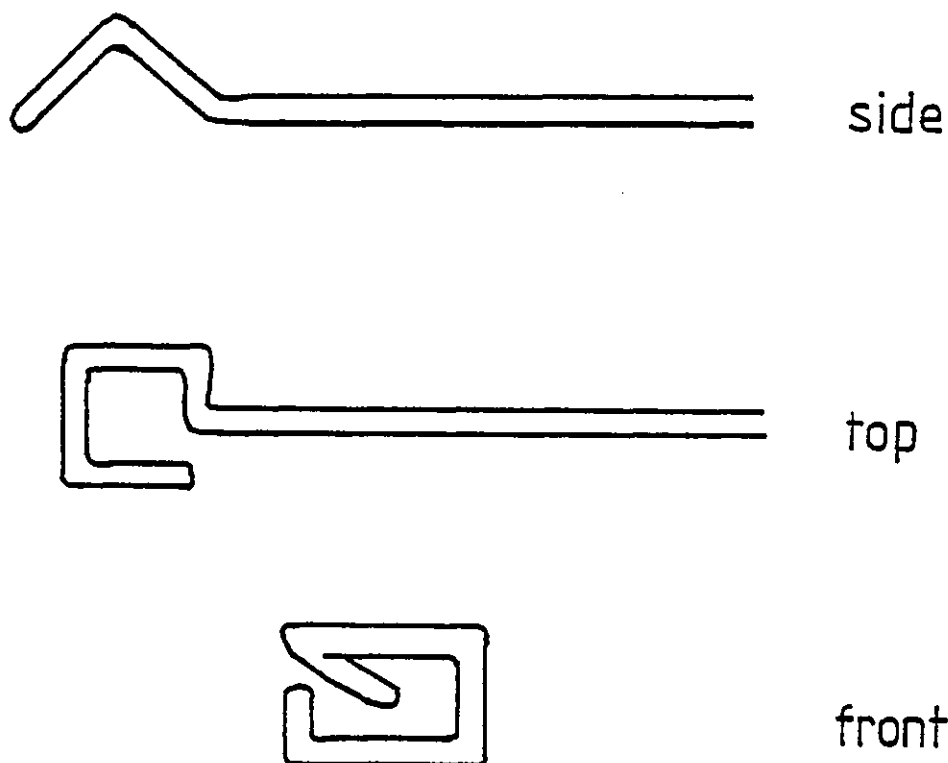


Fig. 4.6 Tungsten wire support for the niobium foil.

The tungsten wire was electrochemically cleaned in saturated NaOH solution, using a voltage of 6V A.C. A lead slab was used for the other electrode. When in the solution a layer of oxide was formed when the electrode was at a positive potential. When at a negative potential the oxide was removed, and, after many such cycles the wire became clean and free from contamination. The malleable niobium foil was simply wrapped around the assembly shown in Fig. 4.5 and pressed into place. The foil became bonded to the tungsten support during the cleaning and degassing routines used to prepare the specimen in vacuo. This

formed a strong, stiff arrangement which allowed reproducible positioning of the niobium foil in the Faraday cage. The long straight support section was developed in order to reduce heat transfer to the probe.

Specimen heating was provided by a thoria-coated tungsten wire filament to the design shown below in Fig. 4.7.

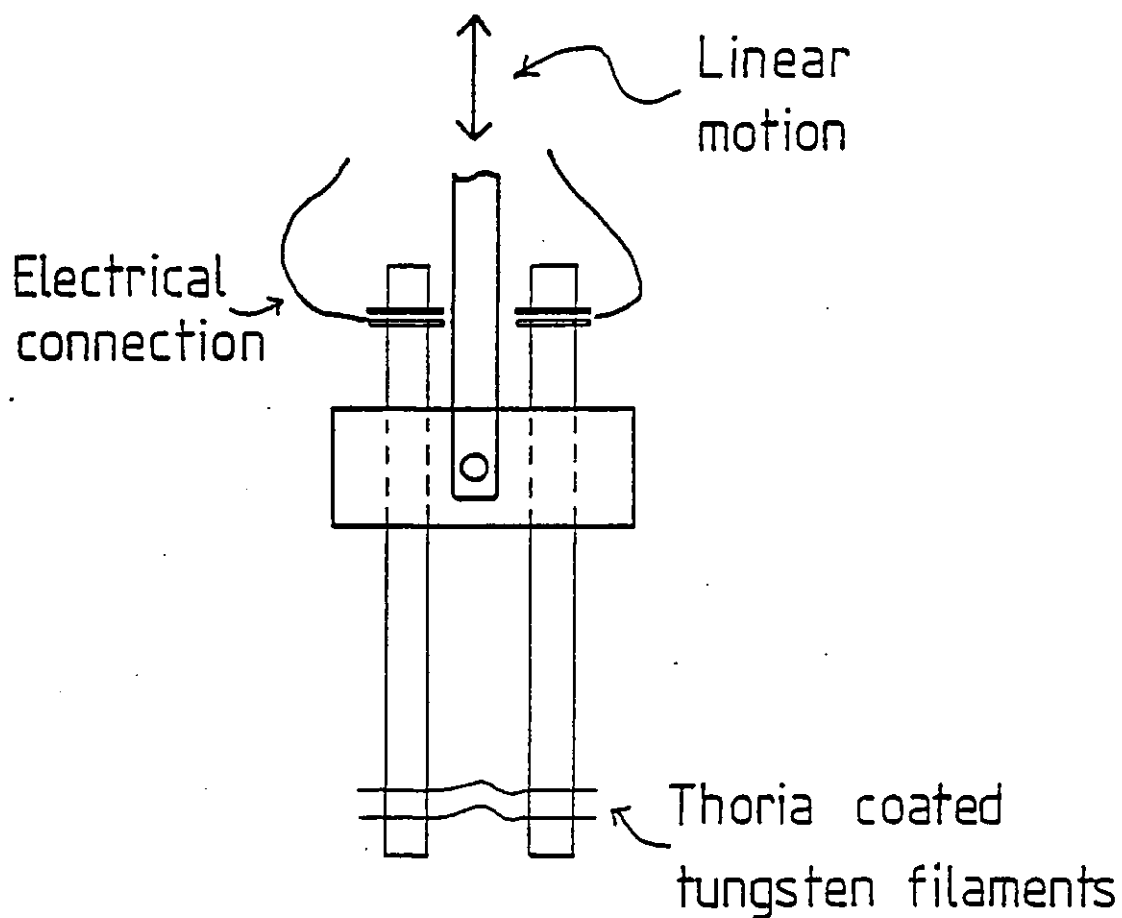


Fig. 4.7 Filament electron source.

One side of the filament was held at earth potential, and current was supplied from a low voltage (7V) system. A high voltage supply provided up to +5kV at currents of up to 100mA. HT was applied to the probe and provided the energy required to accelerate the electrons and so heat the specimen. This arrangement was simple and effective, but had the limitation that emitted electrons were not focused and tended to stray onto the probe and tungsten wire support, causing further outgassing. A focussed electron beam would have been more satisfactory since the energy contained in it could have been directed accurately onto the niobium foil.

CHAPTER 5
THE ULTRA HIGH VACUUM OXIDATION OF NIOBIUM
AS STUDIED BY XPS

This chapter describes those spectra obtained during the interaction of cleaned polycrystalline niobium foils with high purity oxygen. The adsorption was carried out at room temperature and in the pressure range from 1×10^{-8} Torr to 1×10^{-6} Torr.

5.1 ORGANISATION OF THE RESULTS

During this work five separate specimens of niobium were studied. They are described in the text as Specimens 1 - 5 (Spn 1-5) and were studied in chronological order.

The behaviour of various features in the electron emission spectra of Mg K α irradiated niobium were followed during the controlled exposure of the surface to oxygen molecules. These features are listed below:

- a) Nb 3d photoelectron peaks and associated plasmons;
- b) O 1s photoelectron peak;
- c) O KL₂L₂ Auger emission;
- d) Nb M_{4,5} N_{2,3} V Auger emission;
- e) Nb-O valence band.

The Nb 3d peaks were chosen to monitor the oxidation since they are the most intense and narrow feature in the photoelectron spectrum of the metal.

Specimen mounting and other experimental details are described in Chapter 4.

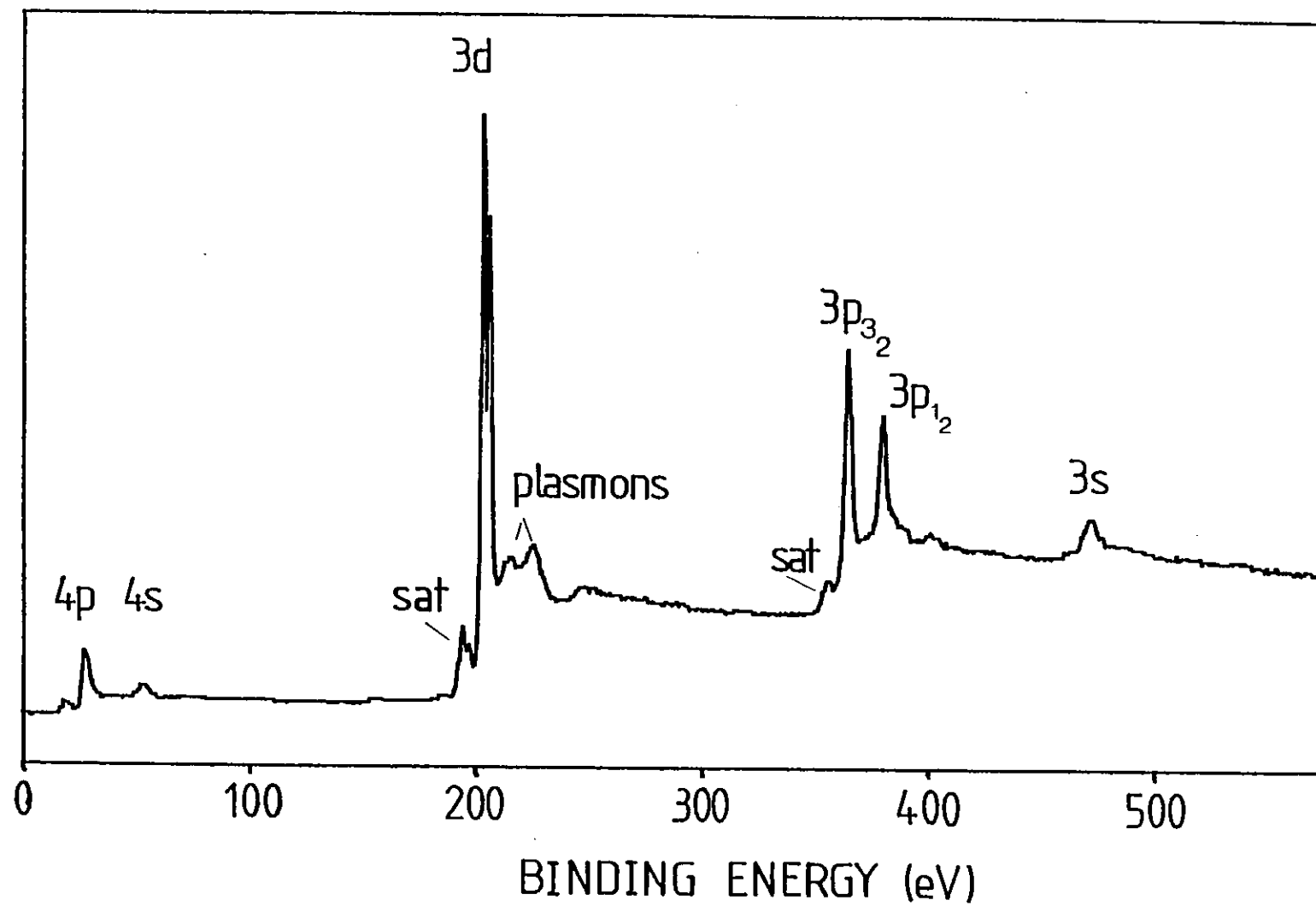


Fig. 5.1 The full spectrum from clean niobium excited by Mg K α radiation.

Spn.	O/Nb ratio	Monolayer %	C/Nb ratio	Monolayer %
1	3.2×10^{-3}	2.8	7×10^{-3}	18
2	5.9×10^{-3}	5.1	10×10^{-3}	26
3	22×10^{-3}	20	8×10^{-3}	21
4	0.17	150	7×10^{-3}	18

Table 5.1 C 1s and O 1s to Nb 3d area ratios for Spn's 1, 2, 3 and 4 and estimated contamination levels expressed as a percentage of a full monolayer.

Of the other common contaminants found on metal surfaces (for example sulphur, phosphorus and silicon) only sulphur was found in the early stages of cleaning a foil. This soon disappeared after a few flashes to 2000 K.

The clean full spectrum obtained at this stage, using Mg K α radiation is shown in Fig. 5.1. The spectrum is from Spn 2 and extends from the valence band to below the O 1s level. The minor peaks as well as the major peaks are identified.

A more detailed examination of the clean surface produced the spectra presented in Fig. 5.2. This shows the O 1s, C 1s and S 2p regions from Spn 2 with a Nb 3d spectrum for comparison. Note the different expansions. These spectra indicate, together with the full spectra of Fig. 5.1 that surfaces were obtained which were basically clean, although contamination due to carbon and oxygen was detected.

Vertical
scale
expansion

x 1 Nb 3d

x 16 S 2p

x 16 O 1s

x 16 C 1s

Fig. 5.2 The Nb 3d, S 2p, O 1s and C 1s regions from a clean niobium surface. Spectra are from Spn 2.

5.2 CLEANING PROCEDURES

The affinity of niobium for oxygen and carbon is very strong, being characterised by the formation of oxides and carbides with high heats of formation. This suggests that some difficulty should be experienced in removing oxygen and carbon from a niobium surface. There have been comments in the literature to this effect (Pantel, R. et al 1977; Lindau, I. and Spicer, W.E. 1974).

Fortunately niobium has a sufficiently high melting point, about 2740 K, such that when a specimen is heated to 2200 K surface oxides both dissolve into the bulk and are evaporated as Nb-O clusters (Pasternak, R.A. and Evans, B. 1967). However, the carbide which has a melting point of 3770 K and graphite (m.p. 3700 K) are more refractory than the metal itself and heating alone was not found to be totally effective in removing this contaminant.

The method of cleaning adopted by the few previous workers who have studied this system has been to simply heat the sample close to its melting point for long periods. This technique has been followed in these studies. Electron beam heating at 4 kV and 40 mA was used to achieve the required temperatures of around 2200 K. The temperature of the sample was monitored by an optical pyrometer. These high temperatures were maintained for periods of only five seconds at one time since prolonged heating produced degassing from the probe (caused by heat transfer along the specimen

support). This degassing then contaminated the surface under preparation; longer heating periods would have been preferred. After several cycles of this flash heating, the surface carbon and oxygen were reduced to a small level and the sample outgassed.

Attempts to reduce the carbon contamination on Spn's 2, 3 and 5 were made by heating the sample to 1500 K in a pressure of 1×10^{-6} Torr oxygen for periods of up to one minute. This proved to be useful since a temporary reduction in the C 1s emission was achieved. However, after several hours in the instrument, the C 1s emission increased due to either CO adsorption from the ambient atmosphere, or diffusion from the bulk. This cleaning procedure resulted, however, in extremely tenaciously adsorbed oxygen atoms, such that the results from Spn's 2 and 3 are from oxygen contaminated surfaces. The quantity of oxygen contamination is estimated to be equivalent to about 5% and 20% of a monolayer respectively. These estimates are based upon equation 2.14 and are thought to be accurate to about $\pm 15\%$.

The experimental ratios of the O 1s and C 1s peak areas relative to the Nb 3d peak area are presented below in Table 5.1. For Spn 6 the surface contamination was monitored using the UPS spectra (Chapter 8).

An estimate of the carbon contamination was gained by carbon monoxide "titration" of the Spn 1 surface. The method employed was as follows. The clean surface was exposed to a pressure of carbon monoxide of 1×10^{-6} Torr for 100 seconds. This was assumed to produce a full monolayer of carbon monoxide - probably more correctly thought of as a half monolayer of both carbon and oxygen atoms. Thus, the peak area associated with half a monolayer of carbon atoms was determined. The contamination peak area could then be compared with this result and an approximate coverage obtained. The relative peak areas for the adsorbate involved in this process are presented below in Table 5.2

	C 1s		O 1s
SPECIMEN PREPARATION	'clean'	CO exposure	CO exposure
PEAK AREA (arbitrary units)	0.6	2.4	7.2
APPROXIMATE PERCENTAGE MONOLAYER COVERAGE	12	50	50

Table 5.2 Estimation of carbon contamination on 'clean' surfaces by carbon monoxide titration for Spn. 1.

The accuracy of this information is probably not high owing to the small peak areas involved, but a contamination level much lower than that formed by carbon monoxide exposure can be deduced. It was noted that the adsorption of carbon monoxide mainly contributed to the lower BE component of the C 1s doublet at a BE of 283.5 ± 0.2 eV. This may be interpreted as indicating

that this component is associated with chemisorbed carbon atoms rather than carbide or graphite.

5.3 CLEAN SURFACE SPECTRA AND THEIR CHARACTERISTICS

The Nb 3d spectrum from a cleaned surface, Fig.5.2 shows the $3d_{5/2}$ and $3d_{3/2}$ peaks at BE's of 202.5 ± 0.2 eV and 205.2 ± 0.2 respectively. This spin-orbit splitting of 2.7 ± 0.1 eV may be compared with that obtained theoretically by Elyashar, N. and Koelling, D.D. (1977) of 2.9 eV, while studying the band structure of niobium. Full widths at half maximum (FWHM) of 0.9 ± 0.1 eV and 1.2 ± 0.1 eV are observed for the $3d_{5/2}$ and $3d_{3/2}$ peaks respectively. This result was obtained with an analyser pass energy of 50 eV and a slit width of 2 mm, giving an analyser broadening of 0.5 eV. The extra width of the $3d_{3/2}$ peak is due to Coster-Kronig transitions from the $3d_{5/2}$ level, which reduces the $3d_{3/2}$ lifetime and hence increases its width as described by the Uncertainty Principle.

Considerable tailing to the lower KE side of these peaks is seen. This phenomena has been of recent theoretical interest (Citrin, P.H. et al 1977; Mahan, G.D. 1967). It is caused by low energy excitations of valence band electrons across the Fermi level, and is a feature of transition metals with unfilled valence bands. These excitations across E_f may occur during the photoexcitation process itself or while the photoelectron is travelling through the metal. In the first case, they are termed "intrinsic" to the photoexcitation event, while in the second case they are termed "extrinsic".

Another feature of the clean surface is the appearance of plasmon losses after the stronger Nb peaks. These too may be either intrinsic or extrinsic to the photoexcitation event and are often observed in spectra from metals. Both surface and bulk plasmon losses are observed, and the surface plasmon is later found to be informative during the oxidation.

5.4 THE OXIDATION OF NIOBIUM

Having obtained a clean surface, as described above, a controlled oxidation of niobium was performed by exposing the surface to known, discrete, quantities of molecular oxygen. In order to monitor the effect of oxygen adsorption on niobium, the intensity, shape and position of the Nb 3d, Nb 3d surface plasmons, Nb $M_{4,5}$ $N_{2,3}$ V Auger, and valence band emissions were recorded. The O 1s and O Auger KL_2L_2 spectra were also carefully observed. The Nb 3d peaks were particularly important since they are both the strongest and narrowest in the niobium spectrum and yielded the most informative data.

Exposures of oxygen were made in laboratory units of Langmuirs where 1 Langmuir of oxygen molecules (1 L O_2) is an exposure of 1×10^{-6} Torr sec. These units have been converted into the number of oxygen atoms which strike unit area of surface. In these units $1 \text{ L O}_2 = 0.72 \times 10^{19}$ oxygen atoms per square metre (O.m^{-2}). The number of niobium atoms per square metre of polycrystalline surface is 1×10^{19} , and so this nomenclature provides a useful scale with which to judge oxygen exposure (Menzel, D. and Fuggle, J.C. 1978).

Exposures of up to 10 L O₂ (7.2×10^{19} O.m⁻²) were made at pressures of 1×10^{-8} Torr; exposures of between 10 and 100 L O₂ were achieved using a pressure of 1×10^{-7} Torr; and higher exposures required 1×10^{-6} Torr. Most of the data to be presented is taken from Spn. 1, with the exception of the Nb Auger spectra, which are from Spn. 2 since their interesting behaviour was not appreciated until later in the work.

In order to facilitate data processing all the spectra were taken using the same parameters for the instrument variables. More precisely the x-ray source was run at 12 kV and 20 mA (half its maximum rating); an analyser pass energy of 50 eV was chosen as the best compromise between sensitivity and resolution; a slit width of 2 mm; the number of scans was a multiple of 25; and the dwell time was 33 ms per spectrum point. There are some exceptions to these conditions and where they occur a note is made in the text. The expansion value which accompanies each spectrum refers to the expansion relative to the clean Nb 3d spectrum for that Spn. The actual experimental results are examined and presented below.

5.4.1 The niobium 3d peaks

The results of oxygen exposures of up to 720×10^{19} O.m⁻² upon a clean niobium surface, as followed by the Nb 3d peaks, are shown in Fig. 5.3. The spectra show several features of immediate interest. Firstly, the resolution of the 3d_{5/2} - 3d_{3/2} spin-orbit gap is reduced after small exposures of oxygen. Secondly, the overall

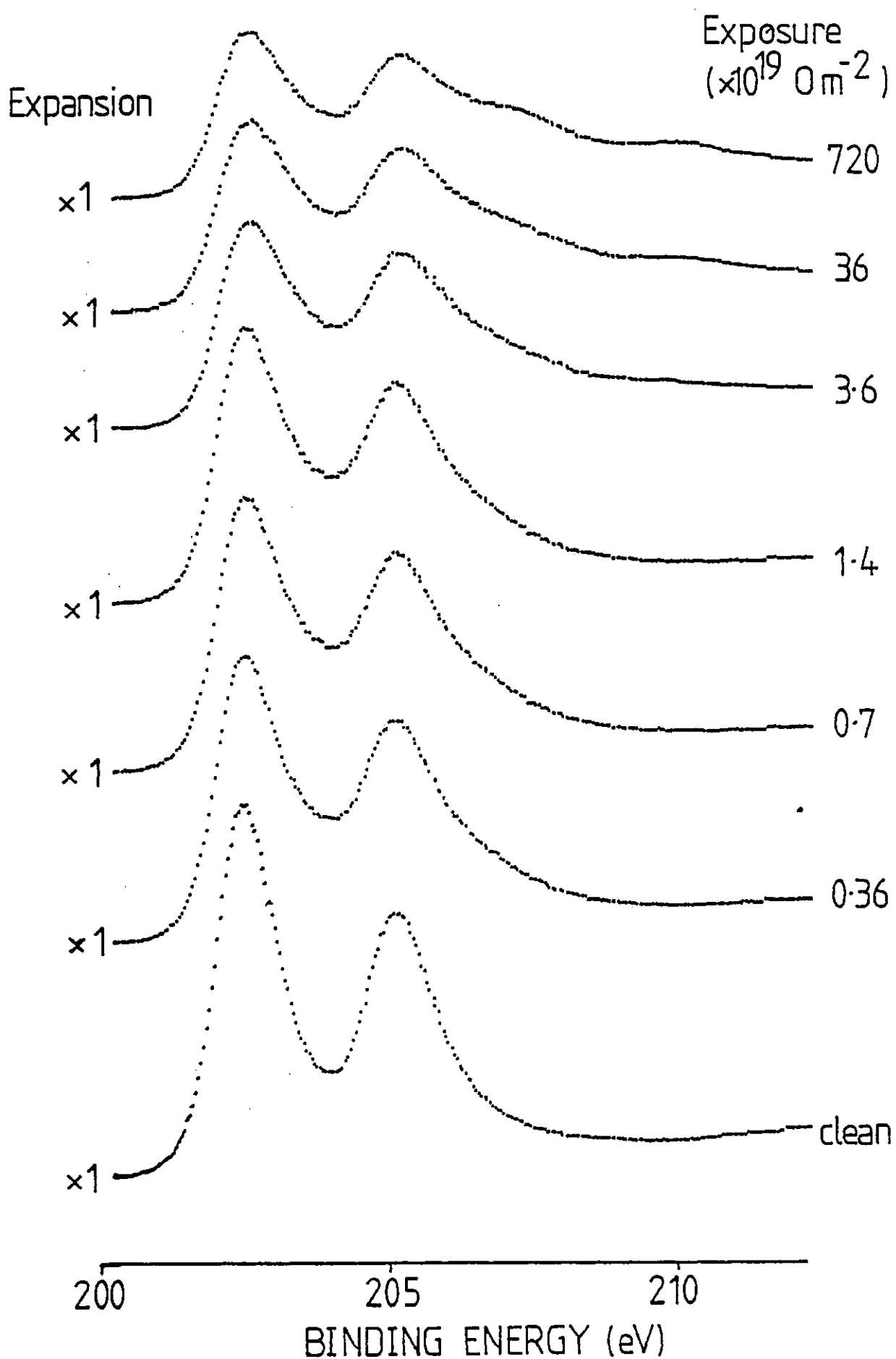


Fig. 5.3 The Nb 3d peaks of clean niobium exposed to oxygen in the exposure regime up to $720 \times 10^{19} \text{ O.m}^{-2}$.

decrease in the intensity of the peaks is of note, and thirdly, the appearance of shoulders, and then peaks, as the exposure is increased.

These higher BE peaks at $207.5 \pm 0.3 \text{ eV}$ and $210.2 \pm 0.3 \text{ eV}$ are assigned to niobium pentoxide, although later data processing also reveals the presence of a lower oxide. The lower oxide has a small chemical shift which displaces the Nb $3d_{5/2}$ emission into the spin-orbit gap, and is responsible for the decrease in resolution in this region.

So it is possible, even at this stage, to positively identify the presence of a thin oxide overlayer on niobium formed in this exposure regime. Chapter 6 deals with the quantitative processing of this data and Chapter 7 with the derived oxidation model.

5.4.2 The oxygen 1s and Auger peaks

The behaviour of the O 1s peak in the exposure regime up to 720 O.m^{-2} is presented in Fig. 5.4, the data being from Spn. 1. Fig. 5.5 shows the O 1s spectra obtained from exposures between 0 and $0.72 \times 10^{19} \text{ O.m}^{-2}$ and cover the expected regime of chemisorption on the metal surface. Note the rapid uptake of oxygen by this reactive metal surface and the slight shift, of about 0.3 eV to higher BE between 0.72 and $72 \times 10^{19} \text{ O.m}^{-2}$. This is also evident in the spectra from Spn's 2 & 3, which are not presented. There is also a slight shift back to lower BE between 72 and $720 \times 10^{19} \text{ O.m}^{-2}$.

Changes also occur in the full width at half maximum (FWHM) as a function of exposure which are observed on all three Spns. At low exposures -

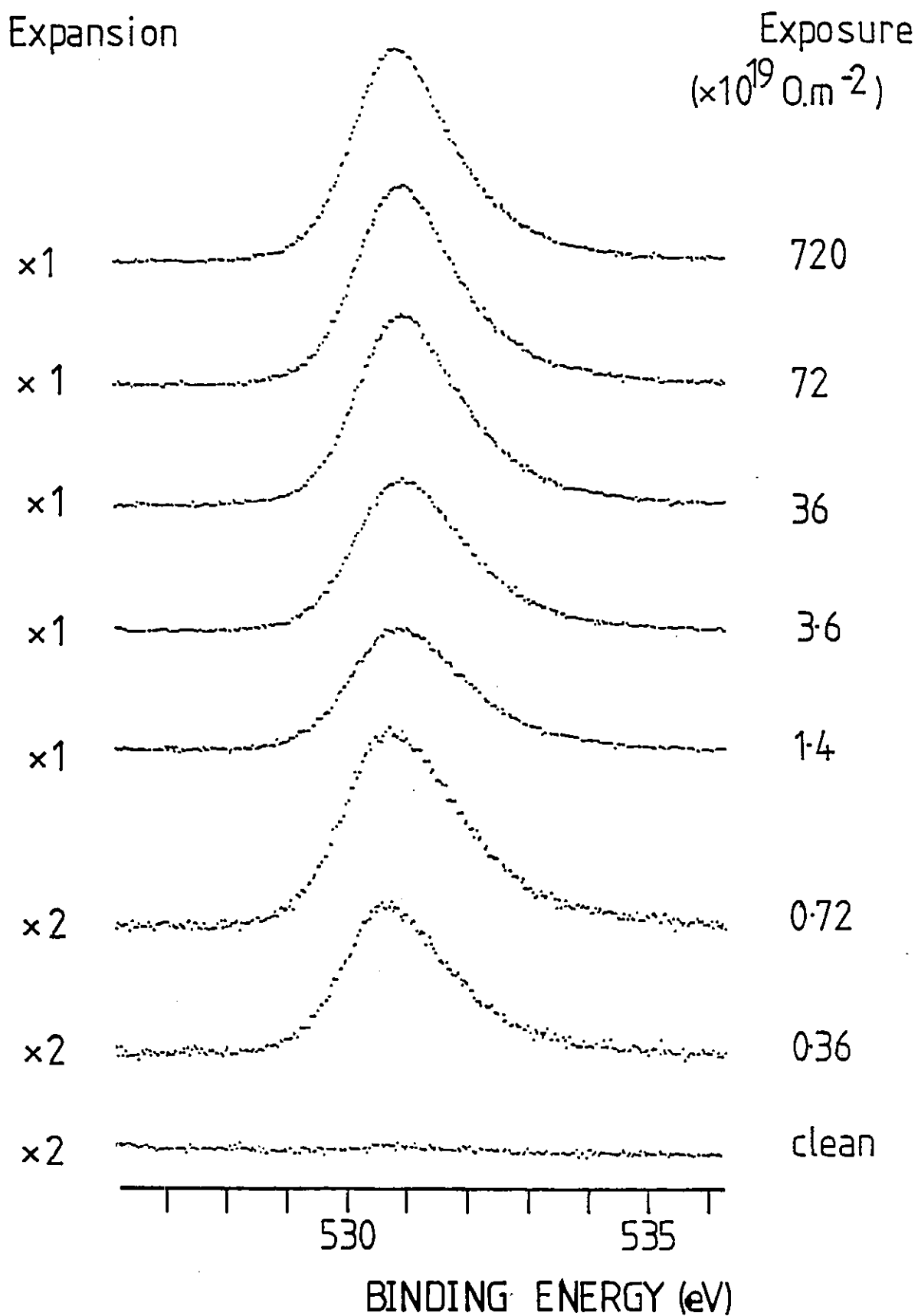


Fig. 5.4 The O 1s spectra from clean niobium exposed to oxygen in the exposure regime up to $720 \times 10^{19} \text{ O.m}^{-2}$.

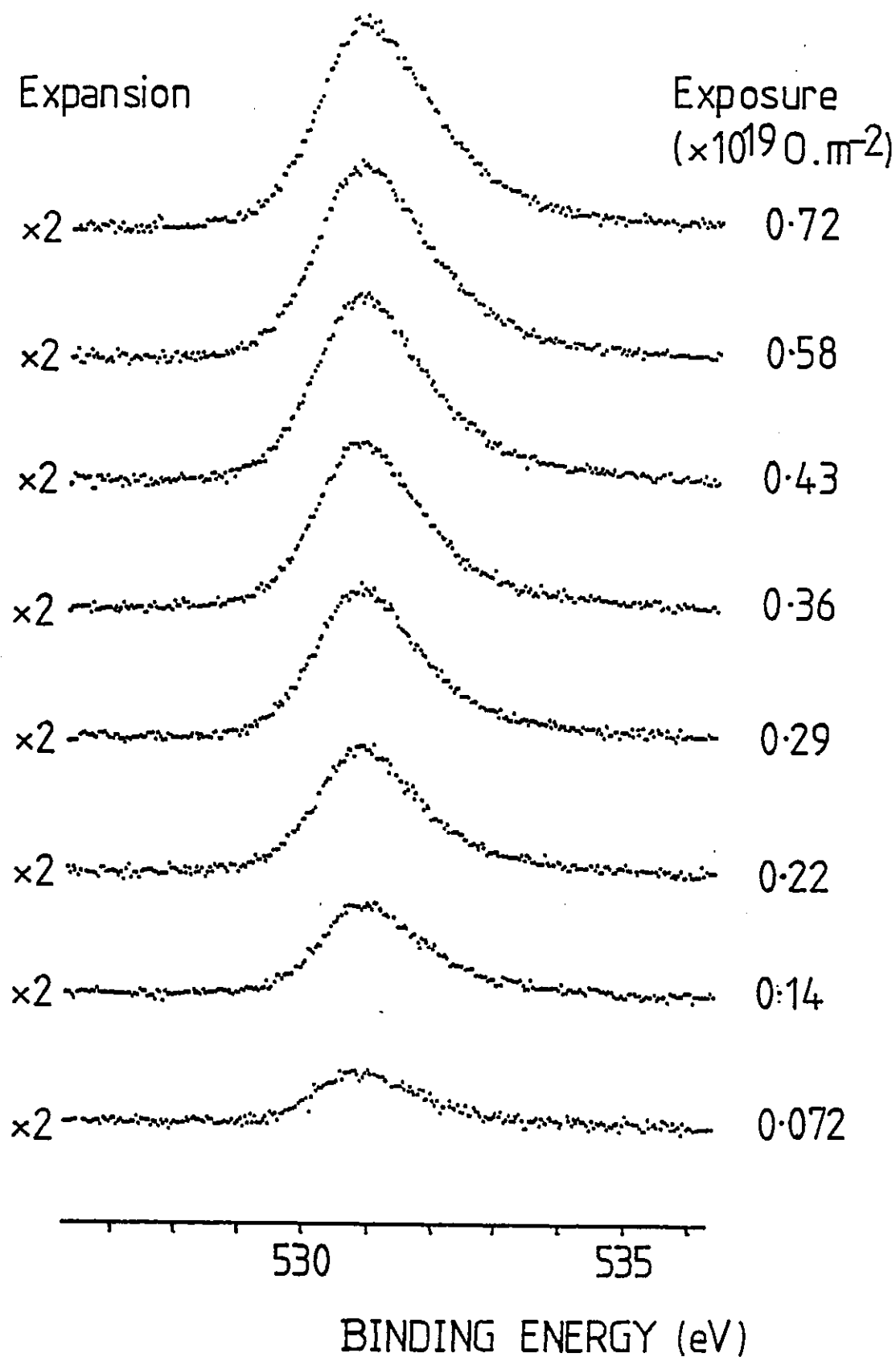


Fig. 5.5 The O 1s spectra from clean niobium exposed to oxygen in the exposure regime up to $720 \times 10^{19} \text{ O.m}^{-2}$.

$0.36 \times 10^{19} \text{ O.m}^{-2}$ - the FWHM value is $2.15 \pm 0.1 \text{ eV}$, whereas at $0.72 \times 10^{19} \text{ O.m}^{-2}$ it has increased to $2.35 \pm 0.1 \text{ eV}$, and at $72 \times 10^{19} \text{ O.m}^{-2}$ the value has returned to $1.95 \pm \text{eV}$. The same general behaviour is observed in the spectra from the other two Spn's. A full listing for Spn's 1, 2 and 3 of the FWHM, BE, and area intensity and asymmetry is given in the Appendix.

The original oxygen Auger spectra are presented in Fig. 5.6 for exposures up to $720 \times 10^{19} \text{ O.m}^{-2}$. These spectra were induced by the Mg K α x-rays and the Bremsstrahlung background. In common with the O 1s data, the oxygen Auger peak shows variations in KE, FWHM and asymmetry with increasing exposure. This information is tabulated in the Appendix and discussed in Chapters 6 and 7. The final KE value of 513.9 eV is the same, within experimental error, for all three Spn's. The peak position shifts to lower KE by over one eV, in the exposure range from 0.36 to $3.6 \times 10^{19} \text{ O.m}^{-2}$ thereafter remaining fairly constant. Another characteristic is the increase and then decrease in FWHM for this Auger peak. Initially, at $0.36 \times 10^{19} \text{ O.m}^{-2}$, the width is $3.4 \pm 0.1 \text{ eV}$ and it then increases to a maximum of $4.2 \pm 0.1 \text{ eV}$ at $1.44 \times 10^{19} \text{ O.m}^{-2}$. Subsequently a small reduction occurs as the surface passivates with a final value of $4.1 \pm 0.1 \text{ eV}$ being observed. Similar trends are noted in Spn's 2 and 3.

The oxygen related data presented above shows that the reactivity of the niobium surface falls continuously with oxygen exposure, becoming relatively unreactive in the exposure range from $4\text{--}14 \times 10^{19} \text{ O.m}^{-2}$ depending upon

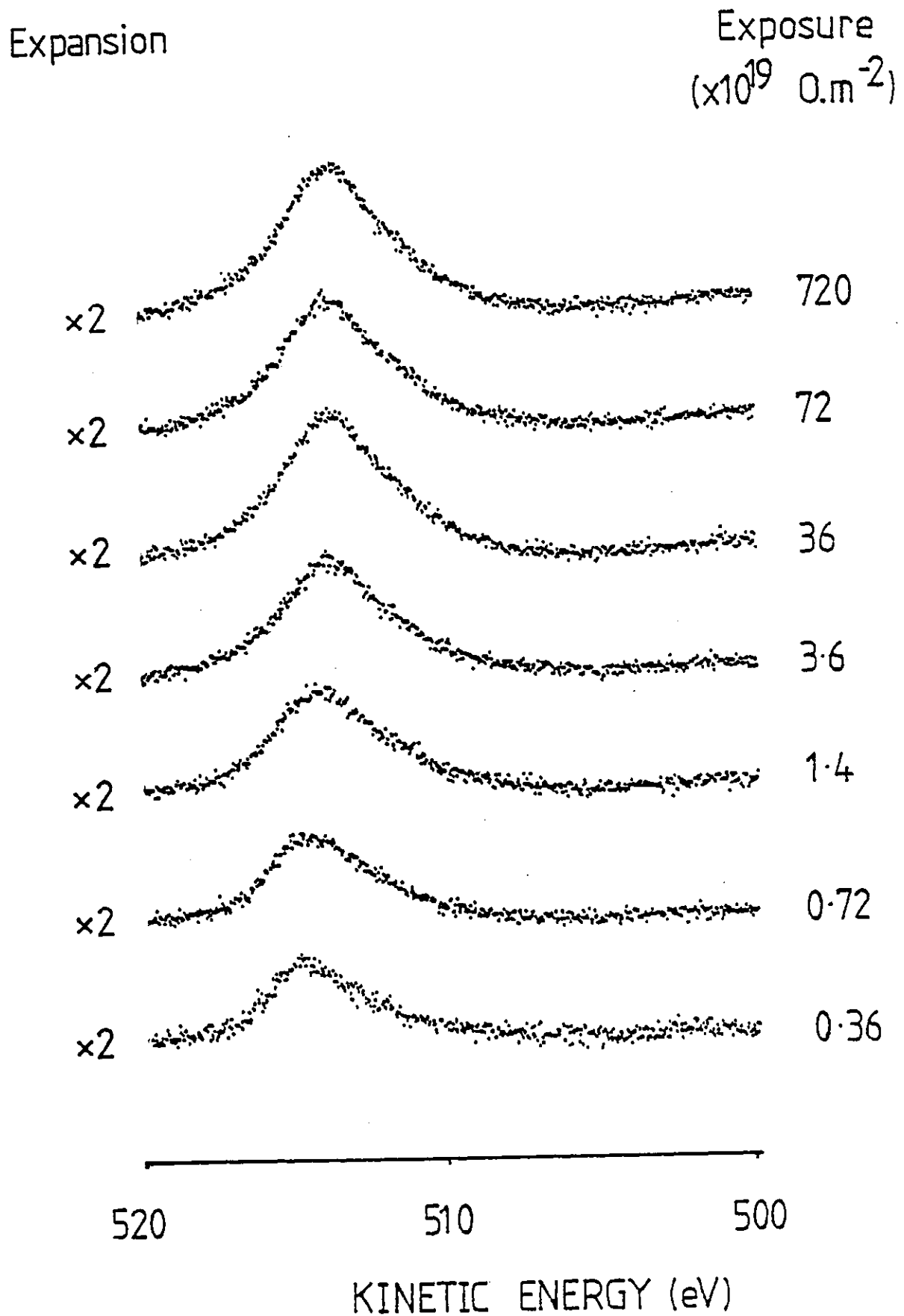


Fig. 5.6 The O Auger spectra from clean niobium exposed to oxygen in the exposure regime up to $720 \times 10^{19} \text{ O.m}^{-2}$.

the specimen. No evidence for substantial quantities of physically adsorbed oxygen molecules is evident in the spectra. Such species would be expected to appear as emission to higher BE with respect to the main peak.

5.4.3 Surface and bulk plasmons

Chapter 2 described the origin of plasma oscillations in free electron metals, and also showed that characteristic oscillations for interfaces may be expected. In this case the interface is the metal-vacuum boundary and the oscillations are known as surface plasmons.

Surface plasmons are observed, together with the bulk losses, on the low KE side of niobium core level peaks. This is shown quite clearly in the wide scan spectrum of Fig. 5.1, especially to lower kinetic energy of the 4p peak. For this peak four distinct losses due to a combination of bulk and surface plasmons are observed before the onset of emission from the 3d level caused by Mg $K\alpha$ x-rays.

For Nb, with five valence electrons, the surface plasmon energy is predicted to be 13.8 eV (bulk plasmon energy at 19.7 eV). This model is based on the assumption that the valence electrons in niobium are free electron like (which they are not), and as a result the theory cannot be expected to produce an accurate estimate of the experimental result. The results shown in Fig. 5.7 for plasmon losses from the 3d peaks, are however in fair agreement with this model estimate. The surface and bulk plasmons for the clean surface, have energies of 10.5 eV

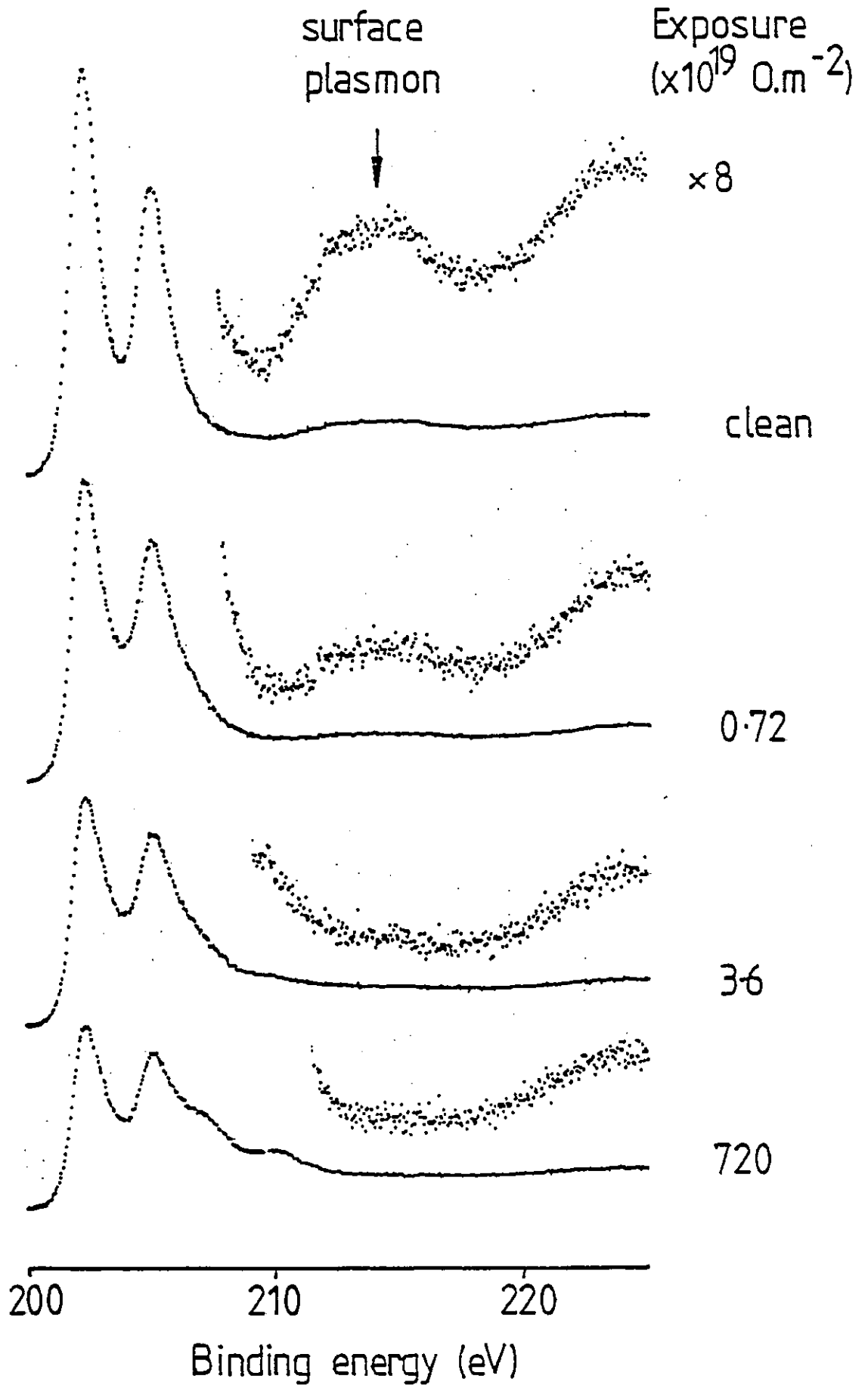


Fig. 5.7

The behaviour of the surface plasmon loss on clean niobium upon exposure to oxygen up to $720 \times 10^{19} \text{ O.m}^{-2}$.

and 21.5 eV respectively.

The assignment of the emission at 10.5 eV to a surface plasmon is supported by the effect of oxygen adsorption. In Fig. 5.7 it can be seen that this emission is reduced to negligible proportions by an exposure of only $3.6 \times 10^{19} \text{ O.m}^{-2}$. The surface plasmon emission is composed of contributions from both the $3d_{5/2}$ and the $3d_{3/2}$ core levels, and this can be distinguished in the spectra.

5.4.4 The niobium Auger transition

Nb has several low KE (100-200 eV) Auger transitions which have been used in this work to complement the higher kinetic energy (1050 eV) XPS results. This is because their lower energy confers more surface sensitivity than the XPS photoelectrons. Unfortunately the transitions are fairly broad and on a substantial background. The strongest of these transitions is responsible for an electron of about 169.7 eV kinetic energy and is labelled $M_{4,5}N_{2,3}N_{2,3}$. It follows the production of a 3d core hole, the filling of this vacancy by a 4p electron and the subsequent ejection of a valence 4d electron.

The Nb Auger peak was monitored during Spn. 2 (with a limited number in Spn. 3) during the controlled exposure of the clean surface to oxygen. Results for this experiment are shown in Fig. 5.8. The adsorption of oxygen causes a considerable drop in peak height and induces a tail to lower KE for exposures of only $0.72 \times 10^{19} \text{ O.m}^{-2}$. This tail becomes a definite peak by $3.6 \times 10^{19} \text{ O.m}^{-2}$, with a KE of $165.2 \pm 0.5 \text{ eV}$ -- a shift to lower KE of 4.5 eV.

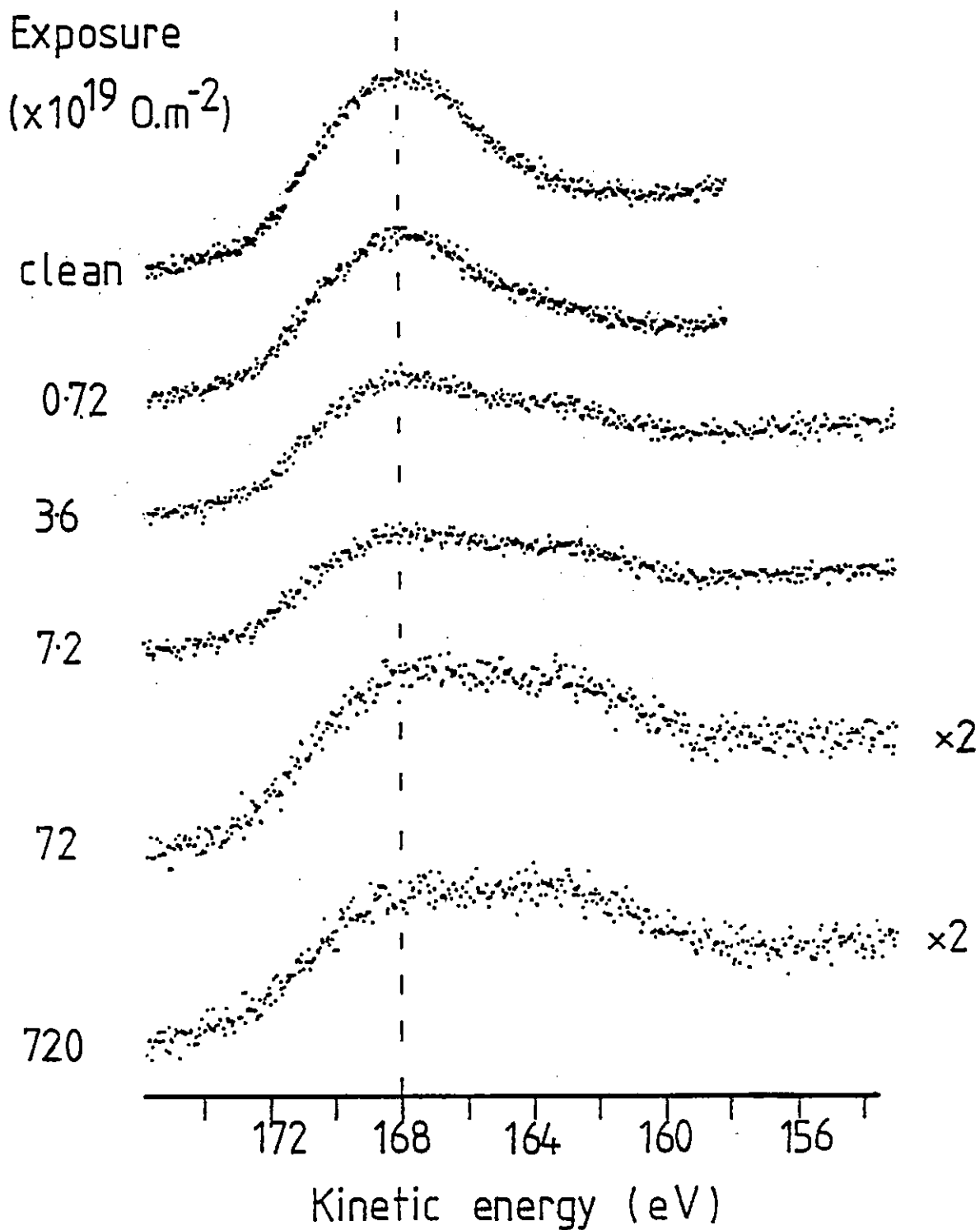


Fig. 5.8 The Nb Auger transition of clean niobium exposed to oxygen in the exposure regime up to $720 \times 10^{19} \text{ O.m}^{-2}$.

Upon further exposure this peak continues to grow, and the original peak shape has taken on a flat topped appearance. The original peak still dominates the total emission by a ratio of about three to two, with respect to the lower KE peak. The second peak at 165.2 eV is interpreted as indicating that the growth of an oxide film has taken place. However, due to the surface sensitivity of these Auger electrons the emission at 169.7 eV is also considered to represent electrons from an oxide, a lower oxide, as well as from metallic niobium. Rieder, K.H. (1980) has also observed this behaviour (with a different interpretation) using electron impact Auger spectroscopy and his results are discussed later.

5.4.5 The valence band

The valence band spectra obtained with Mg K α photons are shown, for various exposures, in Fig. 5.9. Spectra are from Spn. 1 (the only Spn to include this type of data) for exposures of up to $720 \times 10^{19} \text{ O.m}^{-2}$. The clean surface was recorded with only one quarter the number of scans of the others, and as a result has a poorer signal to noise ratio.

The main characteristics of the clean spectrum are a peak at 1.2 eV BE and a shoulder at 2.8 eV BE. An interpretation of these features is given in Chapter 8, where this data is compared with higher resolution UPS studies. Upon adsorption of oxygen no new features appear even at $720 \times 10^{19} \text{ O.m}^{-2}$. The only obvious change occurs in the background at a BE greater than 6 eV. This

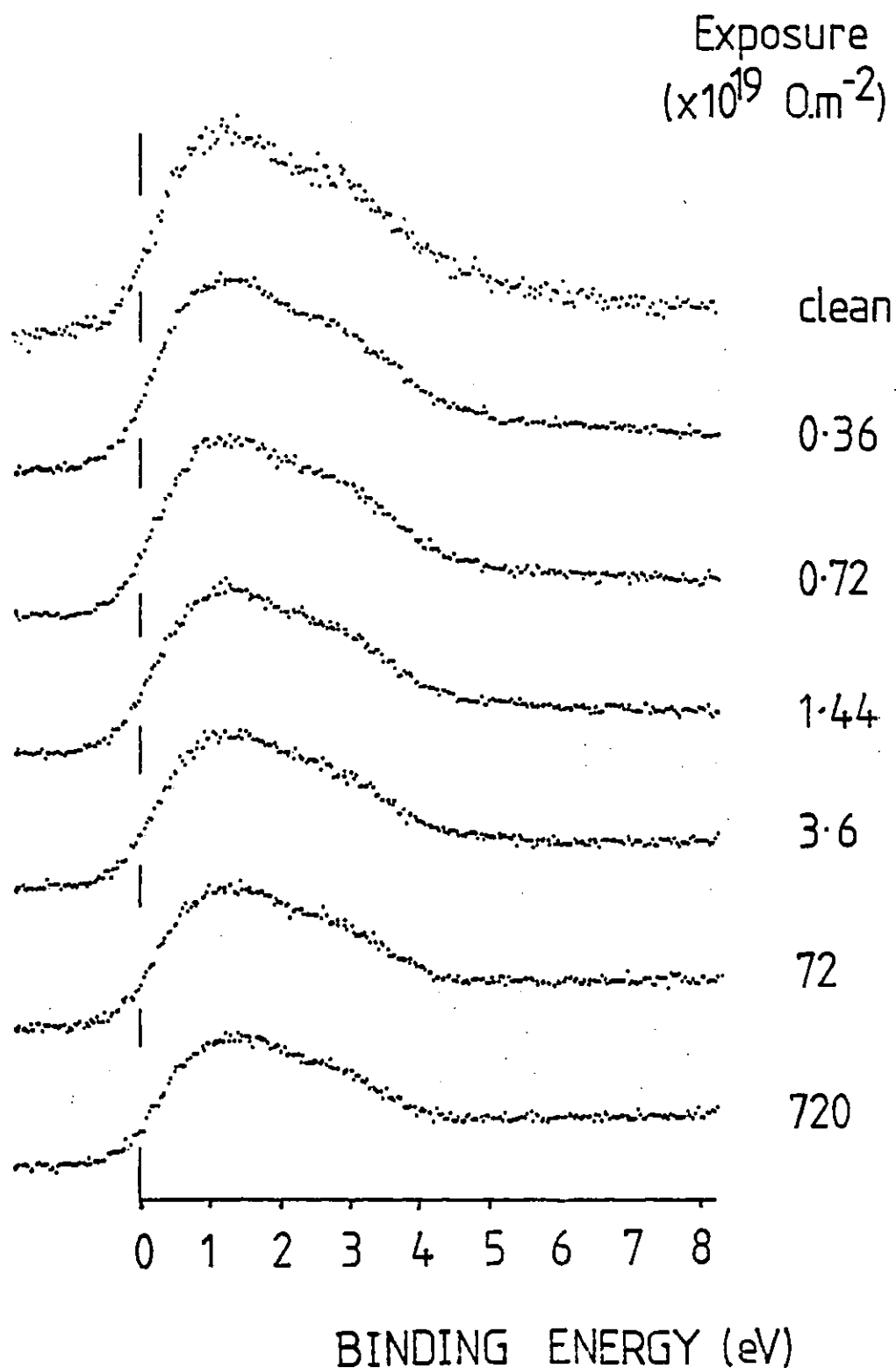


Fig. 5.9 The Nb valence band region of clean and oxygen exposed niobium in the exposure regime up to $720 \times 10^{19} \text{ O.m}^{-2}$.

background is probably the result of emission from oxygen 2p levels. However, the relative cross-sections are in favour of the Nb 4d valence levels, and so the relative emission from oxygen 2p levels is quite small. This situation is reversed at UPS photon energies, where the oxygen 2p levels dominate the spectra.

In fact, the XPS spectra could have been improved by extending the region covered to include properly the O 2p levels. This would have involved scanning to about 15 eV BE, thus allowing a more informative study to have taken place. Despite this limitation the spectra do show that the basic distribution of niobium valence electrons remains the same for exposures of up to $720 \times 10^{19} \text{ O.m}^{-2}$.

5.5 THE HIGH TEMPERATURE NbO SURFACE

While attempting to clean Spn 4 foil of carbon, by heating in oxygen at rather high oxygen pressures (1×10^{-5} Torr) and at high temperature (1800 K), a large amount of oxygen became dissolved in the bulk. This procedure resulted in a smaller carbon signal, but gave a reproducibly large oxygen contamination which could not be removed by flashing to over 2000 K in a vacuum of better than 1×10^{-9} Torr.

A high resolution scan of the Nb 3d peaks, obtained using an analyser pass energy of 10 eV and a slit width of 2 mm, indicated that niobium atoms with a small chemical shift were present. Further analysis, by subtraction of the metallic contribution to the spectrum (see Chapter 6), confirmed that niobium atoms with a

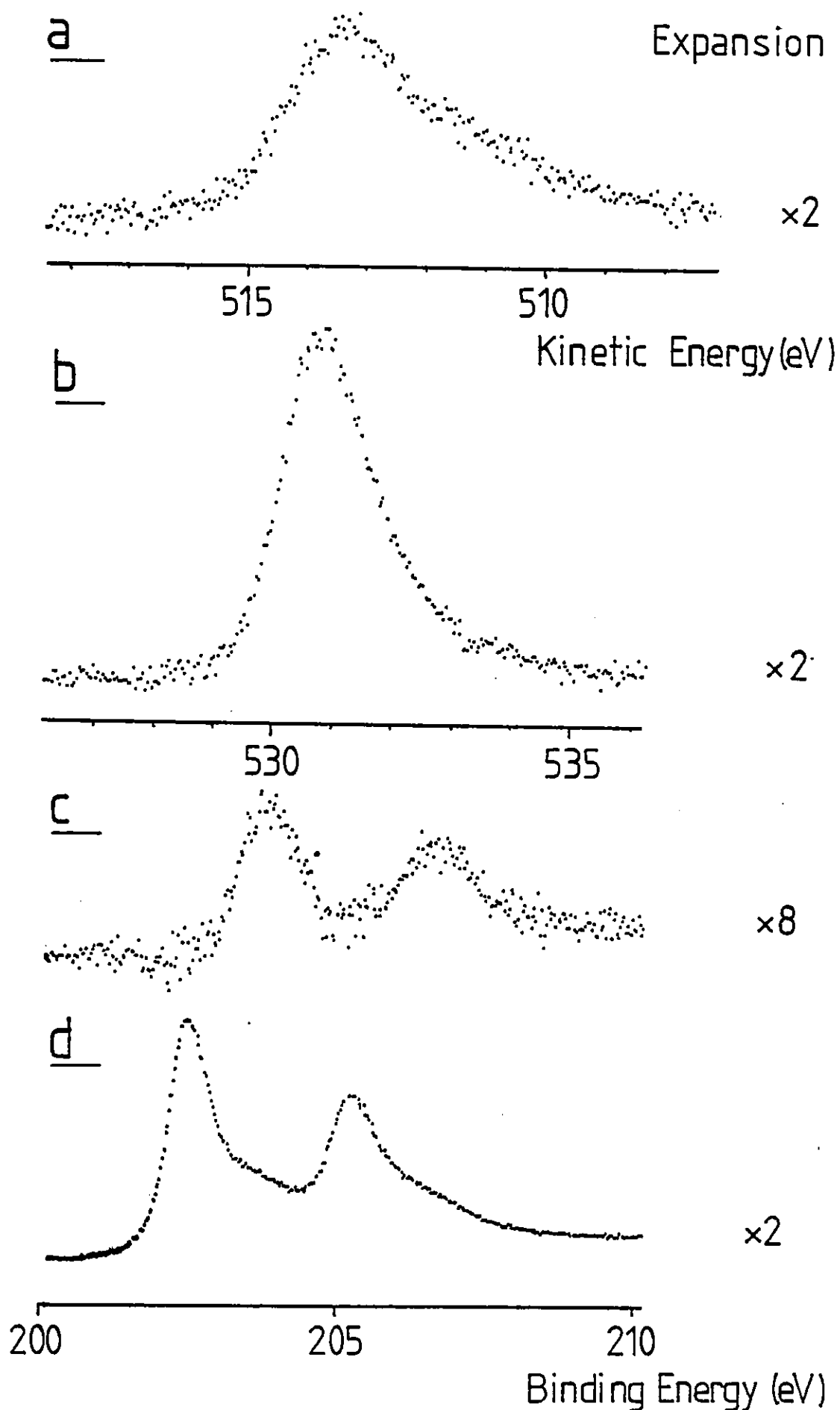


Fig. 5.10 The NbO surface: a) the O Auger emission; b) the O 1s peak; c) the Nb 3d (oxide) spectra; d) the Nb 3d spectra.

chemical shift of 1.2 ± 0.1 eV were present, on the surface. These spectra are shown, together with the O 1s and O Auger peaks, in Fig. 5.10. These spectra are significant as they represent a layer of the lower oxide uncontaminated by higher oxides or other oxygen species. This can be seen by comparing the subtraction spectra, Fig. 5.10.(c), with those analogous spectra obtained from the room temperature adsorption of oxygen molecules, Fig. 6.2. The resolution of the spin-orbit gap between the $3d_{5/2}$ and $3d_{3/2}$ Nb peaks is best displayed in the subtraction spectra of Fig. 5.10.(c), suggesting that the high temperature surface consists mainly of one Nb species.

As described in Chapter 3, Simon, D. et al (1976) have reported the binding energies and chemical shifts for the oxides of niobium. According to these authors, NbO has a chemical shift of 1.3 ± 0.2 eV from the metallic binding energy. On the basis of these results the niobium atoms observed on the surface at Spn. 4 with a chemical shift of 1.2 ± 0.1 eV can be assigned to niobium monoxide, NbO.

At elevated temperatures an equilibrium is established between oxygen atoms dissolved in the bulk and those adsorbed at the surface. There are several reports in the literature of oxygen dissolving into the bulk at high temperatures and reappearing at the surface on cooling (Rieder, K.H. 1980; Dawson, P.H. and Tam, W.C. 1979; Farrel, H.H. et al 1973). The present results support this process and indicate that the precipitated

phase is niobium monoxide. A quantitative discussion is given in Chapter 6.

The characteristic data for the O 1s and O Auger peaks are presented below in Table 5.3 and will be compared with data obtained by oxygen adsorption from the gas phase at room temperature. Further reference data is contained in the Appendix.

	FWHM (eV)	Asymmetry	Kinetic/Binding Energy (eV)
O 1s	1.9	1.23	530.75
O Auger	3.3	1.75	513.4

Table 5.3 Oxygen data for the high temperature NbO surface.

Although a substantial amount of NbO has been formed, equivalent to one monolayer, the Nb 3d surface plasmon has not been completely suppressed. Thus it appears that more than one layer of NbO is required to eliminate the surface plasmon, or that some of the surface remains clean. These ideas are followed up in Chapter 6.

A spectrum of the valence band region obtained by He I photons (21.2 eV) was also taken and is shown in Chapter 8. Taken together with the other UPS spectra in that chapter, it contributes to the information concerning the character of the initial adsorption.

5.6 THE NIOBIUM PENTOXIDE SURFACE

In order to provide accurate information on the pentoxide, and in particular on the BE of the Nb 3d peaks

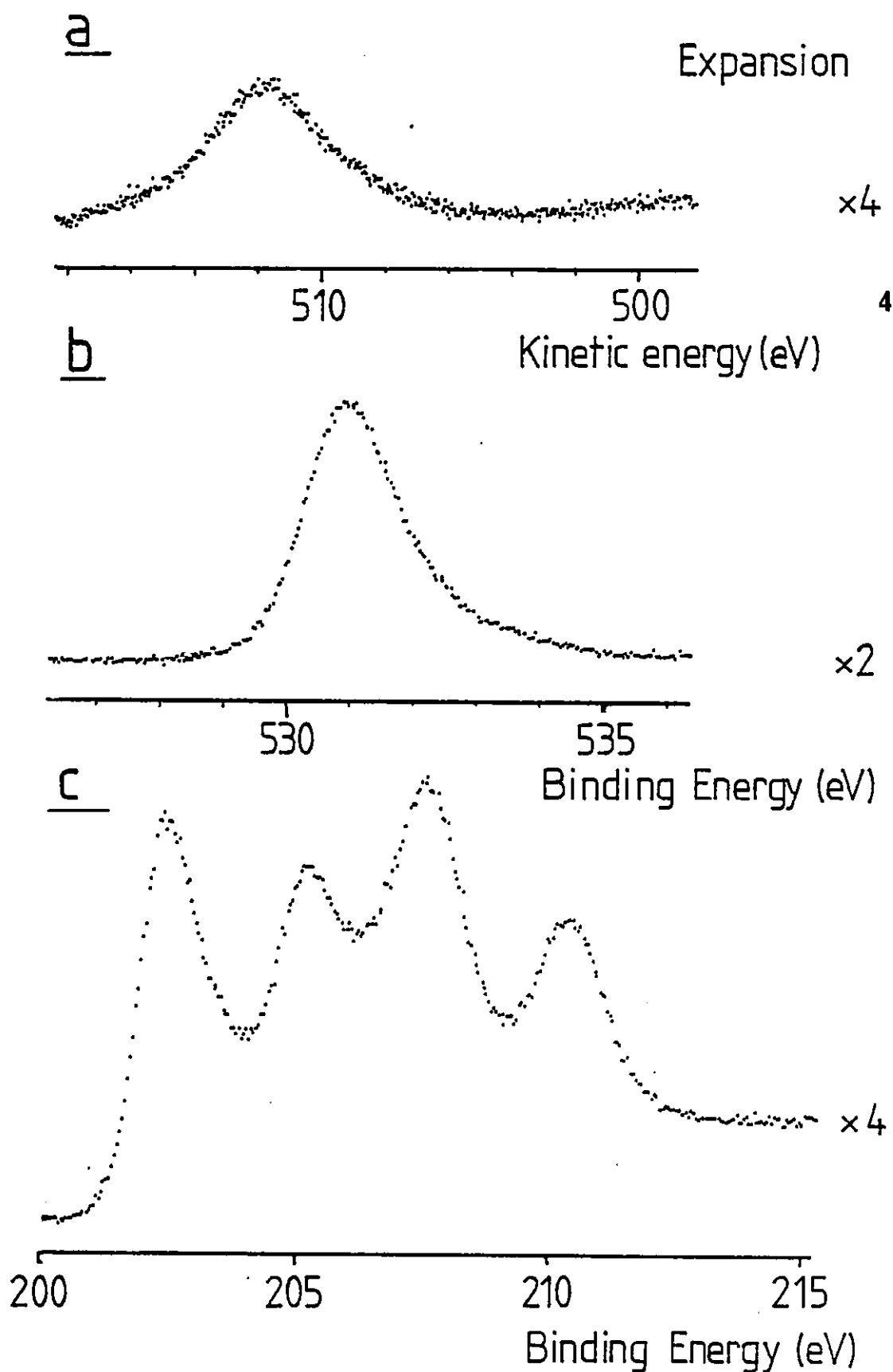


Fig. 5.11 The Nb_2O_5 surface: a) the O Auger emission; b) the O 1s peak; c) the Nb 3d spectra.

in such an environment, a sample foil was left in 0.05 Torr of oxygen for ten days and the resulting Nb 3d, O 1s, O Auger, Nb Auger, He I and Mg K α valence band spectra were recorded.

The surface was found to be contaminated with carbon, probably from the rotary pump oil. Spectra from this specimen are presented in Fig. 5.11 (except for the He I UPS spectrum which is in Chapter 6) and indicate that a layer of pentoxide forms under these conditions. The Nb 3d peaks have a chemical shift of 5.0 ± 0.1 eV with respect to the clean metal peaks. However, the fact that a considerable emission from metallic niobium is still evident shows that the layer formed is thinner than the sampling depth of the technique.

This value of the chemical shift for the pentoxide disagrees slightly with a published figure of Simon, D. et al (1976). Using a thick electrochemically grown pentoxide they obtained a shift of 5.7 eV. This is their tabulated figure. By contrast, other spectra in the same paper consisting of a thin pentoxide formed by gas phase oxidation or electropolishing have a lower chemical shift of about 5.2 eV. For these electropolished and gas phase formed overlayers, some metallic niobium is present in the spectra providing a good reference level. The electrochemically grown films have no such reliable internal standard, and the anomalously high chemical shift may be due to charging of the specimen by 0.5 eV. It may be concluded therefore

that a figure of 5.0 ± 0.2 eV for the chemical shift from metallic niobium to niobium pentoxide is more likely to be correct.

By examination of the spectrum from this well oxidised surface it is also possible to conclude that the dominant oxide formed is the pentoxide. No evidence for the presence of niobium dioxide (NbO_2) is contained in the spectra.

As in the case of the monoxide surface, characteristic values for the two oxygen related peaks (O 1s and O Auger) are tabulated below, Table 5.4. Further data are contained in the Appendix.

	FWHM (eV)	Asymmetry	Kinetic/Binding Energy (eV)
O 1s	1.9	1.11	530.9
O Auger	4.3	1.04	511.9

Table 5.4 Oxygen data for the Nb_2O_5 (gross oxidation) surface of Spn. 5.

This data is relevant to a discussion of the nature of the adsorption layers formed at lower oxygen exposures.

SUMMARY

This chapter has presented the original spectra obtained by the interaction of oxygen molecules on cleaned niobium surfaces. It demonstrates that a rapid uptake of oxygen occurs and that an oxide film is formed. The next chapter deals with the extraction of

quantitative information from these spectra.

CHAPTER 6

XPS DATA PROCESSING AND PRESENTATION

In this chapter, peak intensity information together with peak position and width, where relevant, are compiled and presented for the following emissions: Nb 3d (oxide); Nb 3d (metal); O 1s; O Auger; Nb Auger and Nb 3d surface plasmons.

6.1 Nb 3d CORE LEVEL DIFFERENCE SPECTRA

In order to evaluate the relative intensities of metallic and oxidised contributions to a Nb 3d spectrum, a separation of the two components is required. This has been achieved using a spectrum subtraction technique performed by the PDP 8 minicomputer.

The principle of the method is to take the spectrum of the oxidised surface, together with the cleanest Nb 3d spectrum (Spn. 1) as standard, and perform a point by point subtraction of the clean from oxidised spectra. By this procedure, the emission resulting from atoms in a non-metallic environment is obtained. Unfortunately the direct subtraction of two spectra will not produce a sensible result since the area due to metallic emission in the oxidised sample does not exactly match that of the clean surface. So in general, the approach involves suitably scaling the clean spectrum with respect to the oxidised spectrum in question (Procter, A. et al 1982).

This is achieved in practice by subtracting a clean spectrum of one half magnitude, and then to subtract, for instance, a quarter or eighth spectrum to produce the next

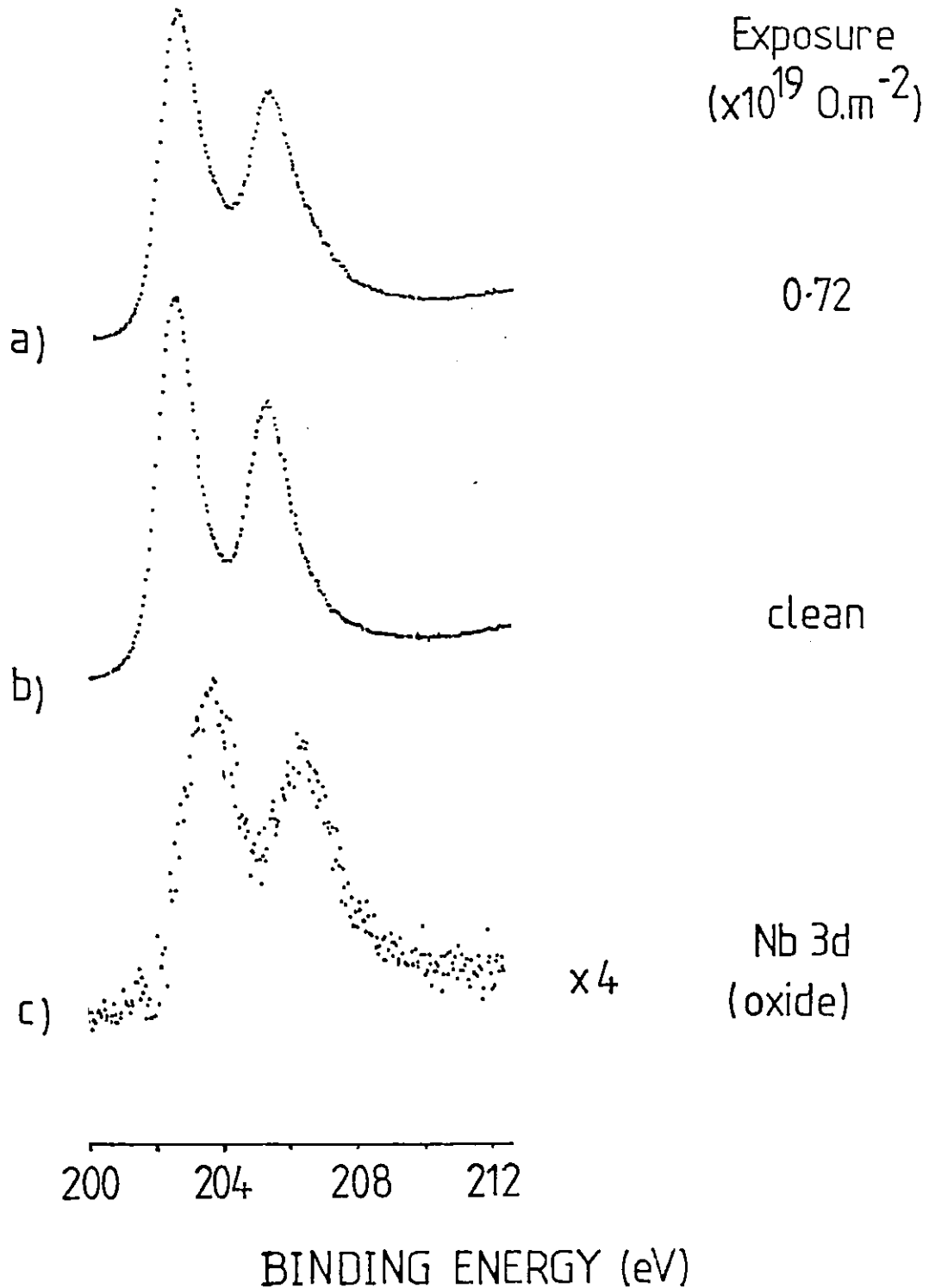


Fig. 6.1

The spectrum subtraction technique applied to obtain a Nb 3d (oxide) difference spectrum (c) from a clean Nb 3d standard (b) and an oxygen exposed Nb 3d spectrum (a).

approximation to the final result. The clean Nb 3d spectrum from Spn. 1 was used in all cases as the standard metal peak shape. The technique is therefore one of iterating towards a final approximation, judged on the basis of avoiding negative peak excursions, by successive subtractions of increasingly smaller fractions of the original clean spectrum. The limitation on the quality of the final result is governed by rounding down errors at low expansions (a computing fault rather than one of the technique). Despite this problem associated with the method, sufficiently accurate results can be obtained and Fig. 6.1 shows a trio of spectra. The spectrum of the original surface together with the clean standard from Spn. 1 are shown. The data is from Spn. 3 for an exposure of $0.72 \times 10^{-19} \text{ O.m}^{-2}$. The raw data from Spns. 1, 2 and 3 have been processed in this manner and the resulting oxide component spectra obtained. Fig. 6.2 shows the difference spectra, referred to as Nb 3d (oxide) spectra, obtained by this method for Spn. 1.

These spectra reveal a great deal of information contained within each original spectra which would otherwise have been difficult or even impossible to recognise. The value of the technique can be seen by comparing the original data, Fig. 5.3, with those in Fig. 6.2. In the original spectra the presence of a lower oxide and its proportion relative to the pentoxide is obscured by metallic emission. However, the subtraction spectra clearly reveal the presence of niobium atoms both with a chemical shift of $1.2 \pm 0.3 \text{ eV}$

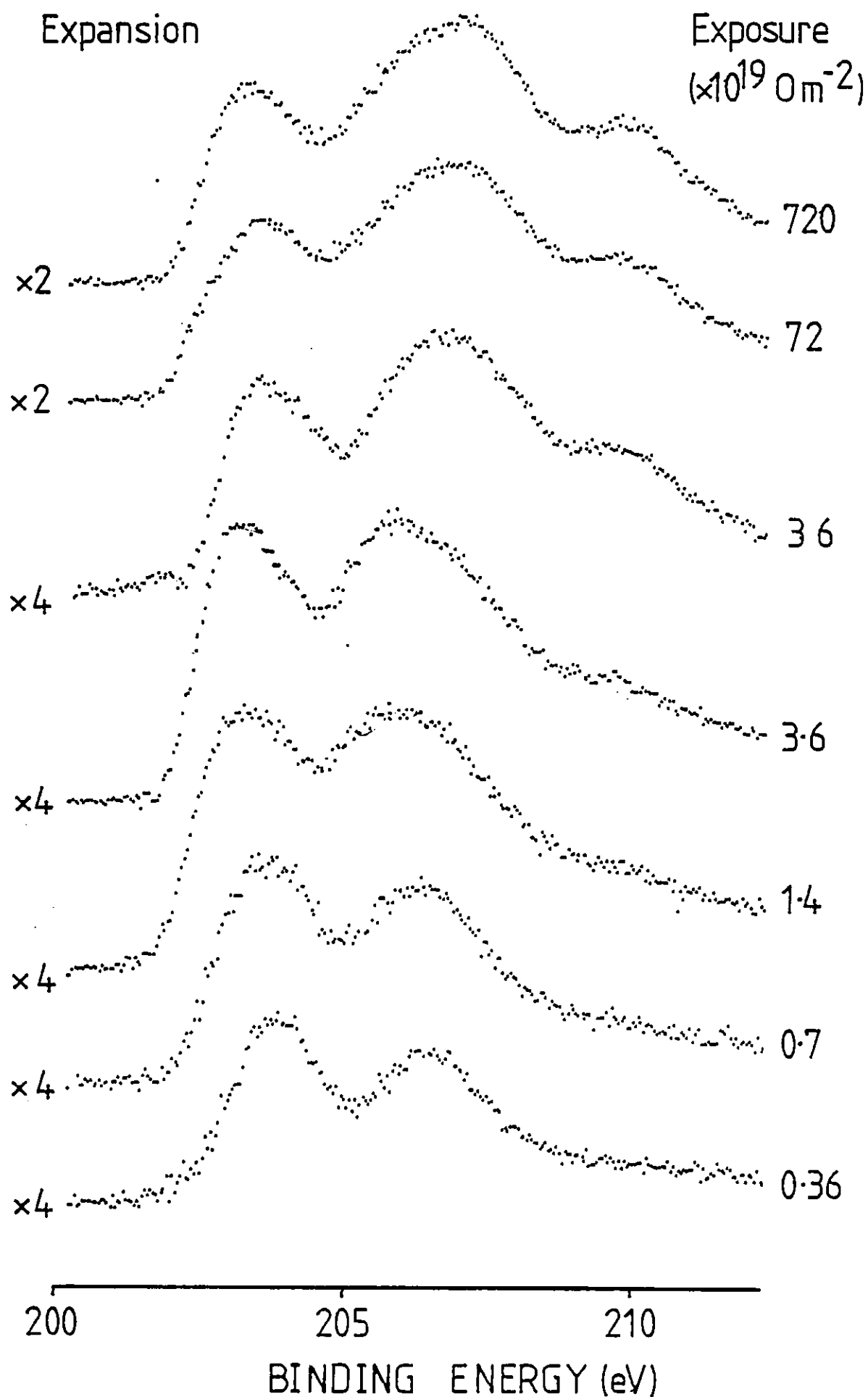


Fig. 6.2 The Nb 3d (oxide) peaks as a function of oxygen exposure up to $720 \times 10^{19} \text{ O.m}^{-2}$.

and 5.0 ± 0.2 eV. These two chemical shifts for niobium are assigned to NbO and Nb₂O₅ as described in Chapter 5.

Fig. 6.2 indicates that the relative intensity of the two oxides varies as a function of exposure. The spectra are slightly complicated by the fact that emission from the two oxides is not well separated i.e. the Nb₂O₅ 3d_{5/2} peak overlaps the lower oxide 3d_{3/2} peak. At an exposure of 0.36×10^{19} O.m⁻² NbO is formed preferentially with a chemical shift of 1.2 ± 0.3 eV from the metallic position. Resolution of the spin-orbit gap is good at this stage in the difference spectra, but soon deteriorates with exposure. This can be seen in the 0.72×10^{19} O.m⁻² spectrum, which also suggests that emission from atoms with a chemical shift of around 5.0 ± 0.5 eV is taking place. By an exposure of 1.4×10^{19} O.m⁻² the pentoxide emission has increased in intensity, although the lower oxide remains predominant. After an exposure of 3.6×10^{19} O.m⁻², the adsorption rate slows down and those changes that do take place in the difference spectra are less rapid than in the earlier stages. Indeed, by peak area measurements described in Sec. 5.2, the total oxide intensity fails to increase after this exposure. To summarise up to this exposure, it has been shown that a thin NbO film forms followed by the gradual appearance of Nb₂O₅ features, showing that an increasing number of Nb atoms are occupying higher oxidation states.

After an exposure of 3.6×10^{19} O.m⁻² the total

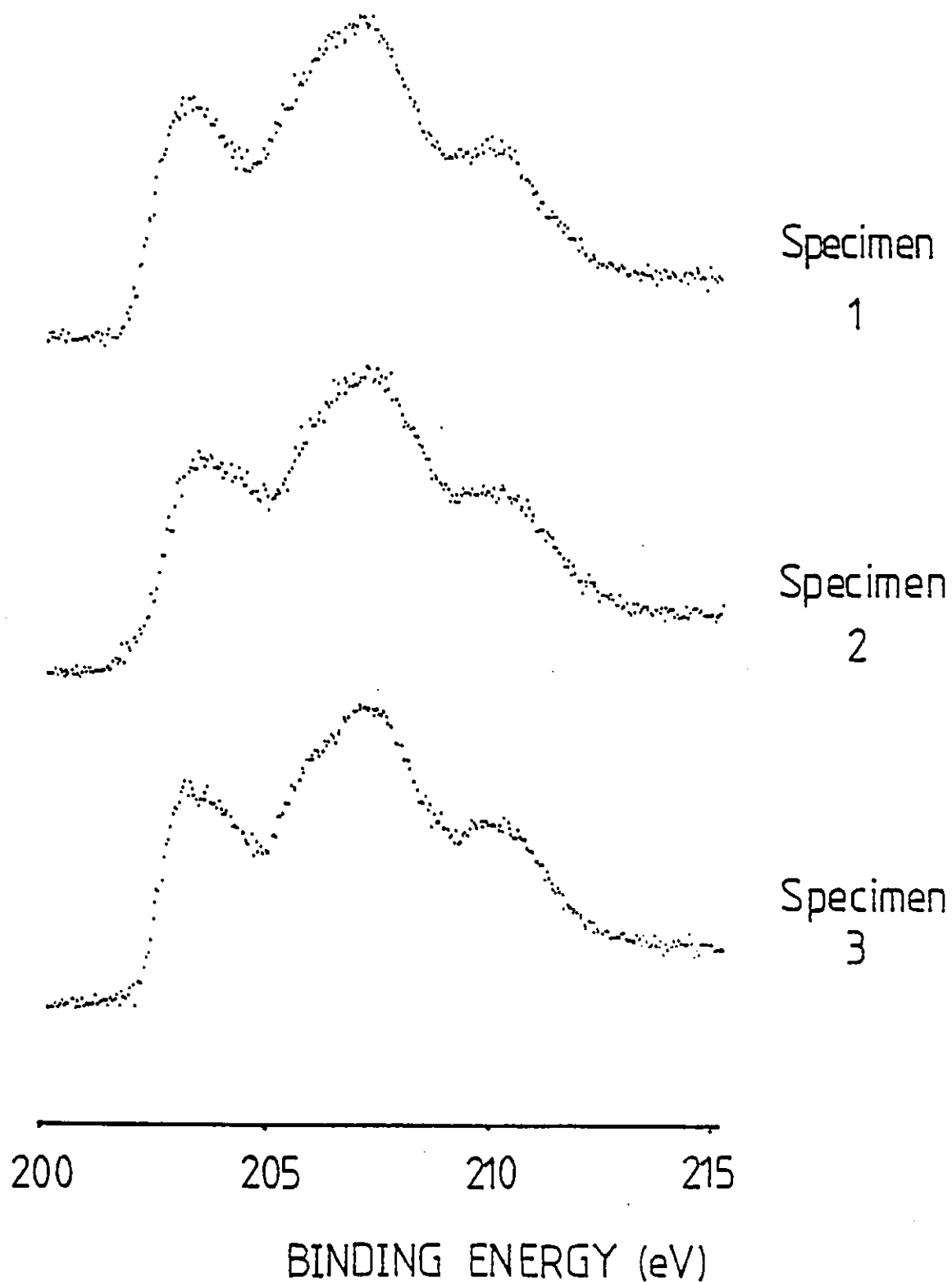


Fig. 6.3 The Nb 3d (oxide) spectra for Specimens 1, 2 and 3 after an oxygen exposure of $720 \times 10^{19} \text{ O.m}^{-2}$.

intensity from oxidised Nb atoms stabilises, and the changes that do take place are concerned with the relative proportions of pentoxide. For Spn. 1 a reduction in absolute intensity in the NbO emission takes place between 3.6 and $36 \times 10^{19} \text{ O.m}^{-2}$ suggesting that the lower oxide is being converted to the pentoxide. The spectrum at an exposure of $72 \times 10^{19} \text{ O.m}^{-2}$ is very similar to that at $720 \times 10^{19} \text{ O.m}^{-2}$, with only a slightly increased pentoxide emission.

For comparison the three spectra for Spns. 1, 2 and 3, at an exposure of $720 \times 10^{19} \text{ O.m}^{-2}$, are shown in Fig. 6.3 to illustrate the close parallels between the final surfaces on the separate foils. Between 3.6 and $36 \times 10^{19} \text{ O.m}^{-2}$ it therefore appears that the mechanism by which oxygen adsorption continues is by oxidation of the monoxide to pentoxide. That continued oxygen uptake does occur can be deduced from peak area measurements on the O 1s and O Auger peaks, described in Sec. 6.2. This figure also shows that only about half the niobium atoms in the initial oxide film are susceptible to further oxidation. Some significance is attached to this point when a description of the final ($720 \times 10^{19} \text{ O.m}^{-2}$) passivation film is presented.

6.2 PEAK AREA DETERMINATIONS

Peak area measurements have been made on the Nb 3d (total intensity); Nb 3d (oxide); O 1s; O Auger; Nb Auger and surface plasmon emissions.

Peak areas were determined by graphing the relevant spectrum on the X-Y plotter, photocopying this original

and then cutting and weighing the area under the peak. If the signal to noise was sufficiently good then no smoothing was carried out. This was the case for the Nb 3d peaks but for the remainder a 13 point Gaussian function smoothed the data producing a reproducible line shape. The choice of a baseline when making area estimate is somewhat arbitrary, but as long as a standard method is followed reliable information may be extracted (Fuggle, J.C. 1977). The method used in this study involved drawing a straight line between the estimated backgrounds on either side of the peak.

Spns. 1 and 2 produced the two major data sets, the information being tabulated in the Appendix, and displayed in Figs. 6.4 to 6.9. Spn. 3 also produced some relevant data. The data is presented in six graphs, one graph for the oxygen related data and another derived from Nb 3d features, for the three Spns involved. Figs. 6.4 and 6.5 display the Spn. 1 information for the Nb 3d and O 1s/O Auger data respectively. Similarly, Figs. 6.6. to 6.9 cover Spn. 2 and Spn. 3 data. The intensity axis is derived directly from the original peak area information and the abscissa is in units of exposure.

The first general point that can be made is that an exposure of about $3 \times 10^{19} \text{ O.m}^{-2}$ represents an important stage in the behaviour of the niobium emission peaks. That is, for exposures below about $3 \times 10^{19} \text{ O.m}^{-2}$ changes take place in the niobium emission intensities whereas above this exposure the Nb 3d (total), Nb Auger,

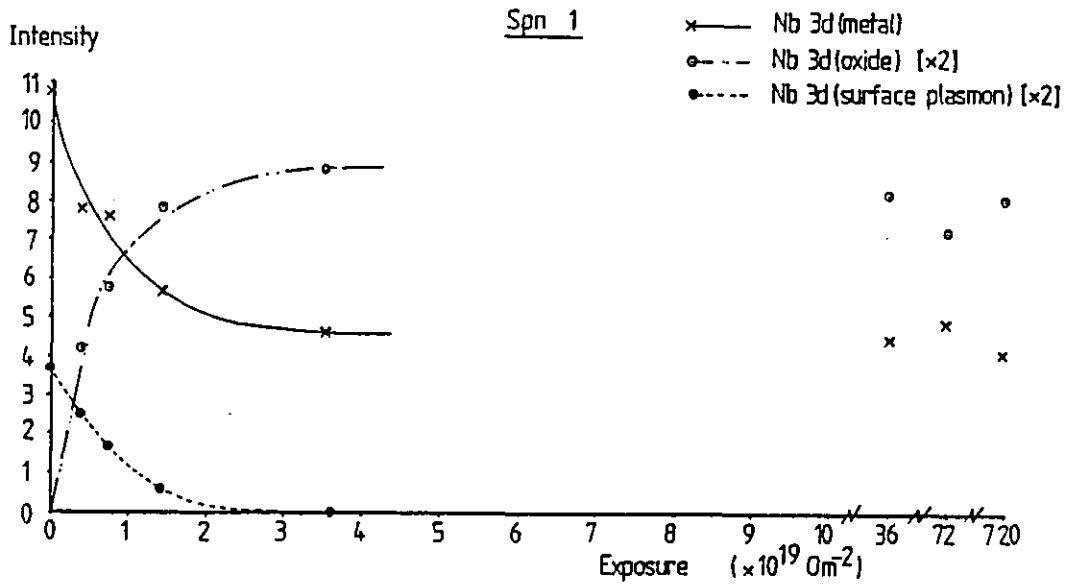


Fig. 6.4 The intensities of Nb3d features for Spn 1 as a function of exposure to oxygen.

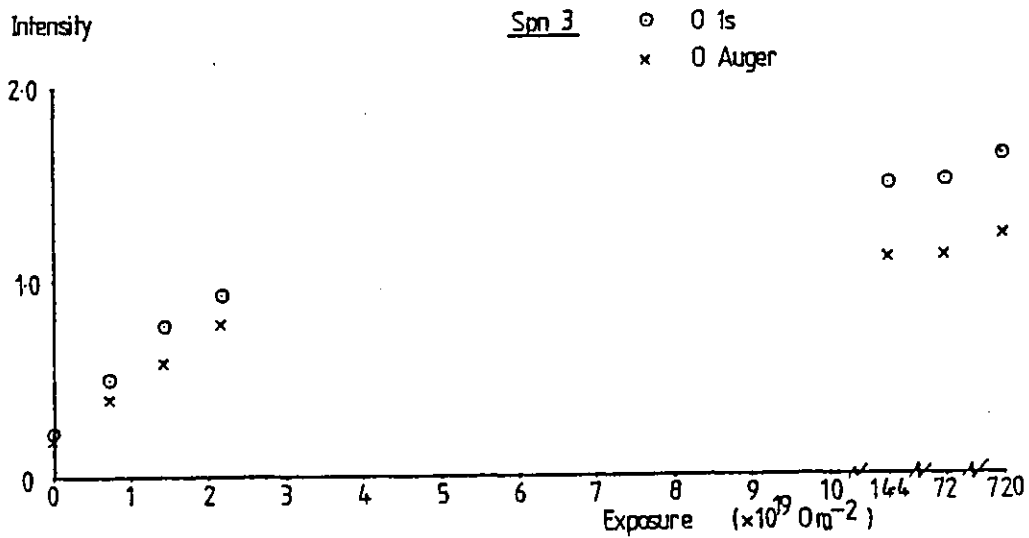


Fig. 6.5 The O 1s and O Auger intensities for Spn 1 as a function of exposure to oxygen.

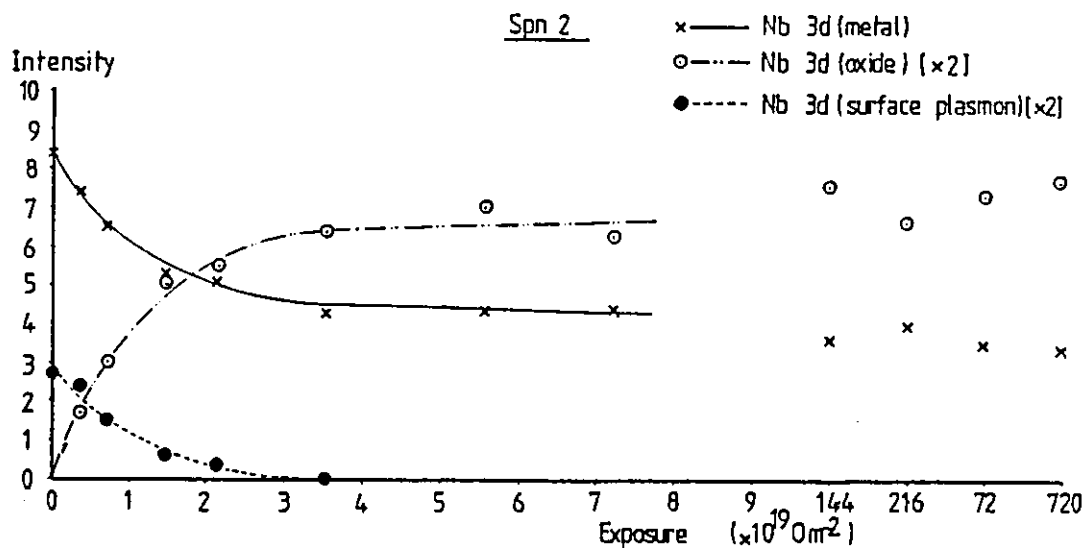


Fig. 6.6 The intensities of Nb 3d features for Spn 2 as a function of exposure to oxygen.

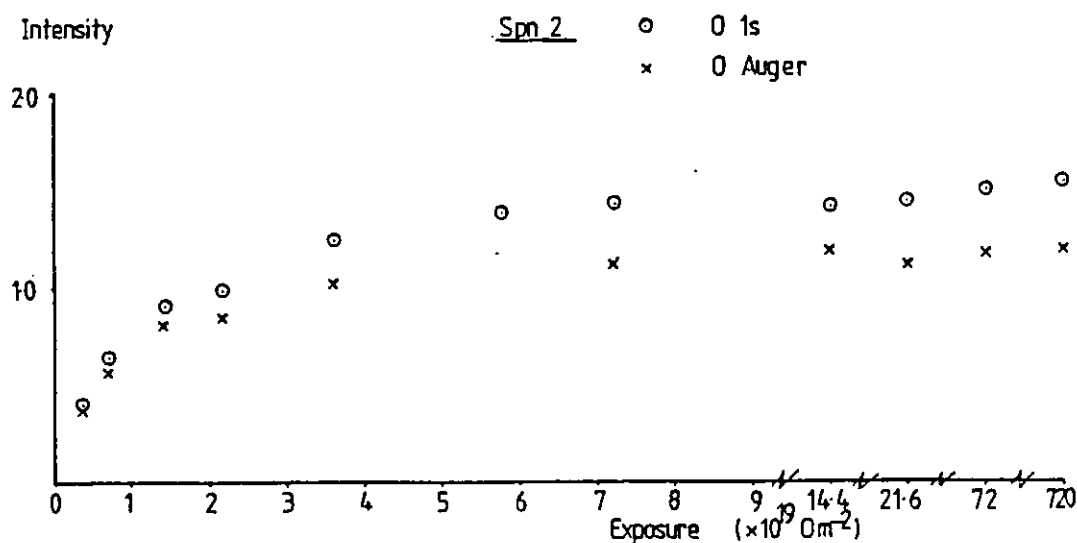


Fig. 6.7 The O 1s and O Auger intensities for Spn 2 as a function of exposure to oxygen.

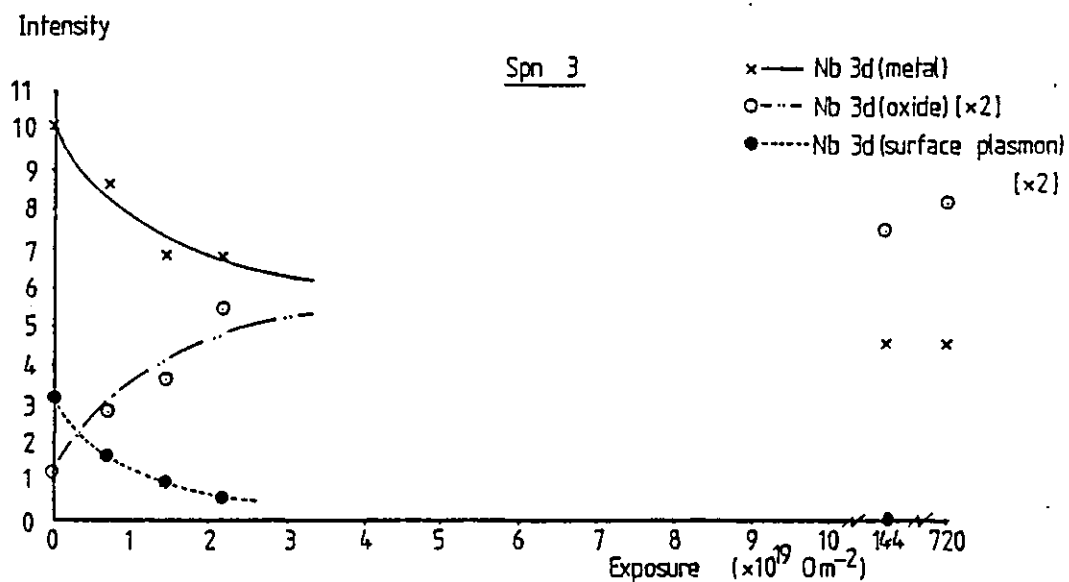


Fig. 6.8 The intensities of Nb 3d features for Spn 3 as a function of exposure to oxygen.

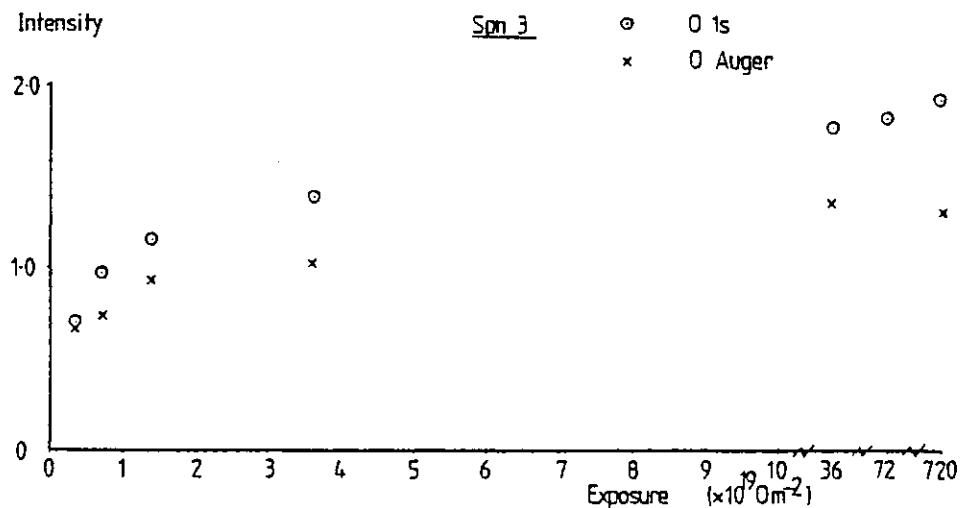


Fig. 6.9 The O 1s and O Auger intensities for Spn 3 as a function of exposure to oxygen.

Nb 3d (oxide) and Nb 3d surface plasmon intensities have achieved peak areas which then remain almost the same until at least $720 \times 10^{19} \text{ O.m}^{-2}$. The surface plasmon intensity is completely quenched by an exposure of $3 \times 10^{19} \text{ O.m}^{-2}$. By comparison, the oxygen related features, O 1s and O Auger, continue to increase beyond $3 \times 10^{19} \text{ O.m}^{-2}$ by around 15%, before saturating at higher exposures. This is interpreted as indicating that further oxidation of the oxide film takes place, in agreement with the changing relative intensities of monoxide and pentoxide peaks shown in Fig. 6.2.

The intensity from unoxidised niobium falls very rapidly upon oxygen adsorption, Figs. 6.4; 6.6; and 6.8, but again this niobium feature stabilises after an exposure of $3 \times 10^{19} \text{ O.m}^{-2}$. Fig. 6.4 for Spn. 1, suggests that no change in fact takes place above $3 \times 10^{19} \text{ O.m}^{-2}$, but the more complete and careful work of Spn.2 shows that an initial attenuation of 45% increases to between 50% or 55% by an exposure of $720 \times 10^{19} \text{ O.m}^{-2}$.

The combined evidence of the Nb 3d (oxide) and Nb 3d (metal) data do not support a simple hypothesis that the adsorption of oxygen proceeds to one monolayer followed by a rapid fall on sticking probability as is the case for noble metals such as copper and silver, but suggest that oxidation occurs beyond the first layer of niobium atoms. This is supported by the formation of chemically shifted components in the Nb 3d and Nb Auger emissions, and the large attenuation of the

unoxidised niobium emission.

The intensity of the Nb 3d (oxide) emission is approximately constant beyond about $3 \times 10^{19} \text{ O.m}^{-2}$ with the possible exception of the oxygen contaminated Spn. 3, demonstrating that by this stage the number of niobium atoms ultimately to be involved in the surface reaction has stabilised. The effect of further oxygen adsorption is to increase the oxidation state of a certain fraction of these niobium atoms as shown in Fig. 6.2, where the monoxide intensity falls after this exposure as the pentoxide peaks increase. This is direct spectroscopic evidence for this process.

The peak area intensities for the O 1s and O Auger features are presented in Figs. 6.5, 6.7 and 6.9 for Spns. 1, 2 and 3 respectively. In Fig. 6.10 the O 1s intensity has been plotted against the logarithm of exposure. The uptake of oxygen behaves logarithmically with exposure up to a certain O 1s intensity. At this O 1s intensity the thickness of the oxide film, as determined in Sec. 6.3, is 0.5, 0.4 and 0.5 nm for Spns. 1, 2 and 3 respectively. This data shows that the mechanism by which oxygen adsorption takes place changes when the film reaches a particular thickness.

In Fig. 6.11 the O 1s intensities for the three specimens has been normalised to that specimens clean Nb 3d intensity. The figure shows that within experimental uncertainty the amount of oxygen in the final oxide film is the same for each specimen. However, the rate at which the final oxide film is built up depends upon the

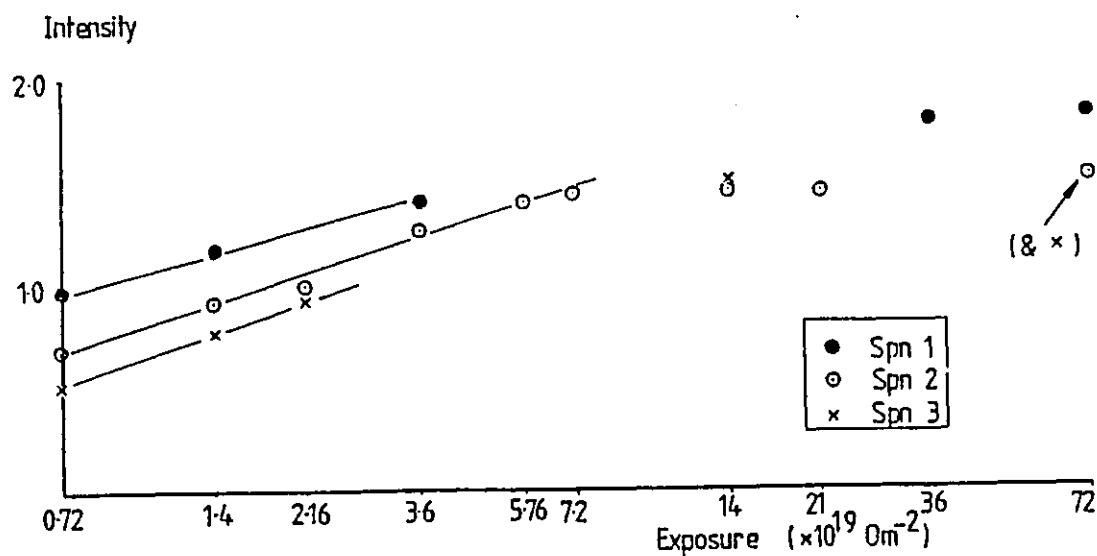


Fig. 6.10 The O 1s intensities plotted against logarithm of oxygen exposure.

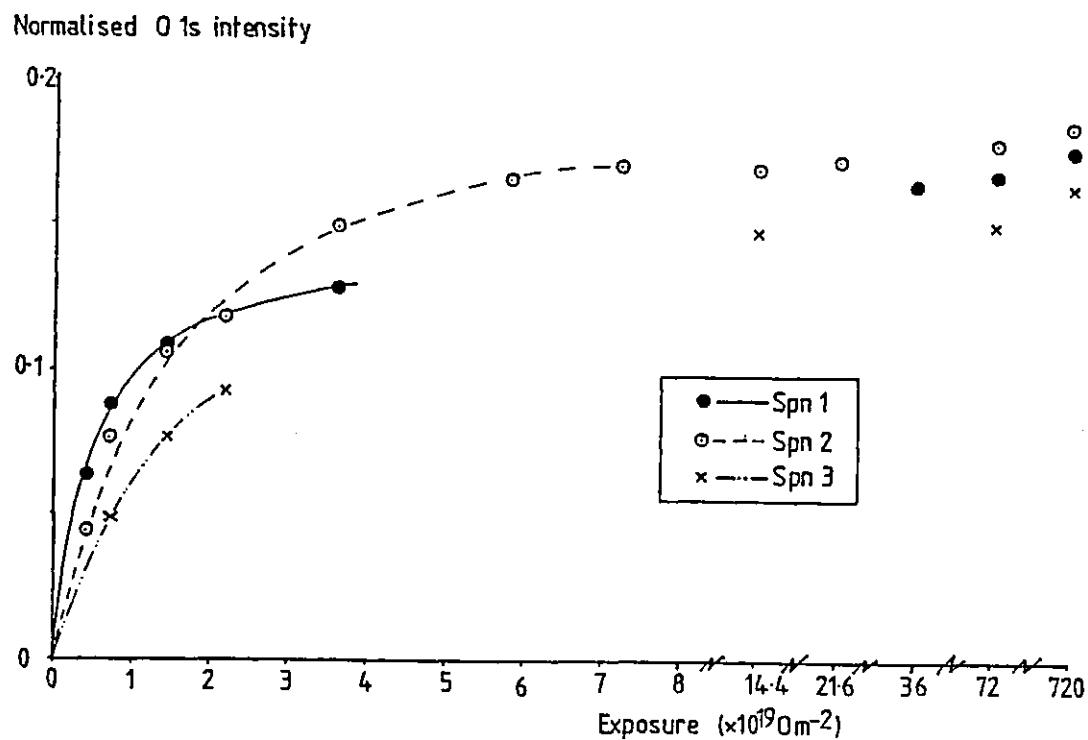


Fig. 6.11 The normalised O 1s intensity as a function of exposure to oxygen in the regime up to $720 \times 10^{19} \text{ O.m}^{-2}$.

cleanliness of the initial surface. The cleanest surface, Spn. 1, has the most rapid initial oxygen uptake followed by Spn. 2 and finally Spn. 3. The initial sticking probability for oxygen increases in the order: Spn. 3 < Spn 2 < Spn 1.

6.3 ESTIMATION OF THE OXIDE FILM THICKNESS

The theory which describes the intensity expected from an overlayer has been presented in Chapter 2, and the following equation will be used to interpret the experimental Nb 3d (metal) intensities as a function of exposure:

$$\ln A = \frac{d}{\lambda \cos \theta} \quad \dots 6.1$$

Equation 6.1 describes the attenuation A (defined as intensity divided by original intensity) of metallic emission by an overlayer of known thickness (d) and mean free path (λ). A full explanation of the symbols and the derivation of the equations has been given in Chapter 2 together with a discussion of their validity. It is concluded that these equations are sufficiently accurate to provide constraints upon the oxidation models that may be considered.

The mean free paths for both niobium and the oxidation overlayer are considered to be effectively the same. A value of 1.3 nm for the Mg K α induced Nb 3d photoelectrons, at a KE of 1050 eV, has been chosen (Evans, S. et al, 1977). Equation 6.1 then becomes:

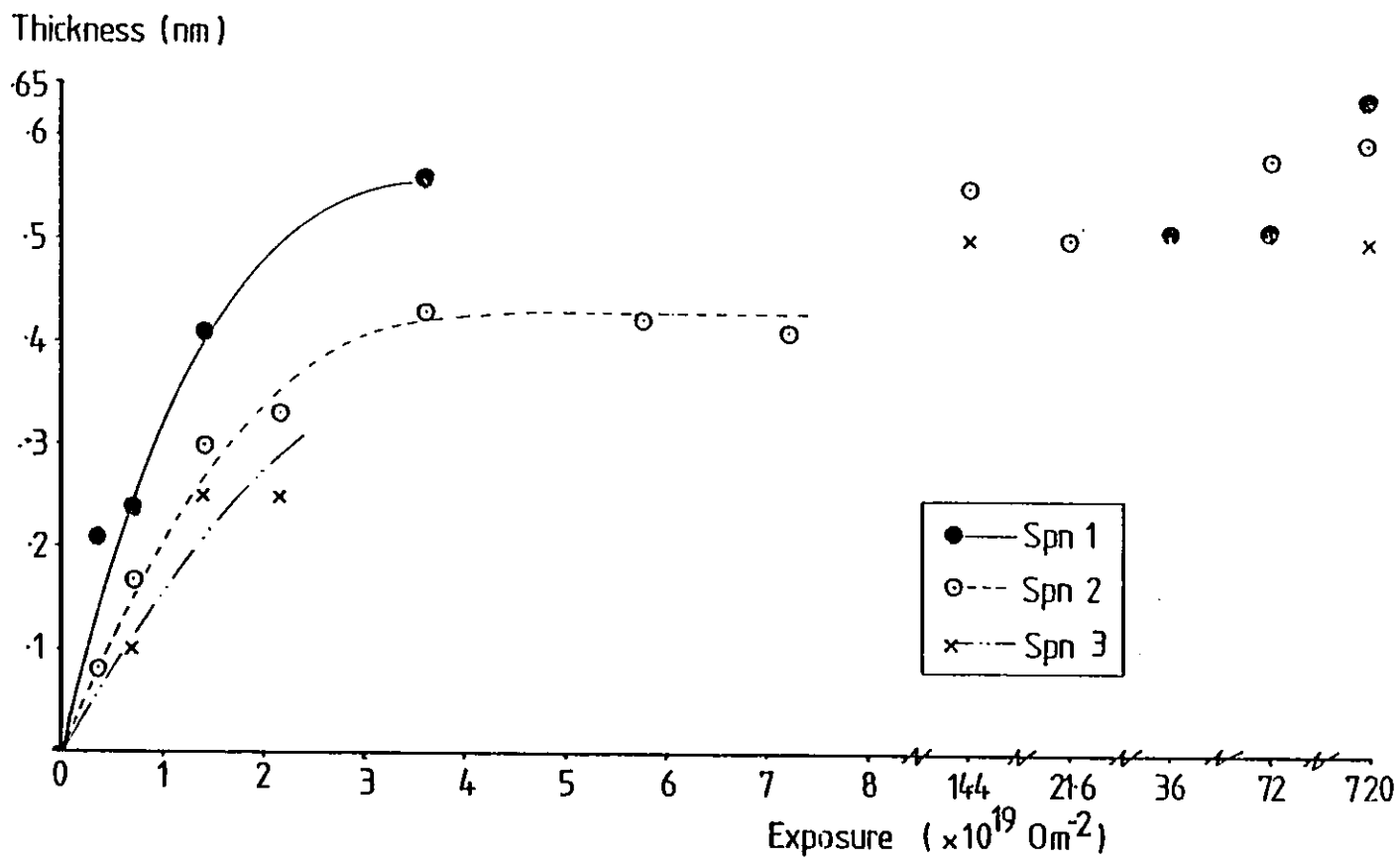


Fig. 6.12 The thickness of the oxide layer as a function of exposure to oxygen in the regime up to $720 \times 10^{19} \text{ O.m}^{-2}$.

$$d = \ln A \lambda_{i,0} \cos \Theta \quad \dots 6.2$$

This equation has been chosen to analyse the experimental data since it does not require a knowledge of the overlayer's stoichiometry, as does Equation 2.12 in Chapter 2. It does, however, require reproducible positioning of the specimen foil as the parameter A involves comparing the clean Nb 3d intensities with subsequent intensities following exposure to oxygen (performed in a separate chamber). This criteria is certainly met as the specimen probe could be positioned within a fraction of a millimetre in the Faraday cage.

The equation has been used to obtain the estimated oxide layer thickness presented in Fig. 6.12. The curves indicate a rapidly thickening layer up to exposures around $3-4 \times 10^{19} \text{ O.m}^{-2}$ followed by a more gradual increase towards larger exposures. At $3 \times 10^{19} \text{ O.m}^{-2}$ a value of between 0.4 and 0.5 nm is suggested which at the final exposures thickens by another 0.15 nm. In the low exposure range (up to $3 \times 10^{19} \text{ O.m}^{-2}$), Spn. 3 does not produce as thick a layer as either Spn. 1 or Spn. 2, but at the higher exposures does achieve similar values. If the data of Spn 2 is considered to be the most reliable, then the overlayer is characterised by a thickness of about 0.4 nm at $3 \times 10^{19} \text{ O.m}^{-2}$ and a thickness of 0.6 nm at $720 \times 10^{19} \text{ O.m}^{-2}$. Spns. 1 and 3 evidently behaved differently to Spn. 2, being more and less reactive respectively. The specimen foil in Spn. 1, was certainly

cleaner than in Spn. 2, while Spn. 3 was known to be more heavily contaminated with stable, high temperature annealed oxygen. It is also feasible that these differences between the three specimens were due to the orientation of different crystal planes at the surface. This must always be a problem with a study of polycrystalline materials of unknown surface structure. Another possible source of systematic error in these results may be uncertainty in the angle of emission (Θ) of analysed electrons.

Despite these variations, the data for the overlayer thickness based upon measured Nb 3d (metal) peak areas does present a reliable model based upon a rapid initial stage of film growth to about 0.4 nm followed by a slower stage which increases the film thickness to 0.6 nm.

6.4 PEAK POSITIONS AND WIDTHS OF THE OXYGEN FEATURES

Information concerning the nature of oxygen adsorption on niobium is also contained in the peak positions and widths of the O 1s and O Auger features, as well as from the Nb 3d peaks discussed above. The peak position and FWHM data for the O 1s and O Auger peaks from Spns. 1, 2 and 3 are tabulated in the Appendix and presented below in Figs. 6.13 to 6.16. Fig. 6.13 illustrates the variation of the O 1s peak in BE as a function of exposure. Estimates of BE's are taken to two decimal places with the second figure being either zero or five. Fig. 6.14 shows the KE for the O Auger peak as a function of exposure; Fig. 6.15 shows the FWHM of the O 1s peak and Fig. 6.16 the FWHM for the O Auger peak.

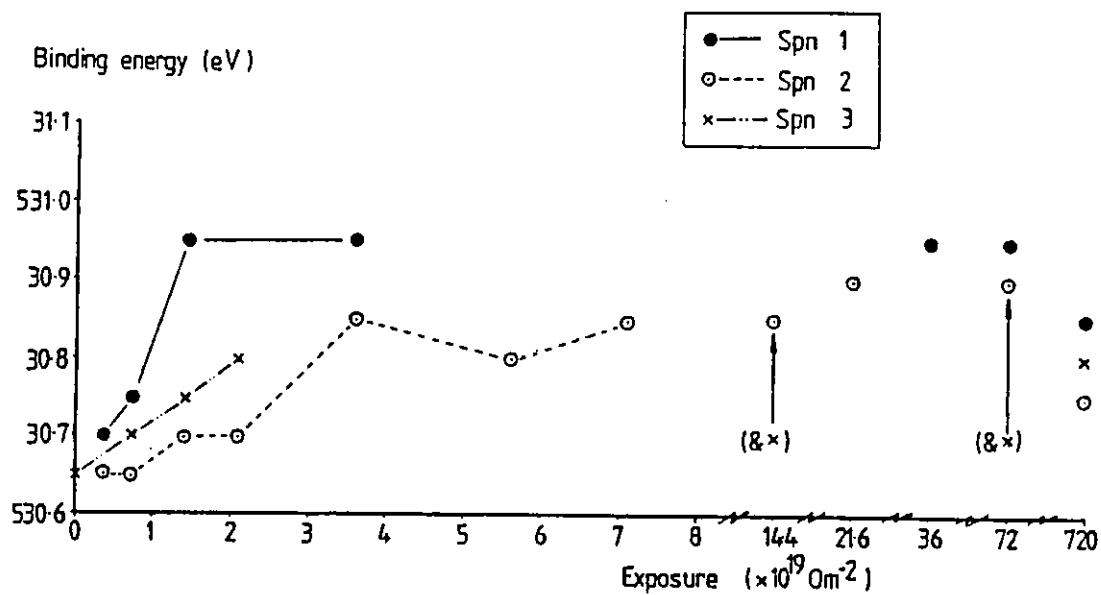


Fig. 6.13 The O 1s binding energy as a function of exposure to oxygen.

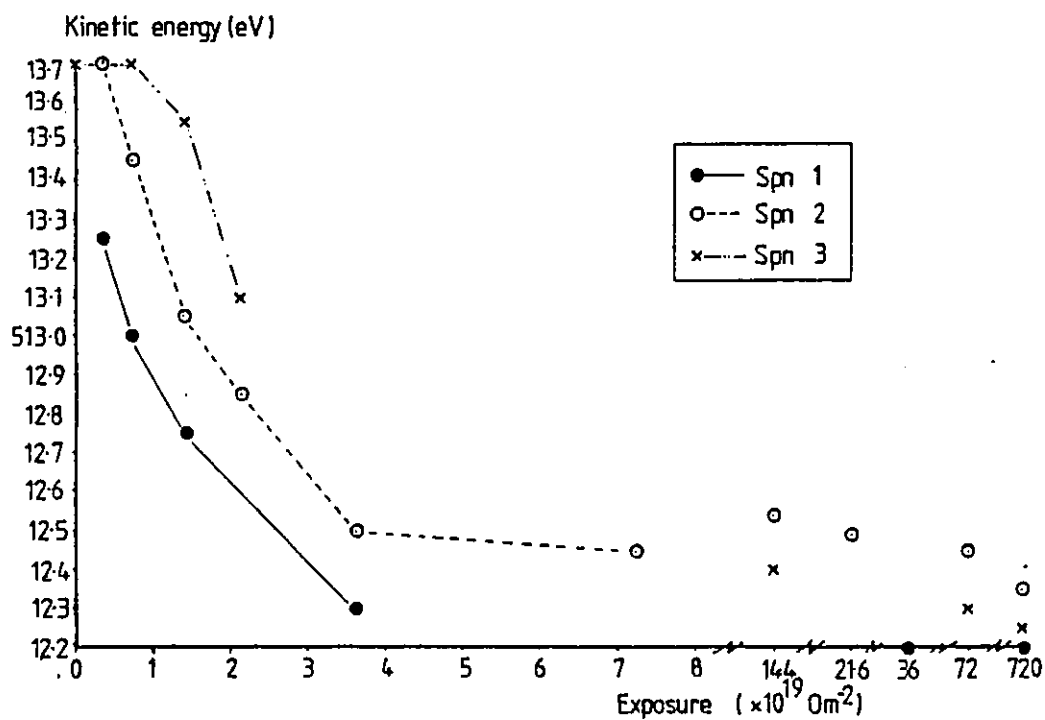


Fig. 6.14 The O Auger kinetic energy as a function of exposure to oxygen.

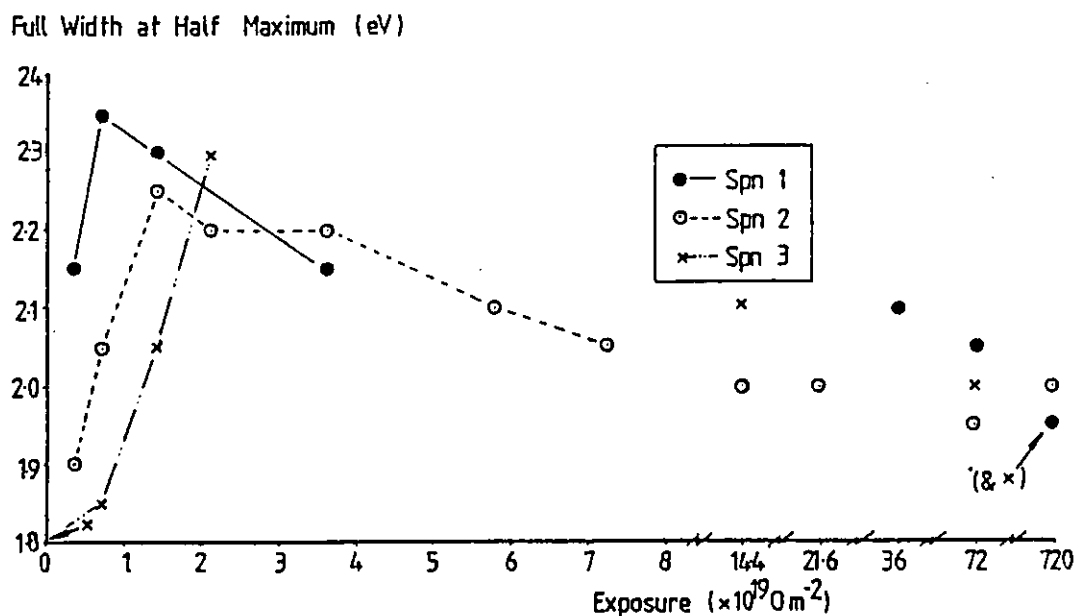


Fig. 6.15 The FWHM of the O 1s peak as a function of exposure to oxygen.

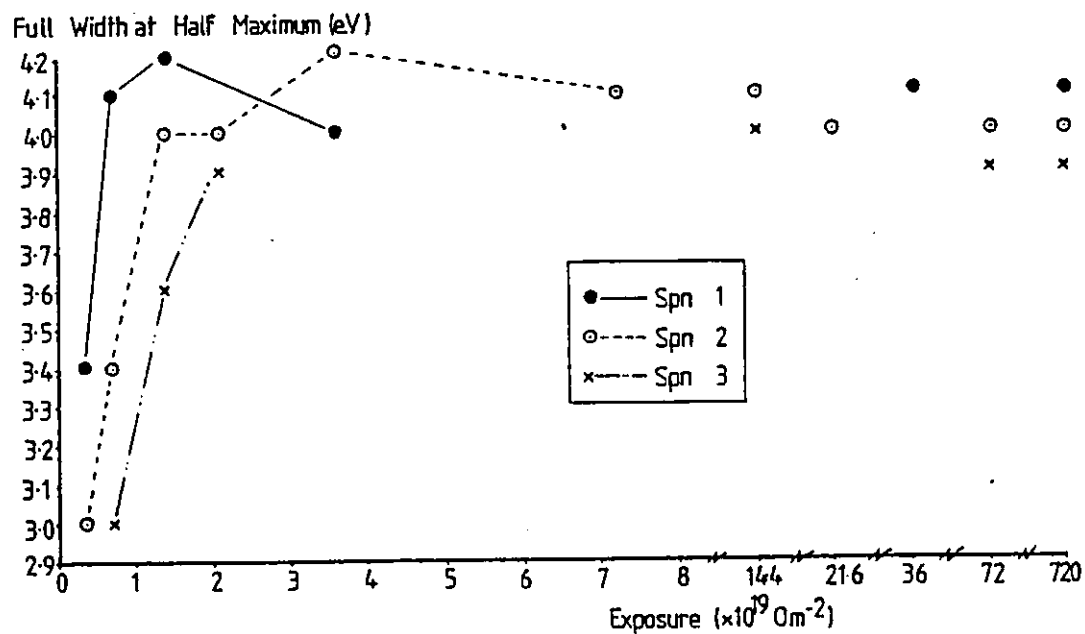


Fig. 6.16 The FWHM of the O Auger peak as a function of exposure to oxygen.

Peak widths are taken to the same accuracy as the BE/KE estimates.

It is clear that a rapid shift to higher BE takes place for the O 1s peak of between 0.15 and 0.20 eV, in the very early stages of the interaction. This rapid shift is completed by about $3 \times 10^{19} \text{ O.m}^{-2}$ and the BE then remains constant up to at least $72 \times 10^{19} \text{ O.m}^{-2}$. A reduction in the O 1s BE by 0.1 eV then takes place in all three Spns for the final exposure of $720 \times 10^{19} \text{ O.m}^{-2}$. These trends can be seen in the original data of Spn. 1 in Fig. 5.4. Variations in FWHM also occur and in this case a maximum is observed around $2 \times 10^{19} \text{ O.m}^{-2}$, with a value of 2.3 eV being typical.

The O Auger data behave similarly to the O 1s peak. The peak KE shifts to lower energies with exposure by one eV - a much larger shift than the core level photoelectron. Changes in the FWHM are also observed, with the most rapid variations taking place in the early stages of exposure. It is evident that Spn. 1 produces the larger FWHM values at lower exposures than is the case for Spns. 2 and 3. This behaviour is also followed for the O 1s peak widths, and will be discussed in Chapter 7.

SUMMARY

This chapter has presented the important Nb 3d (oxide) spectra which demonstrate the presence of niobium monoxide as well as of niobium pentoxide in the oxide film. Estimates of the thickness of the film have been obtained at each exposure. At passivation the oxide film is approximately 0.6 nm thick.

CHAPTER 7

DISCUSSION

In this chapter the information compiled in Chapter 6 is used to propose a model for the oxidation of niobium at low oxygen pressures. The model is then developed using all the available experimental data.

7.1 INTERPRETATION OF THE OVERLAYER THICKNESS IN TERMS OF OXIDE STRUCTURES.

The data contained in Chapter 6 provides the basis for a model describing the behaviour of oxygen molecules adsorbing upon clean polycrystalline niobium surfaces at room temperature. The evidence indicates that adsorption proceeds rapidly leading to the formation of an oxide film 0.6 nm thick. In fact, an initial film 0.45 nm thick is formed, followed by a more gradual growth of a further 0.15 - 0.2 nm. It is also noted that the adsorption of oxygen is logarithmic in exposure up to a certain, Specimen dependent, exposure and thus shows no intensity pause at $3 \times 10^{19} \text{ O.m}^{-2}$, a stage at which the number of oxidised niobium atoms has stabilised. However, other characteristics of the oxygen features such as the FWHM, and KE/BE do show rapid changes up to this exposure followed by more gradual subsequent variations.

Other parameters, based upon niobium features, also show their largest variations up to exposures of about $3 \times 10^{19} \text{ O.m}^{-2}$ followed by much more sedate

behaviour. Such features are the niobium Auger, the surface plasmon and the total intensity of Nb 3d emission. It is concluded that the major oxidation of clean niobium takes place in the initial phase, up to an exposure of $3 \times 10^{19} \text{ O.m}^{-2}$, but that a secondary oxidation then occurs more slowly.

Based upon the lattice parameters of the bulk structures of niobium, niobium monoxide and niobium pentoxide the thickness of one monolayer of each phase would be 0.16 nm, 0.23nm and 0.40 nm respectively. Niobium pentoxide exists in several crystalline forms and a value of 0.40 nm has been taken as being representative. Niobium dioxide has not been included in the compilation since no evidence of structurally significant amounts during the oxidation has been observed.

It can be seen that a double layer of niobium monoxide would satisfy the requirement for a film of around 0.4 - 0.5 nm as two layers of NbO would be 0.46 nm thick. Taken in combination with the subtraction spectra for the Nb 3d peaks which show that a compound with a chemical shift of 1.2 eV (assigned to NbO) dominates the oxide film, it may be concluded that a double layer of NbO is consistent with the available data.

The more gradual thickening of the overlayer at larger exposures is associated with the appearance of substantial contributions from Nb₂O₅ in the Nb 3d (oxide) spectra. This increase in thickness can be accounted

for by postulating a further oxidation of the layer of NbO exposed to the incident oxygen molecules. Such a duplex structure would have a thickness (based upon the bulk lattice parameters) of 0.63 nm. This agrees with a thickness of 0.6 nm suggested by the attenuation of the metallic Nb 3d photoelectrons. The oxide component spectra for the three foils exposed to $720 \times 10^{19} \text{ O.m}^{-2}$ are shown in Fig. 6.3, and do show that approximately equal numbers of niobium atoms occupy NbO and Nb₂O₅ states.

It is difficult for angle integrated XPS to determine the spatial arrangement of two chemical forms on a surface as appears to be the present situation on Nb. Fortunately a study by Rieder, K.H. (1980) using static secondary ion mass spectroscopy (SIMS) has shown that the secondary ion yield from a Nb (100) surface, exposed to $288 \times 10^{19} \text{ O.m}^{-2}$ (400 L O₂) is practically the same as that from a bulk Nb₂O₅ crystal. Since SIMS is sensitive mainly to the outermost surface layer, this evidence supports the model involving an outer layer of Nb₂O₅.

The important conclusions of this model derived from an interpretation of the Nb 3d spectra are:

1. Oxidation to NbO occurs for the top two layers of Nb atoms.
2. The outer NbO layer is then further oxidised to Nb₂O₅.
3. Niobium dioxide (NbO₂) does not contribute to the oxidation.

7.2 DEVELOPMENT OF THE MODEL

The structural model described above has been derived only from a consideration of the Nb 3d spectra. More subtle changes in other features of the XPS spectrum are observed which, when using this model for the oxidation, help to describe the chemical nature of the oxide film. The description of the adsorption process provided by this model can be improved upon and refined when all of the spectroscopic data are studied. The spectra to be discussed in this manner are: Nb Auger; Nb surface plasmons; total Nb 3d intensity; O 1s and O Auger.

7.2.1 Nb Auger

Since a chemical shift is also observed in the Nb Auger MNN emission as well as in the Nb 3d photoelectrons a comparison between the two should prove informative. This is especially so as the two emissions differ considerably in their kinetic energies. While the mean free path for electrons with a kinetic energy of 1050 eV is 1.3 nm, a suitable value for electrons with only 165 eV energy would probably be about 0.5 nm.

In Fig. 5.8 the Nb Auger peak is shown as a function of exposure to oxygen. The main features of the spectra are the appearance of emission at 4.5 eV to lower KE and a reduction in total intensity. At an exposure of $720 \times 10^{19} \text{ O.m}^{-2}$ the shoulder is one-third as intense as the emission at the original peak position. Close examination of the Auger peak at low exposures, e.g. $0.72 \times 10^{19} \text{ O.m}^{-2}$ indicates that, even at this stage,

a tailing of the original peak is taking place. Certainly at $3.6 \times 10^{19} \text{ O.m}^{-2}$ this emission is well defined, and can probably be assigned to Nb_2O_5 as its chemical shift is very similar to that observed in the Nb 3d photoelectron peaks. A feature which is not present in the Nb Auger spectra is a chemically shifted peak due to NbO. This is most probably due to the relatively small chemical shift, as observed in the Nb 3d core level spectra, such that a discrete peak is not observed.

Rieder, K.H. (1980) also observed a shoulder in a high resolution electron excited Auger study of the adsorption of oxygen on Nb (100) and assigned it to the onset of oxidation. Adsorption of oxygen at lower exposures was thought to be 'chemisorptive'. This result shows the problems that can be encountered in Auger spectroscopy when the peak width is relatively large (the Nb Auger is 5 eV wide for the clean surface).

The observed relative area intensity of the pentoxide peak to the metal/monoxide peak at $720 \times 10^{19} \text{ O.m}^{-2}$ is about 4:6. A calculation of the ratio indicates that it should be 6:4, i.e. the Nb_2O_5 peak should be the more intense. The calculation assumes that the mean free path for these electrons is 0.5 nm. However, the calculation does assume that the Auger yield is the same for all the chemical states involved, a possible variable which until recently does not seem to have been considered (Rao, C.N.R. et al 1979). These authors have shown that the $L_{2,3}M_{4,5}M_{4,5}$ transition in the first row

transition elements is very sensitive to the number of electrons in the valence band - the $M_{4,5}$ level. They have also shown how this effect can be of use during studies of the oxidation of these elements, as the intensity of the $L_2M_{4,5}M_{4,5}$ transition falls relative to the other LMM Auger peaks as the oxides are formed and valence electrons are removed.

In the case of Nb, the Auger transition which has been monitored (the strongest - $M_{4,5}N_{2,3}N_{4,5}$), has the final level in the valence band. Now when the oxidation proceeds, and Nb^{5+} ions are formed (Nb_2O_5), the electrons required for the transition are no longer directly available. In fact the constraints on the transition probability may not be as severe as this suggests as cross transitions from the O 2p level could take place. However, the yield of electrons into this peak is reduced and the Nb Auger peak thus appears to be poorly represented by Nb_2O_5 contributions.

These problems are, in fact, general to Auger transitions which involve valence levels. Since the major Auger transitions for the light elements are of this type this problem raises some considerable uncertainties in the analysis of elements such as O, F, Al, Mg, Si, etc. For niobium, the above analysis suggests that the Auger spectra can only be used qualitatively to study the oxidation mechanism.

7.2.2 Surface plasmons

Another feature of the niobium photoelectron spectrum which can provide some insight into the

oxidation is the surface plasmon observed on the Nb 3d peaks. The primary data are shown in Fig. 5.7 at exposures of up to $720 \times 10^{19} \text{ O.m}^{-2}$. The measured intensities are presented in Figs. 5.4, 5.6 and 5.8 for Spns. 1, 2 and 3 respectively.

The behaviour of the surface plasmon follows the pattern set by the other spectral features, in that the most rapid change in intensity occurs up to an exposure of $3 \times 10^{19} \text{ O.m}^{-2}$. In this case the intensity at $3 \times 10^{19} \text{ O.m}^{-2}$ is effectively zero. The decay of the surface plasmon intensity may reflect directly the number of remaining oxygen free surface niobium atoms. That some surface plasmon intensity does remain at exposures of over $1 \times 10^{19} \text{ O.m}^{-2}$ (the exposure when a complete monolayer of NbO could theoretically exist) suggest that two complete NbO layers are required to eliminate the surface plasmon, or that some adsorbate free sites still populate the surface. The true explanation of the persistence of the surface plasmon probably involves both possibilities as bulk NbO is a good electrical conductor suggesting that a single monolayer of NbO may support a plasmon. Alternatively the existence of a complete monolayer of NbO seems unlikely since this structure is very reactive and double layer formation probably commences before a complete monolayer has been formed.

7.2.3 Total Nb 3d intensity

The third feature of the XPS data which deserves some attention is the total Nb 3d intensity, the data

being tabulated in the Appendix. This once again follows the pattern of a fall in intensity by $3 \times 10^{19} \text{ O.m}^{-2}$ followed by a more gradual decline towards higher exposures. In this case the formation of oxide on the surface reduces the number of niobium atoms in the sampling depth. This is equivalent to considering the flux of photoelectrons to be reduced due to the oxygen atoms acting as additional scattering centres.

That most of the drop in intensity occurs by $3 \times 10^{19} \text{ O.m}^{-2}$ adds further evidence to the model that most of the Nb atoms ultimately to be involved in the oxidation are involved by this stage. The Nb Auger total intensity also falls in the same exposure regime as the Nb 3d peaks, but the reduction is about 30% of the original intensity instead of about 15% as for the Nb 3d peaks. The larger fall in this case reflects the greater surface sensitivity associated with the low energy Auger electrons.

7.2.4 O 1s and O Auger

The data on these peaks is presented in the following figures:

- Fig. 5.4 O 1s spectra from Spn. 1
- Fig. 5.6 O Auger spectra from Spn. 1
- Fig. 6.5)
- Fig. 6.7) Peak area data
- Fig. 6.9)
- Fig. 6.10 O 1s peak area vs. logarithm of exposure
- Fig. 6.12 Normalised O 1s peak areas.
- Figs. 6.13 FWHM and BE/KE data
- to 6.16

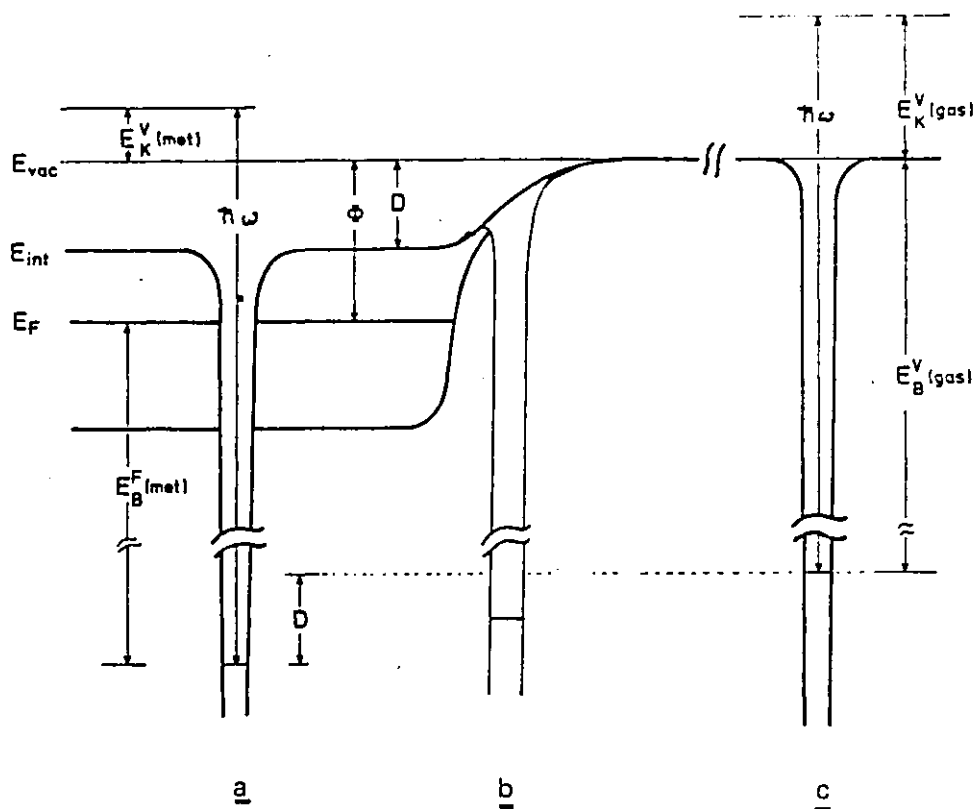


Fig. 7.1

The electrostatic potentials influencing the core level binding energies of an atom a) in a solid, b) in the surface region and c) in the gas phase.

The main features displayed by the oxygen peaks are a rapid increase in the 1s BE; a 1 eV shift to lower KE for the Auger peak; and increases in the FWHM for the two emissions with exposure to oxygen, followed in the core level by a slight narrowing. All of the major changes take place at low exposures. Before an interpretation of this information is presented a brief review of the causes of such shifts in BE/KE's is given.

A diagram of the relationship between the important potentials involved in adsorption on a metal surface is shown below in Fig. 7.1, taken from Menzel, D. (1978). For a gas phase photoexcitation event the reference level is the vacuum potential of the instrument. In the case of an atom in a solid it is the Fermi level. However, for adsorption on a surface the potential varies rapidly across the surface and the problem arises of deciding upon a suitable reference level. For adsorbed atoms the reference level will lie somewhere between these two limits and may lead to the observation of a low BE relative to similar atoms in the bulk. This situation is represented by the centre atom in the figure, although this may not be a good model of the Nb-O system. An equally complex problem arises if the atom becomes incorporated within the top layer of the metal surface, as has been suggested for the Nb-O system by Pantel, R. et al (1977).

As well as the physical position of an atom with respect to the potential variations in the surface region, the chemical environment influences the measured

BE and KE's. This is observed very easily in the Nb 3d core level shifts between metal and the oxides, but more subtle effects may also occur on a smaller scale.

These effects primarily influence initial states although they may also perturb the degree by which the final state ion is relaxed, and hence the measured kinetic energy of the photoelectron. Both of these factors could be of the required order of magnitude to produce the O 1s and O Auger shifts observed in the present work. The approach taken here to discuss these shifts is to consider the initially low O 1s BE and high O Auger KE as representing oxygen atoms in a particular surface configuration. As the NbO high temperature surface (Spn. 4) O 1s and O Auger values are similar to those observed after low exposures to oxygen, a tentative similarity between the two surfaces is proposed. These ideas are supported by the work of Pantel, R. et al (1977) who observed a $c(2 \times 2)$ LEED pattern on Nb (100) due to oxygen migration from the bulk at high temperatures. The surface potential of this structure was found to be very similar to that produced by low exposures of oxygen at room temperatures. Although a $c(2 \times 2)$ pattern was not seen by Pantel, R. et al on Nb(100) at room temperature, Usami, S. et al (1977) did report this pattern on Nb(100) in a similar study. Pantel, R. et al concluded that the reduced surface dipole for the two surfaces was due to incorporation of oxygen atoms into the first niobium layer. The low surface potential and the low O 1s BE

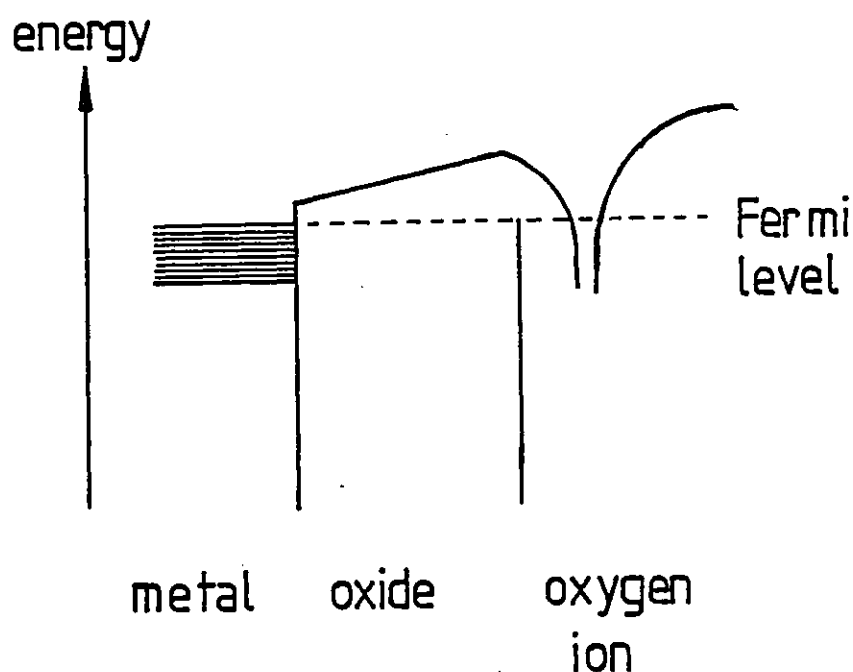


Fig. 7.2 Negative charge localised at the oxide-vacuum interface influences the inner potential through the oxide layer.

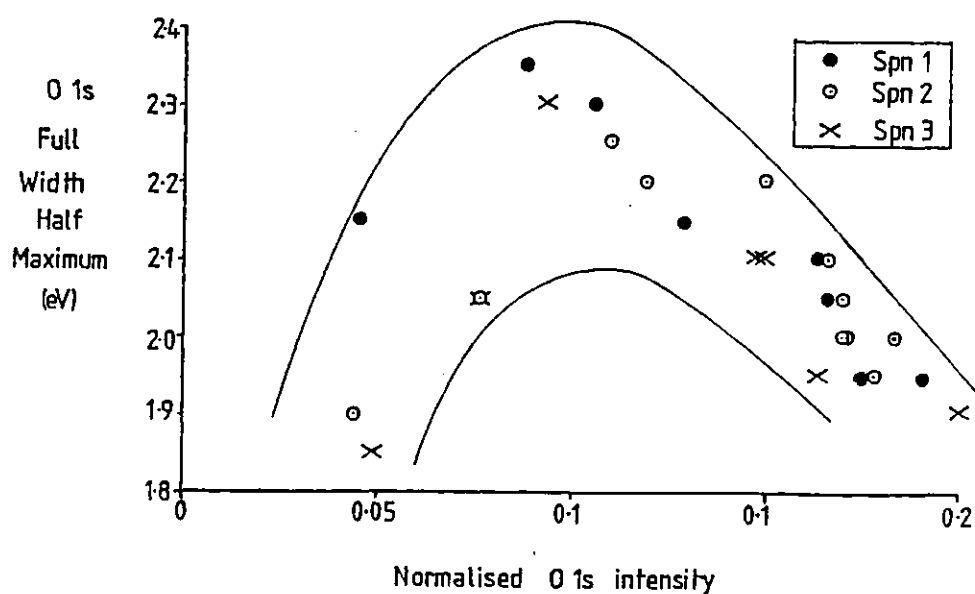


Fig. 7.3 The relationship between the full width at half maximum height of the O 1s peak and its normalised intensity.

and high O Auger KE's are probably related phenomena associated with a single layer of NbO on a Nb substrate.

The small reduction in the O 1s BE that is observed for all the specimens at an exposure of $720 \times 10^{19} \text{ O.m}^{-2}$ is considered to be evidence for band bending in the oxide overlayer. This effect is well known in semiconductor technology and has recently been noted during the formation of thin oxide layers on Cr(100) and Cr(111) by Peruchetti, J.C. et al (1978 and 1979) and for thin films of oxide on polycrystalline Mg by Fuggle, J.C. (1977). It is caused by the presence of negative charges at the oxide/vacuum interface raising the inner potential of the film and so reducing the binding energy of all the atoms in the film. Fig. 7.2, below, illustrates the suggested arrangement of the surface charges in such a situation.

For the oxidation of niobium the effect is relatively small, only 0.1 eV, compared to the two studies mentioned above where shifts of around 0.5 eV occurred. This shift should be noted for all the peaks in the spectrum, but no other feature is sufficiently narrow for the shift to be readily observed. Fuggle, J.C. estimated that a shift of 0.5 eV would require $5 \times 10^{13} \text{ atoms cm}^{-2}$ with a net charge of only one third that of an electron.

Large changes in the FWHM values for the O 1s and O Auger peaks are of interest. These peaks rapidly increase in width with exposures up to about $3 \times 10^{19} \text{ O.m}^{-2}$ and then more gradually decrease with higher exposures.

The width of the peaks for the final film is greater than for the NbO and Nb₂O₅ surfaces alone probably reflecting the composite nature of the final film. In a similar manner the maximum peak widths around exposures of $1 - 3 \times 10^{19} \text{ O.m}^{-2}$ may reflect a particularly wide variation of chemical environments for the oxygen atoms.

An interesting feature of the FWHM graphs is that the initial presence of oxygen contamination, probably in the form of high temperature NbO, displaces the attainment of maximum FWHM to higher exposures. Thus for Spn. 1, the maximum value is achieved at an exposure of only $0.72 \times 10^{19} \text{ O.m}^{-2}$, whereas Spn. 3 requires an exposure of $2.2 \times 10^{19} \text{ O.m}^{-2}$, and Spn. 2 is intermediate. In Fig. 7.3 the data is replotted as FWHM as a function of normalised O 1s peak area (normalised to the clean Nb 3d peak area for the relevant specimen) then the data all lie in a band. This suggests that it is a certain concentration of oxygen atoms that gives rise to a particular FWHM. The maximum FWHM value occurs at a coverage of oxygen which corresponds to a peak area approximately one half the final uptake peak area. The peak area corresponds to a concentration of oxygen atoms equivalent to about one monolayer, at which stage a range of chemical states for oxygen coexist. One such state is likely to be the low exposure NbO monolayer structure. Another candidate must be the first nuclei of the NbO double layer structure. Islands of this structure must be forming possibly at defect sites such as grain boundaries and surface steps. The surface at

this stage may be characterised by the breaking up at well ordered NbO monolayers caused by the nucleation and growth of the double layer NbO oxide layer.

7.2.5 Oxygen adsorption in the chemisorption regime

The behaviour of adsorbates in the exposure regime where less than a monolayer is formed is often referred to as the region of 'chemisorption'. In order to examine this regime in more detail a set of O 1s spectra were obtained from the Spn. 1 surface for exposures up to $0.72 \times 10^{19} \text{ O.m}^{-2}$. The original spectra are shown in Fig. 5.5.

The kinetics of the adsorption in the submonolayer regime have been investigated by plotting $-\ln(1-x)$ against exposure, where x is the peak area. This procedure tests the possibility that the O 1s intensities are approaching a limiting value exponentially and the test is derived from first order kinetics. The data is presented in Fig. 7.4. The $1.44 \times 10^{19} \text{ O.m}^{-2}$ exposure result was not obtained at the same time as the data for exposures up to $0.72 \times 10^{19} \text{ O.m}^{-2}$. It has been obtained by multiplying the $0.72 \times 10^{19} \text{ O.m}^{-2}$ intensity obtained during the submonolayer study by the ratio of the O 1s intensities for exposures of 1.44 and $0.72 \times 10^{19} \text{ O.m}^{-2}$ obtained during exposures up to $720 \times 10^{19} \text{ O.m}^{-2}$. These two sets of data were obtained from Spn. 1 at different times.

The graph shows that there are two distinct reaction stages linked at an exposure of $0.36 \times 10^{19} \text{ O.m}^{-2}$. The change of slope takes place at a significant

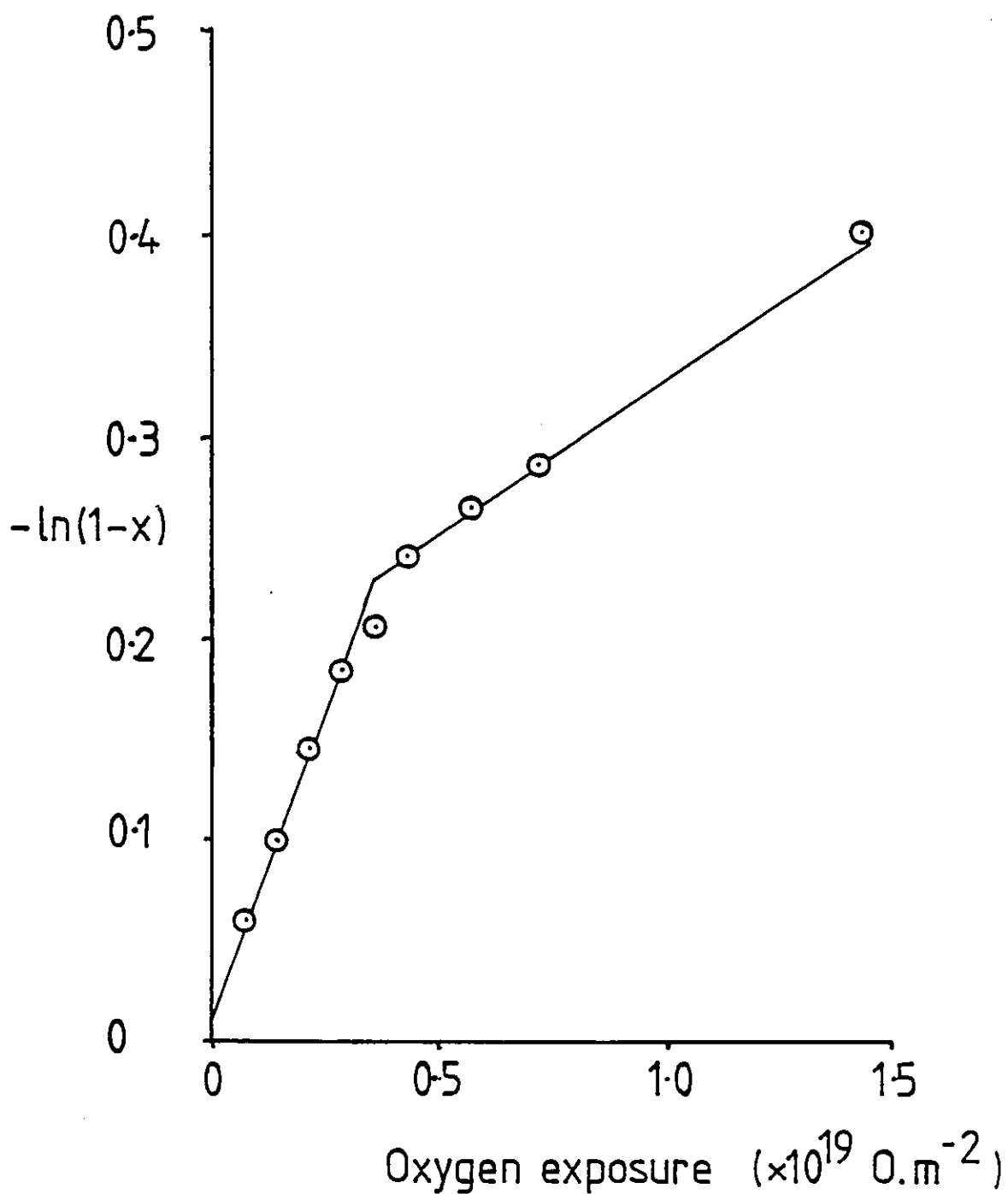


Fig. 7.4 A plot of the function $-\ln(1-x)$, where x is the 0 1s peak area, against oxygen exposure in the regime to $0.72 \times 10^{19} \text{ O.m}^{-2}$ for Specimen 1.

exposure, as Pantel, R. et al noticed that the minimum in the surface potential for the Nb(100) and Nb(110) faces occurred at exposures of 0.36 and $0.42 \times 10^{19} \text{ O.m}^{-2}$ respectively. For the Nb(100) face this is one half of the available sites (assuming unity sticking probability) and for the Nb(110) face this is one third the available sites. Hence it seems likely that this change in slope reflects the same process as is responsible for the surface potential change.

The slope of the kinetic graph decreases above this exposure showing that the sticking probability this surface is less than on the clean surface. Pantel, R. et al were able to observe LEED patterns from these low exposure structures and suggested some oxide over-layers that would be compatible with the LEED results. The structures that they proposed were basically NbO layers arranged epitaxially on the metal substrate (see Chapter 3). In this respect, their results confirmed the presence of NbO at low exposures.

SUMMARY

A model for the adsorption of oxygen on niobium has been proposed. A double layer of NbO is formed initially the outer layer of which is then further oxidised to Nb_2O_5 . A field gradient can be observed across the oxide film at passivation caused by negative charges at the oxide-vacuum interface. A change in the mechanism of oxygen adsorption occurs at an exposure of $0.3 - 0.4 \times 10^{19} \text{ O.m}^{-2}$.

CHAPTER 8

ULTRA VIOLET PHOTOELECTRON SPECTROSCOPY

This chapter describes and presents those spectra obtained from an ultra violet photoelectron spectroscopy (UPS) study of the initial oxidation of niobium. The radiations used were primarily He I and He II. Clean and oxygen exposed surfaces were studied and comparisons made with published band structures and previous UPS work.

8.1 UPS OF CLEAN POLYCRYSTALLINE NIOBIUM FOIL

UPS spectra were obtained from Spn. 2 using He I, He II and Ar I photons. The method of mounting specimen foils and of cleaning them were exactly the same as for XPS work described above. The UPS work in fact followed directly the XPS data of Spn. 2. The surface contamination on Spn. 2 was 5% for oxygen and 26% for carbon (expressed as percentage of a full monolayer).

A selection of valence band spectra from clean niobium surfaces taken over a range of photon energies are shown in Fig. 8.1. An unclean surface was characterised by emission below about 4 eV BE and low Fermi level (E_F) intensity.

In Fig. 8.2 He I spectra obtained by Miller, J.N. et al (1978) is shown together with a theoretical band structure calculated by Louie, S.G. et al (1976).

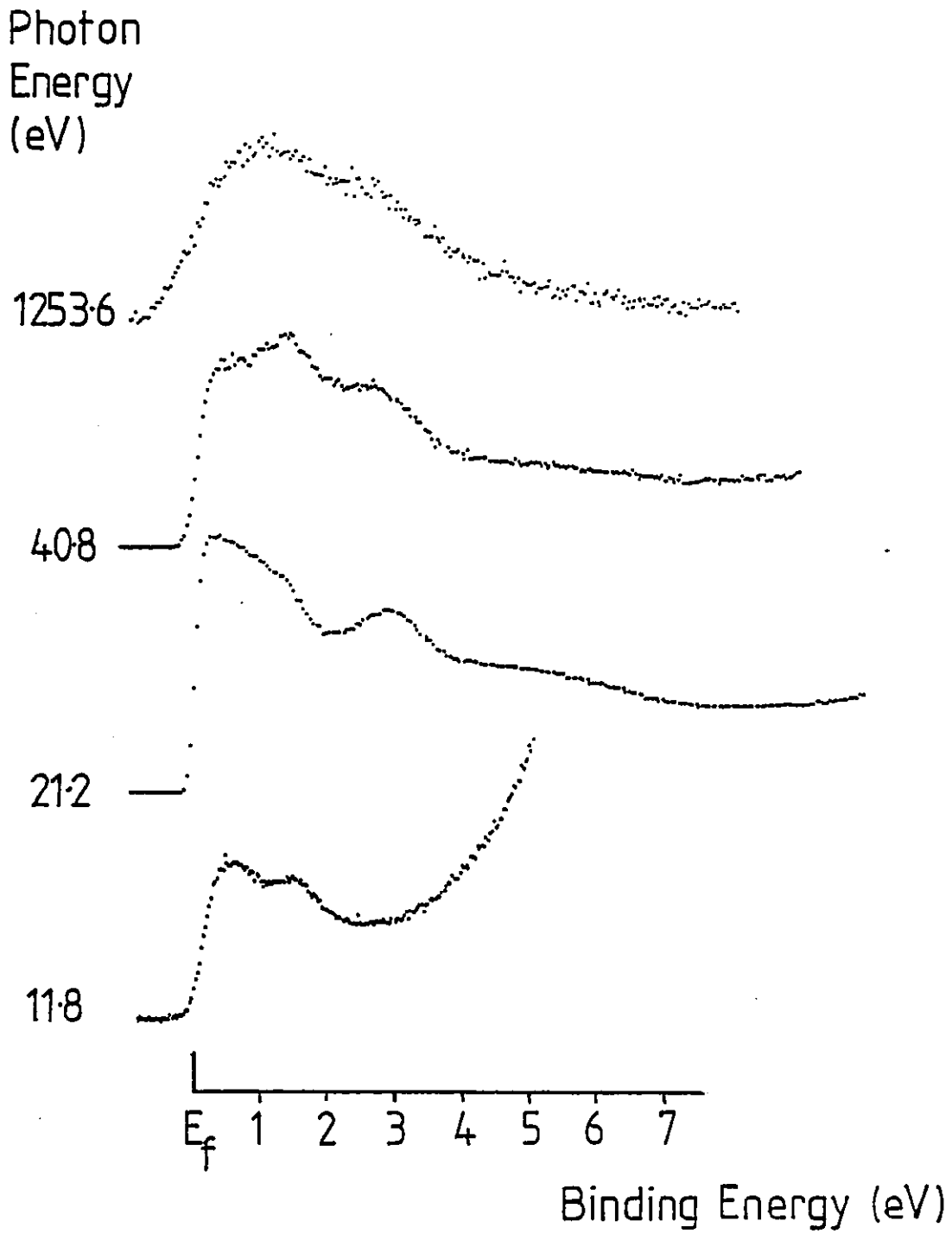


Fig. 8.1

The photoelectron spectra using photon energies of up to 1253.6 eV of the valence band of clean niobium.

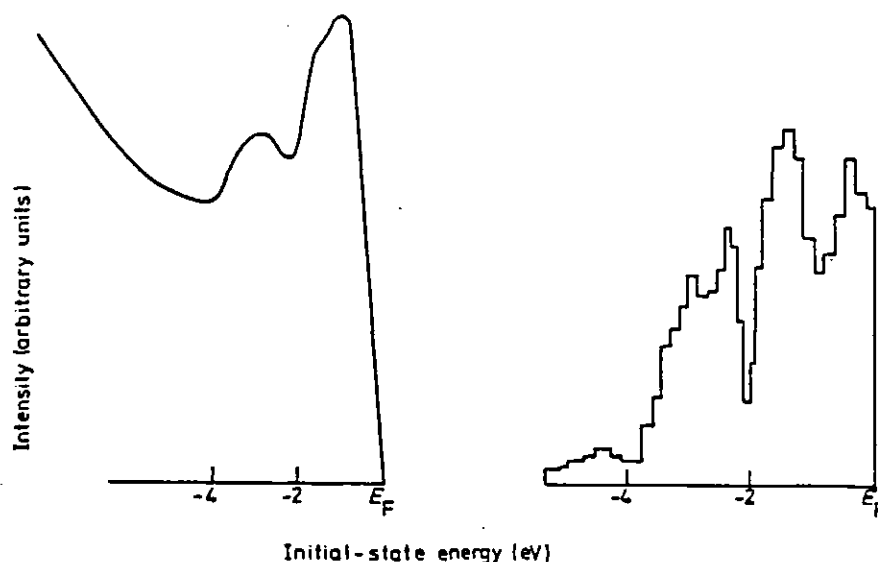


Fig. 8.2 He I UPS spectra from niobium from Miller, J.N. et al (1978) and a theoretical bulk density of states calculated by Louie, S.G. et al (1976)

It can be seen that the theoretical work is in good agreement with the spectra in Fig. 8.1. This is particularly true for the He II and Mg $K\alpha$ excited valence band spectra, as modulations in the spectra introduced by varying matrix elements (Chapter 2) are reduced at high final state kinetic energies.

The breakdown of orbital character in the band structure has been described by Elyashar, N. and Koelling, D.D. (1977). The deepest lying level at about 2.8 eV is an s-d admixture with only a slight p contribution; the second peak at 1.2 eV BE is a pure p-d mixture; and the peak very close to E_F is again a

p-d mixture with some f character.

Referring to Fig. 8.1, some changes between spectra obtained at different photon energies can be discerned. At 21.2 eV the gap between the first two bands (E_F and 1.2 eV) is not clearly resolved, whereas at 11.8 eV it is well defined. The deep level at 2.8 eV BE is not observed at all in the 11.8 eV spectrum, but is an obvious feature of the spectra at higher energies.

The absence of a peak, using photon energies of 11.8 eV at E_F , has also been noted by Lindau, I. and Spicer, W.E. (1974). Using photon energies of 10.2 eV these authors clearly observed the peak. This rapid modulation in the strength of the emission over a small photon energy range was interpreted as evidence for the operation of bulk optical selection rules.

The cause of the poor resolution of the gap at 1 eV/BE at He I and He II energies compared to at Ar I energies may be explained by the work of Louie, S.G. et al (1977). These authors studied theoretically the electronic states at an ideal Nb(100) surface. Their findings indicate that the local density of states (LDOS) at the surface is considerably different to the bulk. Their results are reproduced below in Fig. 8.3.

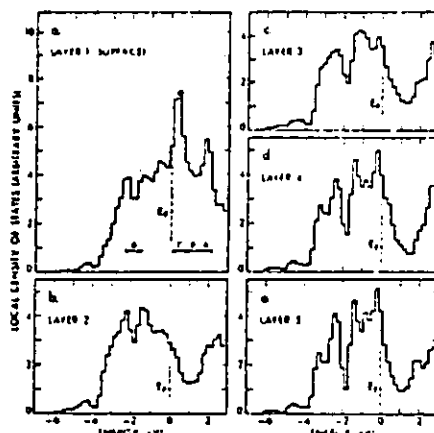


Fig. 8.3 The theoretical layer by layer density of states according to Louie, S.G. et al (1977) for an ideal Nb(100) surface.

The uppermost surface layers appear to have local density of states structures which do not contain sharp features. The spectra may be understood if the data obtained with 21.2 eV and 40.8 eV photons contains larger contributions from the surface layers than the 11.8 eV spectrum. Since the lower KE electrons will have a longer mean free path (perhaps twice as long) then an increased surface sensitivity for the He I spectrum may be expected.

Louie, S.G. et al (1977) claim that the lack of structure in the top few atomic layers is caused by occupied surface resonances and states and also partly owing to distortions of the bulk wave functions.

The information obtained on the clean polycrystalline niobium surfaces by UPS supports the theoretical studies of the band structure. A more thorough examination of the electronic structure of

niobium could be made using angle resolved UPS from single crystal specimens.

8.2 THE INITIAL OXIDATION OF NIOBIUM STUDIED BY ULTRA VIOLET PHOTOELECTRON SPECTROSCOPY

Clean niobium surfaces were prepared in the same manner as for the XPS studies. Oxygen dosing was accomplished in exactly the same manner.

The He I (21.2 eV) spectra of oxygen exposed surfaces are shown in Fig. 8.4. Exposures of 0, 0.72, 1.4, 2.16, 72 and 720 x 10¹⁹ O.m⁻² are presented. It can be seen that a sharp reduction in emission close to the Fermi level; the disappearance of the gap at 2.3 eV and the appearance of O 2p level are associated with small oxygen exposures. The reduction in emission near E_F for exposures of only 0.72 x 10¹⁹ O.m⁻² suggests that this emission may be due to a surface state or resonance. The general reduction in resolution of the Nb 4d band indicates that, even for small exposures, the electronic environment of surface Nb atoms is being perturbed.

The dominant peak in the spectra is the O 2p feature centred at low exposures on a BE of 5.8 ± 0.1 eV. At an exposure of 0.72 x 10¹⁹ O.m⁻² the O 2p band is a narrow single peak asymmetric towards higher BE. The spectrum is similar to that obtained from the high temperature annealed NbO surface, the He I spectrum of which is shown later in Fig. 8.7. At 1.4 x 10¹⁹ O.m⁻² the general features evident at 0.72 x 10¹⁹ O.m⁻² are more obvious, with the Nb 4d band maximum now at 1.2 eV BE instead of at E_F . The O 2p band continues to grow with

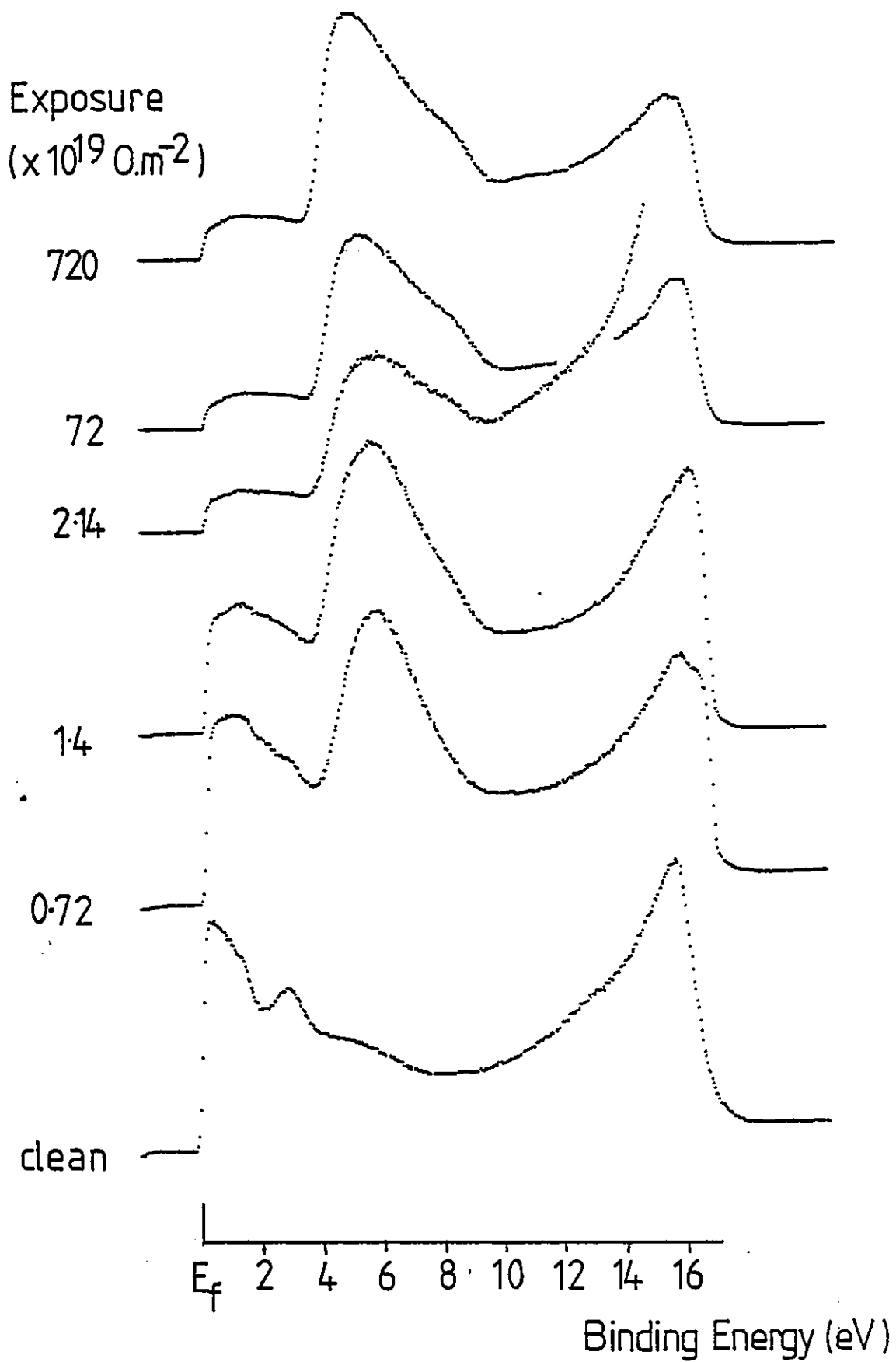


Fig. 8.4 The He I photoelectron spectra of clean niobium exposed to oxygen in the exposure regime up to $720 \times 10^{19} \text{ O.m}^{-2}$.

exposure and a definite shoulder towards high BE develops. The peak maximum remains at 5.8 eV BE.

At an exposure of $2.16 \times 10^{19} \text{ O.m}^{-2}$ the shoulder on the main O 2p peak is sufficiently strong that an estimate of its BE may be made. The value is $8.0 \pm 0.2 \text{ eV}$. Emission from the Nb 4d band continues to decrease and most of the structure is lost. A small but sharply defined Fermi level reflects the presence of underlying metallic niobium. It is worth noting that the inelastic background reaches a maximum relative intensity at this exposure, since the O 1s core level peak has a maximum FWHM in this exposure range, see Sec. 6.4.

At an exposure of $72 \times 10^{19} \text{ O.m}^{-2}$ the O 2p band is very clearly resolved into two components, with BE's of $5.4 \pm 0.1 \text{ eV}$ and $8.0 \pm 0.2 \text{ eV}$ respectively. The overall peak width is now quite large, at nearly 4 eV, and the secondary electron background has reduced in intensity. From this exposure onwards the only changes are a continuous increase in O 2p band intensity, a shift in the peak to lower BE and a reduction in the Nb 4d band emission.

In order to complement this He I data, He II (40.8 eV) spectra were also taken of exactly the same surfaces as described above for He I. They are shown in Fig. 8.5. The spectra are particularly interesting for two reasons.

Firstly, the O 2p band shows the same general behaviour at 40.8 eV photon energy as at 21.2 eV, except that the high BE shoulder becomes a feature of equal

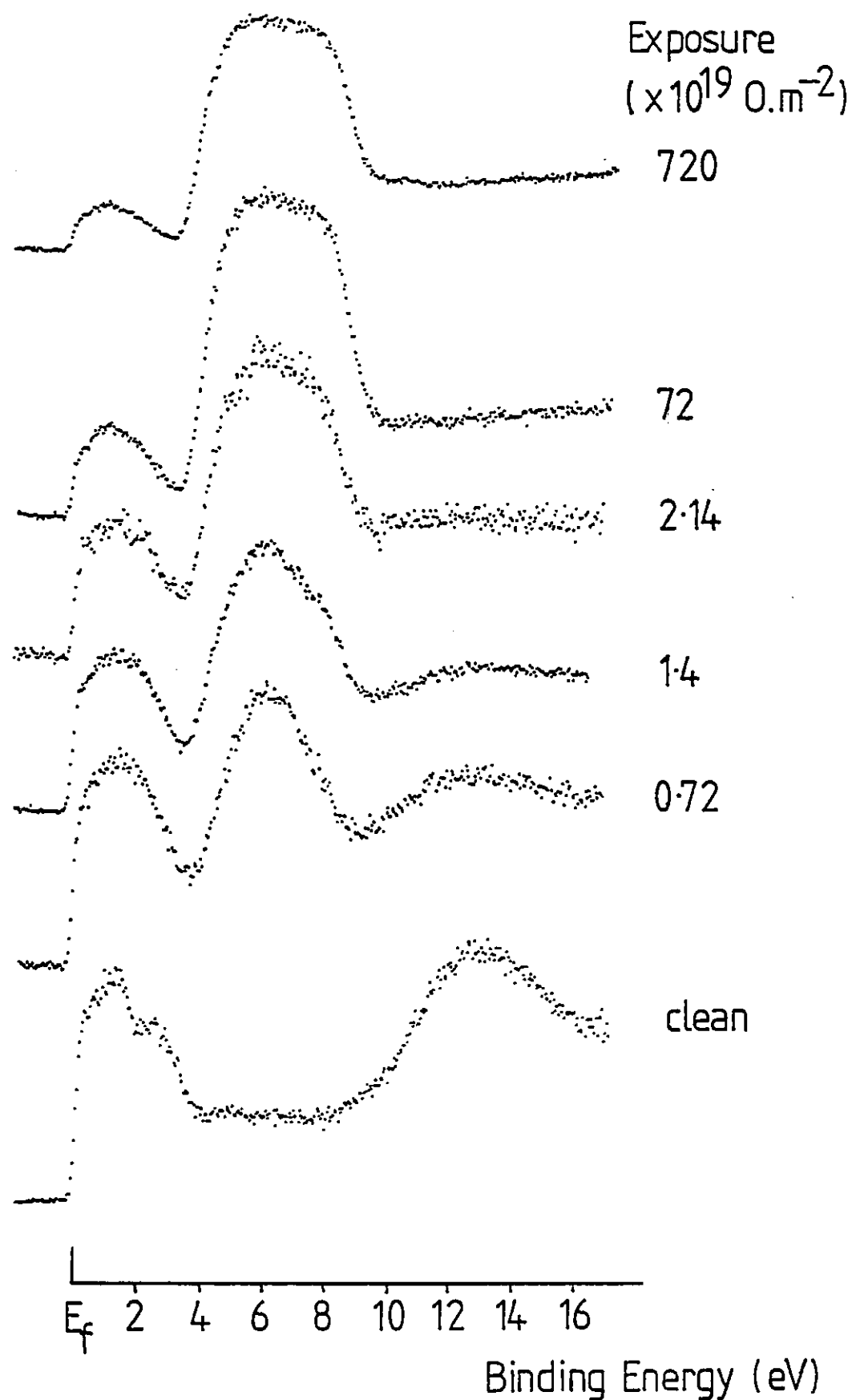


Fig. 8.5

The He II photoelectron spectra of clean niobium exposed to oxygen in the exposure regime up to $720 \times 10^{19} \text{ O.m}^{-2}$.

intensity to the 5.8 eV BE peak. This results in a transition from a single narrow peak at low exposures to a flat topped structure at an exposure of $720 \times 10^{19} \text{ O.m}^{-2}$. The peak maximum appear to be exactly the same as at He I photon energies.

Secondly, a very broad feature at an apparent BE of 15-17 eV is a prominent emission from the clean surface, but by an exposure of only $2.16 \times 10^{19} \text{ O.m}^{-2}$ it has been completely eliminated. This peak is due to low energy $\text{N}_{2,3}\text{N}_{4,5}\text{N}_{4,5}$ Auger electrons with a KE of about 26 eV, caused by ionisation of the 4p level (BE 34 eV) followed by emission of a 4d electron as the 4p hole is filled. This peak and its great sensitivity to adsorbates has also been observed by Usami, S. et al (1977).

For completeness the effect of oxygen adsorption upon the Ar I photoemission spectrum has been recorded. It is shown, together with the only other published Ar I spectrum of 'clean' Nb, in Fig. 8.6. The alternative spectrum is from Lindau, I. and Spicer, W.E. (1974), from an electron beam evaporated thin Nb film. It is clear that their spectrum is not representative of clean niobium.

The leading peak in the clean Ar I spectrum is sensitive to adsorbates, and suggests that a proper interpretation of photoemission spectra should include more than just volume photoemission alone. This conclusion can be reached since at these low kinetic energies, around 10 eV, the mean free path will be about 2 nm. Thus the surface contribution to the spectrum

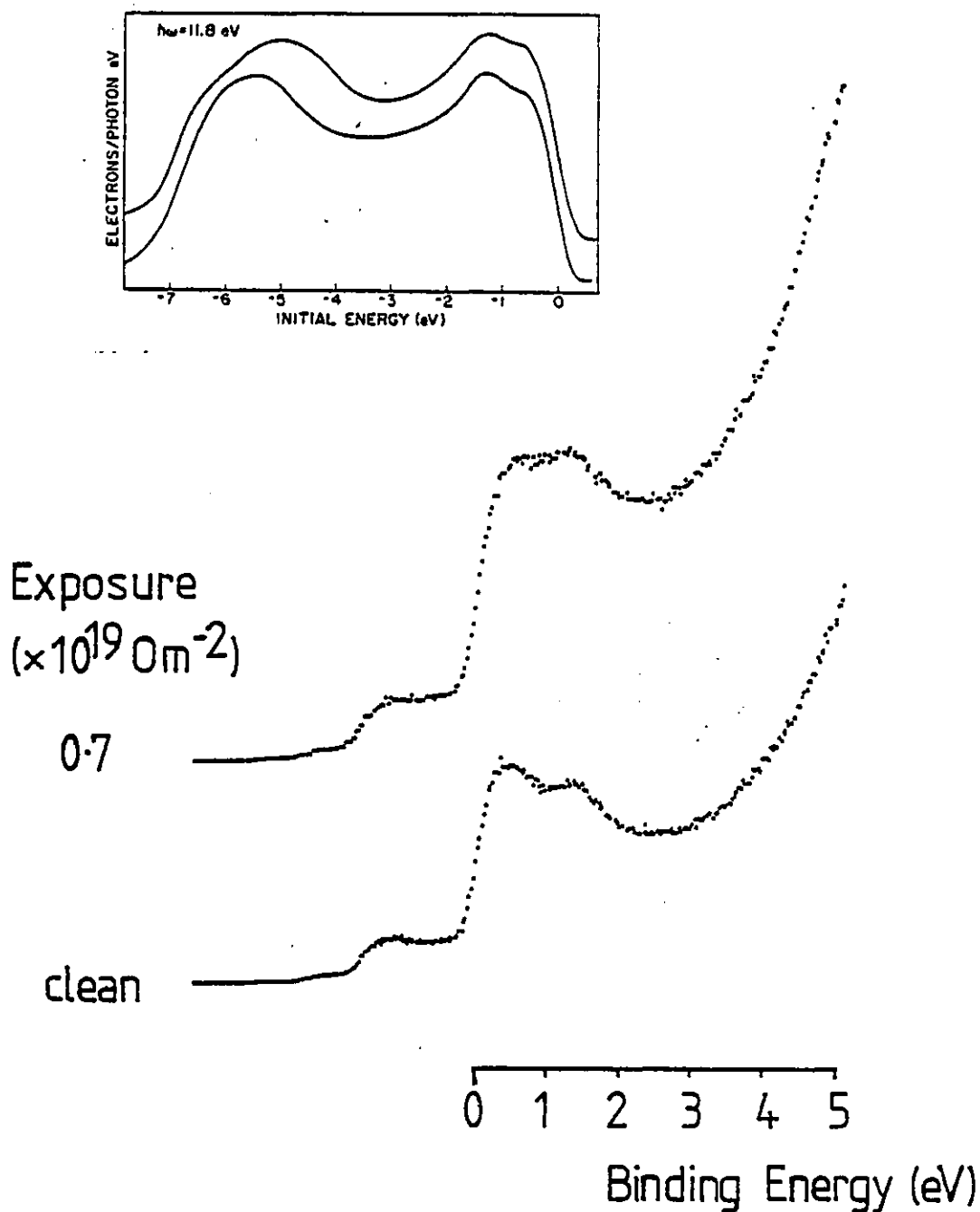


Fig. 8.6

Ultra violet photoelectron spectra obtained using Ar I radiation of clean and oxygen exposed niobium surfaces. The insert shows the spectrum of 'clean' niobium, as obtained by Lindau and Spicer (1974).

appears to be anomalously high, and it seems reasonable to invoke a contribution from the surface photoeffect (through the third term in Equation 2.3) especially as the photon energy (11.8 eV) is very close to the surface plasmon energy (12.5 eV).

8.3 THE UPS OF THE NbO AND Nb₂O₅ SURFACES

The He I spectra of the NbO, high temperature annealed surface, and the Nb₂O₅, gross oxidation surface were taken in order to complement the spectra produced by low oxygen exposures. The spectra are presented in Fig. 8.7.

The spectra suggest a similarity between room temperature oxygen exposed surfaces, Fig. 8.4, and those produced by high temperature segregation from the bulk.

The grossly oxidised surface shows as expected, that the density of states near E_F is low. The small emission that is observed is probably due to underlying metal. An interpretation of the emission below about 4 eV BE would be of dubious value since contamination contributes to the spectrum in this region.

8.4 INTERPRETATION OF THE UPS SPECTRA

The He I and He II spectra from all of the surfaces, show the two distinct regions of emission. One has been assigned to Nb 4d electron states and the other to O 2p derived levels.

The XPS results indicate that oxidation proceeds by the formation of a double layer of NbO followed by further oxidation of the outermost layer to Nb₂O₅. The final state is therefore one layer of pentoxide above

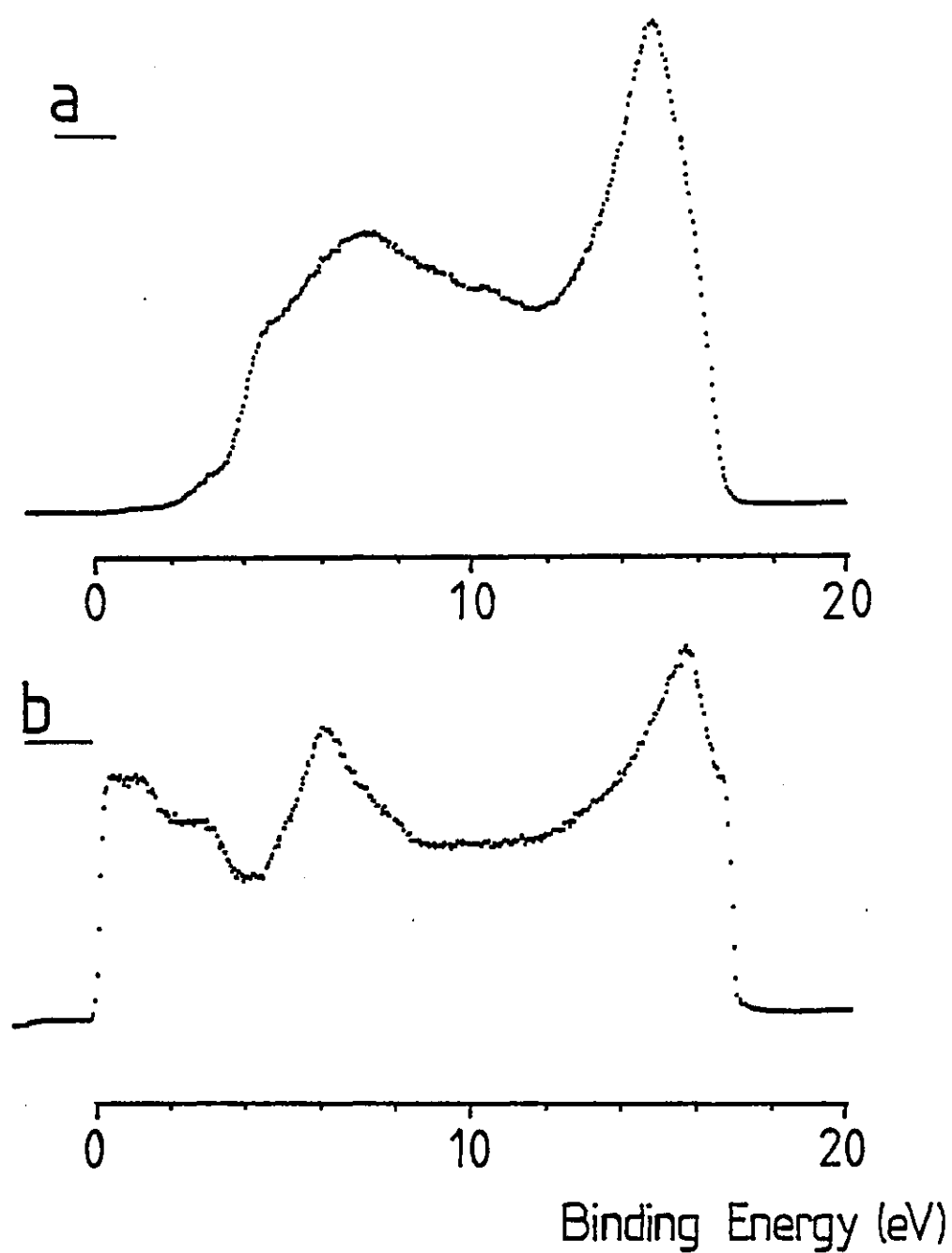


Fig. 8.7 Ultra violet photoelectron spectra obtained using He I radiation of a) the Nb_2O_5 surface and b) the NbO surface.

another layer of monoxide. The UPS data distinguishes a state at an exposure of $0.72 \times 10^{19} \text{ O.m}^{-2}$ which is characterised by a single peak at 5.0 eV BE, followed at higher exposures, $2.14 \times 10^{19} \text{ O.m}^{-2}$, by the appearance of a second peak at 8.0 eV BE.

This behaviour is interpreted as indicating the formation of a two-dimensional adsorption layer followed by a three-dimensional structure. The two bonding levels observed in both He I and He II UPS spectra at high exposure is consistent with that of many bulk oxides. These include the following three: TiO_2 , RuO_2 and IrO_2 whose high resolution valence band spectra are presented in Fig. 8.8, taken from Riga, J. et al (1977).

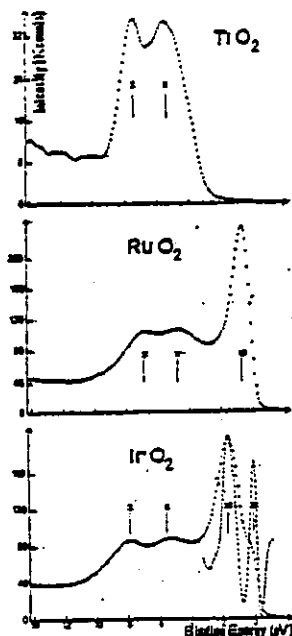


Fig. 8.8 X-ray photoelectron spectra of the oxides TiO_2 , RuO_2 and IrO_2 showing two bands associated with the O 2p level between 4 and 8 eV binding energy.

Two bands, labelled I and II, are observed of approximately equal intensity centred on 7 eV BE. For RuO_2 and IrO_2 the remaining metal d electrons occupy bands close to E_F . The deepest O 2p band, band I, is assigned by Riga, J. et al (1977) to σ type orbitals derived from suitable metal and oxygen atomic orbitals. Band II is composed of π type M-O orbitals. A similar description of electronic bands in NbO_2 , MoO_2 and RuO_2 has recently been given by Beatham, N. and Orchard, A.F. (1979). It is interesting to note that the XPS valence band spectrum for the Nb_2O_5 surface also displays these two levels in the O 2p band.

Similar results to the UPS spectra in this study have been obtained by Gewinner, G. et al (1978) during the low temperature oxidation of the Cr(111) surface; by Fuggle, J.C. during the oxidation of evaporated Mg films; by Brundle, C.R. (1977) on oxidised iron films and by Johansson, L.J. et al (1977 and Private Communication) on evaporated Ti films. All of these studies produced low oxygen exposures a narrow O 2p band which at higher exposures transformed into a broader band with two or more components. The He I spectra of Fuggle, J.C. (1977) are strikingly similar to the present results. The saturated surface gives a well defined peak at 5.0 eV BE with a shoulder at about 8.0 eV BE, the relative intensities of which are similar to the Nb-O system. Fuggle also notes that these two peaks are at equal intensity at He II energies. It is worth pointing out that since the final oxide formed

upon Mg is MgO, this double peaked result must be a characteristic of bulk MgO, as predicted by band structure calculations.

Theoretical calculations of the band structure of NbO have been carried out by Gubanov, V.A. et al (1978) which predict a broad double peaked structure to the O 2p band, confirmed by UPS measurements.

It appears therefore that a double peak in the O 2p band is consistent with both NbO and Nb₂O₅. The narrow single peak appears to be best assigned to isolated oxygen atoms incorporated within the first Nb layer and to two-dimensional surface monolayers in which the broad O 2p bands of bulk oxides do not form. This approach is in contrast to that of Miller, J.N. et al (1978) in their He II study of the room temperature oxidation of niobium foil. Their results are presented below, in Fig. 8.9

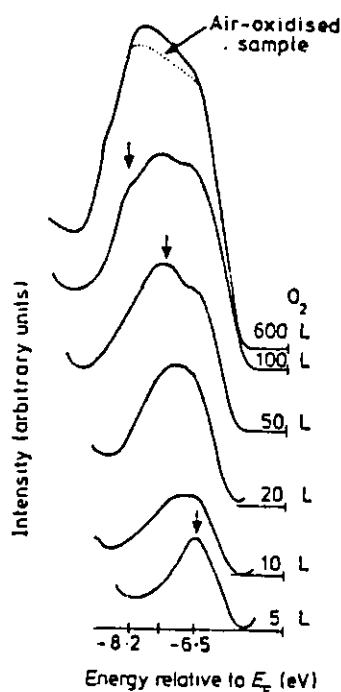


Fig. 8.9 The UPS spectra of Nb oxidation taken from Miller, J.N. et al (1978)

The formation of a broad band of O 2p states is in line with the present results. However, at 50 L O₂ (36×10^{19} O.m⁻²) the deepest lying peak becomes the most intense and at 100 L O₂ (72×10^{19} O.m⁻²) a third peak appears. At 600 L O₂ (430×10^{19} O.m⁻²) a spectrum similar to the air exposed sample was obtained. Their interpretation of these three peaks (marked by arrows) assumes that each peak may be assigned to a particular oxide. Fortunately for this simplistic approach niobium does have three well defined oxides - monoxide, dioxide and pentoxide. The presence of three peaks in the UPS spectrum was therefore correlated with the three oxides by Miller, J.N. et al (1978).

The similarity of the air exposed sample to the 600 L O₂ (430×10^{19} O.m⁻²) spectrum probably indicates that this discrepancy could be caused by water contamination of the oxide film. The water may have been present either in the oxygen supply or generated by an ion pump or Ti getter film upon exposure to oxygen.

8.5 THE BEHAVIOUR OF THE N_{2,3}VV Nb AUGER PEAK

In addition to the photoelectron spectra produced by the incident u.v. photon flux, an Auger transition with some interesting properties is observed. This Auger electron feature has a KE of about 26 eV and is an N_{2,3}N_{4,5}N_{4,5} transition. It is only observed in He II spectra since ionisation of the 4p (N_{2,3}) level must first occur (the BE is 33 eV). The remarkable feature of this emission is that it is reduced to almost negligible intensity after an exposure of only

$2.2 \times 10^{19} \text{ O.m}^{-2}$.

This behaviour has also been noted by Usami, S. et al (1976) in an AES-LEED study of the Nb(100) surface. These authors observed that the peak disappeared after an exposure of $6 \times 10^{19} \text{ O.m}^{-2}$. No interpretation was presented, but a speculative explanation is given below.

There are two mechanisms which acting together may explain the super surface sensitivity of this particular electron emission feature of niobium:

1. The first supposes that this Auger transition only occurs with reasonable probability from surface atoms.
2. The second mechanism involves chemical effects modulating the transition probability.

Mechanism 1.

Muller, J.E. et al (1978) have described theoretically the density of available state up to 60 eV above the Fermi level for the 4d transition metals. In general these authors find that peaks in the unoccupied density of states occur (just above E_F 1) and at energies of 20 eV and 40 e V. These peaks correspond to 4d, 5p and 5f orbital energies. A valley in the density of states is found between these peaks and in particular at energies around 30 eV. These features were also found experimentally by x-ray absorption measurements.

If this minimum does exist then the probability for promotion of any electron to an energy near 26 eV will be reduced. This is equivalent to matrix effects

in photoemission. However, in the surface layer an electron may be promoted to an energy of 26 eV and be emitted in the vacuum direction without any requirement to satisfy constraints set by bulk band structures.

It is possible that this $N_{2,3}N_{4,5}N_{4,5}$ Auger transition is influenced by these effects, such that an anomalously large fraction of the Auger yield is emitted from surface atoms.

Mechanism 2.

It has recently been shown by Rao, C.N.R. et al (1980) that the transition probability for Auger electrons involving valence levels depends upon the number of electrons in the valence band. These authors have shown that, for the first row transition metals and their oxides, the intensity of the LVV Auger electron depends upon the number of valence electrons. In the present work it has been suggested that the relative intensities for the $M_{4,5}N_{2,3}V$ Auger peaks between the Nb_2O_5 and NbO/Nb features cannot be used quantitatively to estimate oxide thickness. This is because the fully oxidised Nb^{5+} ion formally has no remaining 4d electrons able to take part in the transition.

A similar mechanism may be taking place when the $N_{2,3}VV$ Auger peak observed in the He II spectrum is considered. As the valence band is both the second and third electron level involved in the transition the effects may be quite considerable.

The proposed mechanism for the extreme surface sensitivity of this Auger peak is as follows. Upon

oxygen adsorption to the first monolayer coverage (about an exposure of $0.72 \times 10^{19} \text{ O.m}^{-2}$) the outer layer of Nb atoms have some of their electrons removed by the oxygen atoms. This brings about a large reduction in the Auger transition probability through mechanism 2. Mechanism 1, complemented by oxygen scattering in the absorbed layer prevents a significant Auger yield from the underlying niobium atoms.

In combination these two effects appear to explain the high surface sensitivity of this Auger transition. Similar surface sensitivity for very low energy Auger electrons (nearly always involving valence levels) has been observed for other systems. The adsorption on a monolayer of Cs onto Mo eliminates the 29 eV Auger electron (Thomas, S. and Haas, T.W., 1971).

If the above discussion is correct then the intensity of this low energy Auger electron is proportional to the number of unoxidised niobium atoms in the uppermost layer. This information shows that about 20% of the surface sites remain oxygen free after an exposure of $0.72 \times 10^{19} \text{ O.m}^{-2}$. By comparison the Nb 3d surface plasmon falls in intensity by only about 50% at this exposure. It can therefore be concluded that the double layer of NbO, described in Chapter 7, is required to completely eliminate the surface plasmon. This stage is reached at exposures of $3-4 \times 10^{19} \text{ O.m}^{-2}$.

SUMMARY

The UPS work presented above illustrates the

amount of information that can be obtained on the surface electronic structure of materials. This is especially true if XPS measurements are performed on the same system.

It is concluded that a single O 2p peak indicates two-dimensional oxides or isolated oxygen ions on a surface. The formation of a second deeper level indicates that three-dimensional or 'bulk' oxide structures have formed. Low energy Auger electrons have been observed in the He II spectra. These electrons are very surface sensitive and can be correlated with oxygen free areas of the niobium surface.

CHAPTER 9

THE MECHANISMS OF OXYGEN ADSORPTION ON NIOBIUM AND A COMPARISON WITH OTHER METALS

This chapter presents a description of the oxide structures formed when oxygen adsorbs on niobium at room temperatures and at low pressures.

9.1 THE NATURE OF OXYGEN ADSORPTION ON NIOBIUM AT ROOM TEMPERATURE AND LOW PRESSURES.

The basic spectra of chapter 5 have been presented; processed to provide derived data in chapter 6; individual features of the spectra have been discussed in chapter 7 and the UPS data presented in chapter 8. This material is now brought together to present, in terms of both structure and kinetics, the mechanism of the adsorption of oxygen on niobium.

For a particular microarea of the surface the reaction takes place in several well defined stages.

1. Initial incorporation of oxygen atoms into the top surface layer to form an ordered overlayer (up to an exposure of $0.4 - 0.5 \times 10^{19} \text{ O.m}^{-2}$). Formation of a second overlayer structure with double the oxygen concentration then takes place (up to an exposure of $1 \times 10^{19} \text{ O.m}^{-2}$).
2. This surface then reacts with more oxygen to produce a second oxide layer of essentially NbO (up to an exposure of $3 - 5 \times 10^{19} \text{ O.m}^{-2}$).
3. A third gradual reaction then occurs to form

a Nb_2O_5 monolayer. The resulting duplex oxide layer - $\text{NbO}/\text{Nb}_2\text{O}_5$ - is stable to further oxygen exposure at room temperature and low pressures.

The above series of events probably takes place at separate rates for different crystal planes and at defective surface sites resulting in an overlap of the various phases of the reaction for individual parts of the surface. Thus Nb_2O_5 photoelectron peaks are observed at a stage when the NbO double layer is still building up. However, the sequence of events probably holds true for an individual part of the surface. These various stages are discussed more fully below.

9.2 ADSORPTION IN THE MONOLAYER REGION.

For extremely low exposures of oxygen, adsorption takes place randomly leading to a disordered overlayer. Incorporation occurs as shown by the surface potential measurements of Pantel, R. et al (1977). At higher surface coverages a relatively open ordered structure based upon a layer of NbO forms. This gives a $c(2 \times 2)$ LEED pattern on Nb(100), (Usami, S. et al 1977), and a complex pattern on Nb(110), (Pantel, R. et al 1977). The structure is formed up to exposures of about $0.4 - 0.5 \times 10^{19} \text{ O.m}^{-2}$ after which a more compact overlayer, still based upon NbO, is formed. Usami, S. et al (1977) observed the gradual fading of the $c(2 \times 2)$ spots on Nb(100) and their extinction by about $4 \times 10^{19} \text{ O.m}^{-2}$. Pantel, R. et al (1977) for Nb(110) observed the formation of a surface structure with double the

original periodicity in one lattice dimension. The O 1s BE for these monolayers of NbO on Nb has a characteristically low value, while the O Auger peak has a high KE. The O 2p region observed by UPS is represented by only one band centred at a BE of about 5 eV. Chemically shifted Nb 3d emission is observed which is associated with atoms in an environment similar to NbO. In the kinetic interpretation of the O 1s peak areas at less than $1 \times 10^{19} \text{ O.m}^{-2}$, a kink in the curve is observed at exposures of $0.4 - 0.5 \times 10^{19} \text{ O.m}^{-2}$ which agrees with the observed LEED/surface potential measurements of Pantel, R. et al (1977).

Possible structures for the first and second oxygen overlayers are shown in Figure 9.1. The building up of the second, more dense oxygen overlayer is associated, on Nb(110), with a return to the original "clean surface" surface potential. Pantel, R. et al (1977) suggested that this implies that the original incorporated oxygen atoms returned to the same plane as the uppermost Nb atoms so as to present no net dipole. However, a puckered structure could also produce a surface with a surface potential the same as the clean metal.

The close relationship between the two low exposure surface layers and low index faces of NbO shows that in the case of niobium there is no separate "chemisorption" phase before oxide formation. Indeed since the bulk oxides are the most stable arrangements for combinations of Nb and O atoms it may not be so

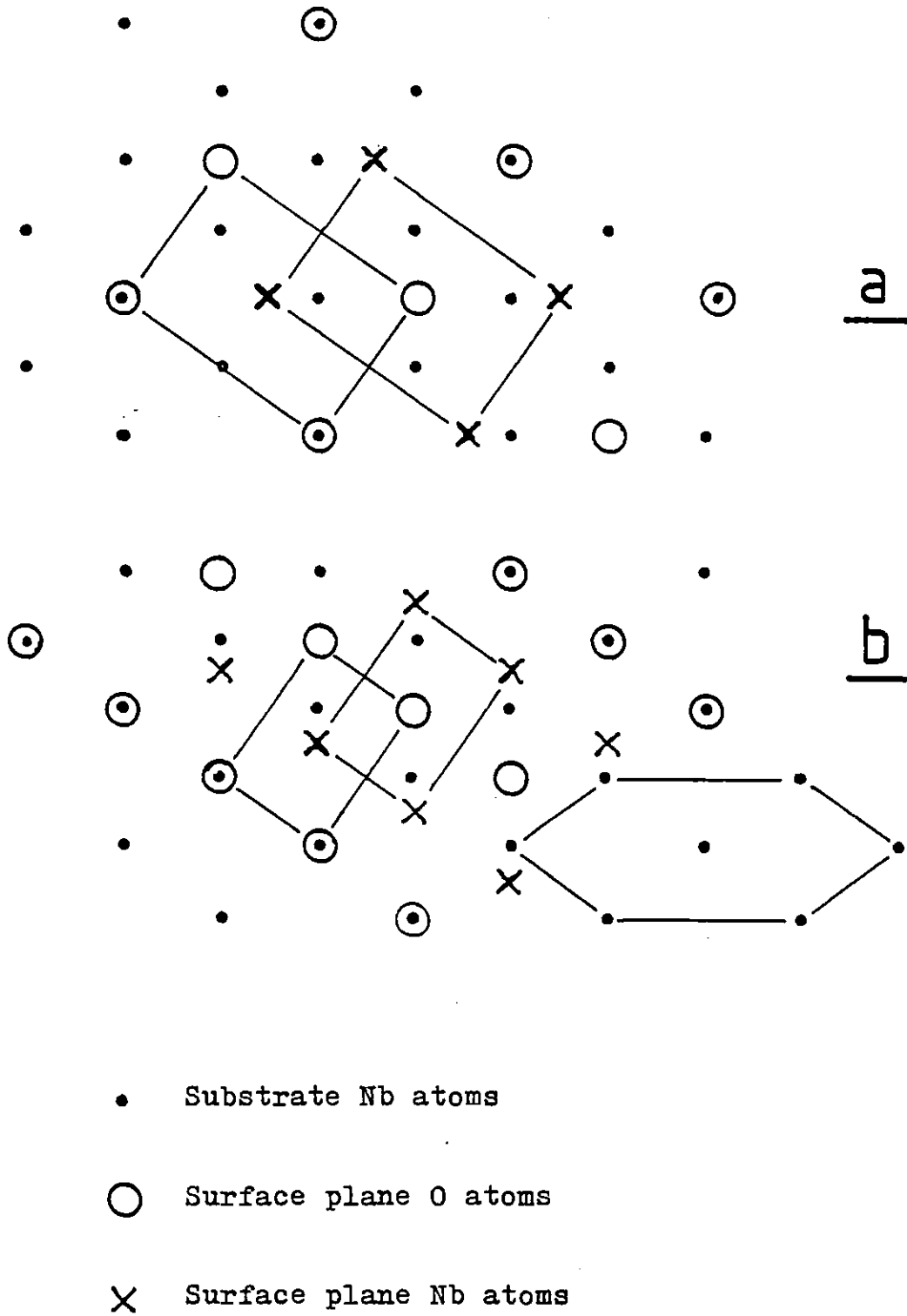


Fig. 9.1 a) Open oxygen surface structure and
 b) a compact oxygen structure
 according to Pantel (1977).

surprising that two dimensional surface phases are based upon the bulk oxide structures. This is particularly true for those metals, such as niobium, which have oxides with high heats of formation. In other metal-oxygen systems lower oxides may be difficult to observe by XPS owing to line width or other spectroscopic problems, and are, as a result, not considered. Thus intermediate oxides, (represented by small chemical shifts) formed during the "chemisorption" phase of an oxidation, may be quite common but generally overlooked. This is particularly true of reactive metal oxidation e.g. Ti, Zr, Mo, Cr, Al, etc.

In a study of the initial oxidation of polycrystalline aluminium Carley, A.F. and Roberts, M.W. (1978) showed that a chemically shifted Al 2p peak, with a chemical shift intermediate between Al metal and Al_2O_3 , was formed upon the chemisorption of oxygen. This intermediate state has also been described by Flodström, S.A. et al (1976). In addition to this spectroscopic data, work function measurements by Roberts, M.W. and Wells B.R. (1969) on aluminium are similar to the work of Pantel, R. et al (1977). In both studies an initial lowering of the work function (or equivalently the surface potential) occurred followed by a work function increase as the oxidation proceeds. Furthermore both sets of data were interpreted in terms of oxygen incorporation into the metal lattice.

Carley, A.F. and Roberts, M.W. (1978) considered that the Al 2p shift intermediate between Al and Al_2O_3

was associated with a Al-O surface compound of low stoichiometry formed by place exchange, which transformed to Al_2O_3 at higher oxygen exposures. In this respect the behaviour of niobium and aluminium are similar.

9.3 FORMATION OF THE NbO DOUBLE LAYER

Following the formation of the dense NbO monolayer structure the surface potential measurements of Pantel, R. et al (1977) show a linear increase with exposure up to about $3 - 4 \times 10^{19} \text{ O.m}^{-2}$. During this phase XPS measurements of this study show that the oxide thickness increases to around 0.45 nm. The Nb 3d (oxide) spectra are dominated by emission from NbO type atoms. The O 2p region studied by UPS shows the appearance of a second band at a binding energy of 8eV. The intensities for the Nb 3d (total), Nb 3d (oxide), Nb Auger and Nb 3d surface plasmons produce their greatest changes as a function of exposure up to an exposure of about $4 \times 10^{19} \text{ O.m}^{-2}$.

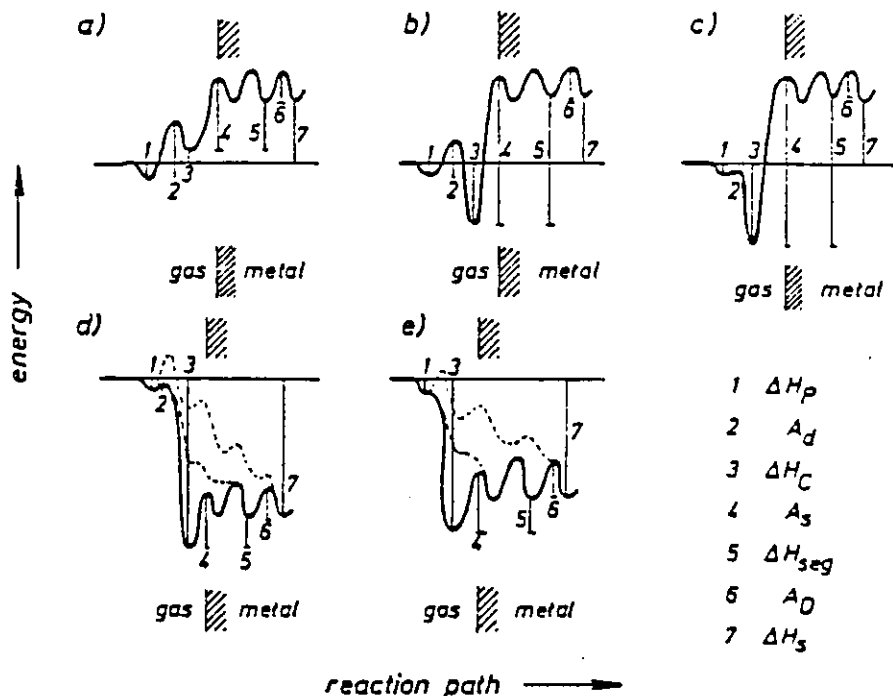
Pantel, R. et al (1977) were able to demonstrate that the second oxygen layer was built up, irrespective of pressure, in five minutes. These authors considered the second oxygen layer to be a chemisorption layer formed on top of the first complete oxygen monolayer. The present results indicate that this second layer is in fact a further layer of NbO. The resulting overlayer is thus a double layer of NbO.

That the growth of the second NbO layer is independent of pressure, suggested to Pantel, R. et al that one of two possible mechanisms may be responsible

for the oxygen adsorption.

1. Catalytic sites for oxygen molecule dissociation exist which control the rate of the adsorption, or
2. Suitable sites for oxygen molecule adsorption are formed at a constant rate independent of the pressure. These sites are then immediately occupied by an oxygen atom.

The present results cannot directly support one or other of these two mechanisms. However, if the adsorption of oxygen results in double layer formation then a mechanism by which oxygen sorption takes place must be invoked. Diffusion by place exchange of oxygen into the second Nb layer would account for the known facts. Pantel, R. et al (1977) found that the process was temperature dependent suggesting that an activation energy was required. Diffusion of a thick oxide layer into bulk niobium readily occurs at less than 900 K (dull red heat) as observed in the preliminary cleaning routine, and reported by Reider, K.H. (1980) and Pasternack, R.A. and Evans, B. (1967). Oxygen atoms incorporation is quite widespread (Roberts, M.W. and Wells, B.R. 1967) and has even been reported for oxygen on Cu(100) at intermediate temperatures by Hofman, P. et al (1978). For a reactive metal incorporation or place exchange could well occur at lower temperatures, and provide the mechanism by which a double layer is formed.



where ΔH_P is the heat of molecular chemisorption.
 A_d is the activation energy for dissociation of gas molecules on the surface.
 ΔH_C is the heat of dissociative chemisorption.
 A_s is the activation energy for surface penetration.
 ΔH_{seg} is the heat of segregation.
 A_D is the activation energy of bulk diffusion.
 ΔH_s is the heat of solution.

Fig. 9.2 Schematic energy-reaction path diagrams for endothermal systems (a) - (c), and exothermal systems (d) and (e).

Metal	$\Delta H_s/A_D$
Ti, Zr, Hf	- 1.7
V, Nb, Ta	- 1.3
Mo, W	+ 1.0
Re, Fe, Ni	+ 0.4

Table 9.1 Ratio of heat of solution H_s to the activation energy of bulk diffusion for a selection of metals (Fromm and Mayer 1978).

If the mechanism is temperature dependent then it could be tested by experiments at liquid nitrogen temperatures. Although this has not been done in the present work, Fromm, E. and Mayer, O. (1978) have found that the amount of oxygen adsorbed on large area clean, niobium films is between 3 - 4 times less at 77 K than at 300 K.

A diagram of the possible states involved in a gas-metal reaction for the case of a reactive metal is presented in Fig. 9.2, one of five such diagrams suggested by Fromm, E, and Mayer, O (1978). These authors defined a reactive system as one in which the exothermic heat of solution ($\frac{1}{2} \text{O}_2 (\text{gas}) \rightarrow \text{O}_{(\text{metal})}$) is greater than the activation energy for bulk diffusion: $\Delta H_s/A_D > 1$. The Nb - O system has a particularly high $\Delta H/A_D$ ratio of around -3.5. Table 9.1, presents some representative values for some selected gas-metal systems.

On the basis of this thermodynamic approach alone, the oxidation of niobium should continue indefinitely since it is energetically favourable. That a continuous reaction with oxygen does not occur shows that kinetic factors limit the oxidation process.

At low oxygen exposures $0.5 \times 10^{19} \text{ O.m}^{-2}$, it is apparent that oxygen atom incorporation into the first layer of niobium atoms takes place. This process creates an open, NbO related monolayer structure and is characterised by a surface dipole. This is a particularly reactive configuration since it involves exposing niobium

ions to incoming oxygen molecules. This reactivity leads rapidly to the second, dense, NbO based monolayer completed around $1 \times 10^{19} \text{ O.m}^{-2}$. The formation of the second layer of NbO (at an exposure of $3 - 4 \times 10^{19} \text{ O.m}^{-2}$) then occurs by penetration of the underlying niobium layer by oxygen atoms from the first layer by place exchange. In a similar manner to the initial adsorption at $0.5 \times 10^{19} \text{ O.m}^{-2}$, the process creates reactive sites at the surface which are rapidly occupied by oxygen atoms. Thus a second NbO layer may be built up, with the rate limiting step being the penetration of oxygen atoms into the second niobium layer, as shown in Fig. 9.3. For a third layer of NbO to be formed, oxygen must penetrate from the second layer creating oxygen deficient sites. As these sites in the second layer are not in direct contact with the gas phase, they are not filled rapidly by oxygen atoms and the reaction fails to proceed.

The formation of a double layer of oxide, before the sticking probability falls to 10^{-2} , may be a widespread phenomena associated with metal oxidation at low pressures and at intermediate temperatures. Tantalum displays very similar adsorption behaviour to niobium (Fehrs, D.C. and Stickney, R.E. 1976) implying a reconstruction of the top two layers. Molybdenum also adsorbs two monolayers of oxygen at room temperatures (Bauer, E. and Poppa, H. 1979), as well as displaying a decrease in work function for initial exposures of oxygen. These two metals are

nearest neighbours of niobium in the periodic table, but double layer formation, by place exchange, may occur on other reactive metals. Some possible candidates are Fe (Brundle, C.R. 1977), Ni at 77K (Norton, P.R. et al 1977), Cr(100) on which a coverage of 2.3 monolayers was estimated by Peruchetti, J.C. et al, (1979); and Al evaporated films (Benndorf, C. et al 1977). There are many other systems where results are only described rather vaguely in terms of 'thin' oxide layers, or where the oxide layer is described as being between 0.6 and 0.8 nm thick. Unfortunately, in these cases the use of only thickness units, instead of a model involving the number and type of oxide layers, reduces the value of the work, as it is less easy to compare with other related systems.

In conclusion it can be stated that double layer formation is a likely stage in the oxidation of reactive metals, and that the process may be quite widespread.

9.4 THE SECONDARY PARTIAL OXIDATION OF THE NbO FILM TO Nb₂O₅.

Exposures of oxygen above $3 - 4 \times 10^{19} \text{ O.m}^{-2}$ present the NbO double layer with additional oxygen atoms. The O 1s peak area continues to increase demonstrating that further adsorption does occur. However, the Nb(oxide) area stabilises at this point. The characteristic of this regime is that a Nb 3d component at higher binding energy becomes significant. The Nb Auger peak also has a tail towards lower kinetic energy. These features are due to niobium pentoxide.

By $72 \times 10^{19} \text{ O.m}^{-2}$ the NbO and Nb₂O₅ emissions are of approximately equal intensities. This section deals with the possible mechanisms responsible for this behaviour.

The surface potential measurements of Pantel, R. et al detected the presence of physically adsorbed molecules on the surface following exposures greater than those required to form the NbO double layer. This was achieved by monitoring the drop in surface potential as soon as the supply of oxygen was stopped. Such behaviour, they concluded, was strong evidence for physically adsorbed oxygen species in equilibrium with the gas phase. Such species might well form a suitable precursor state for the oxidation of the NbO double layer since they have a comparatively long residence time on the surface. However, there is no evidence that such species are involved, and it is possible that oxygen molecules incident directly from the gas phase may play an important role.

Niobium pentoxide displays several crystal structures based upon a common basic unit. This is a NbO₆ octahedral cluster and oxide structures are constructed of units joined at edges and corners, but not at faces. Fig. 9.4, taken from Cotton and Wilkinson (1972) illustrates the general arrangement.

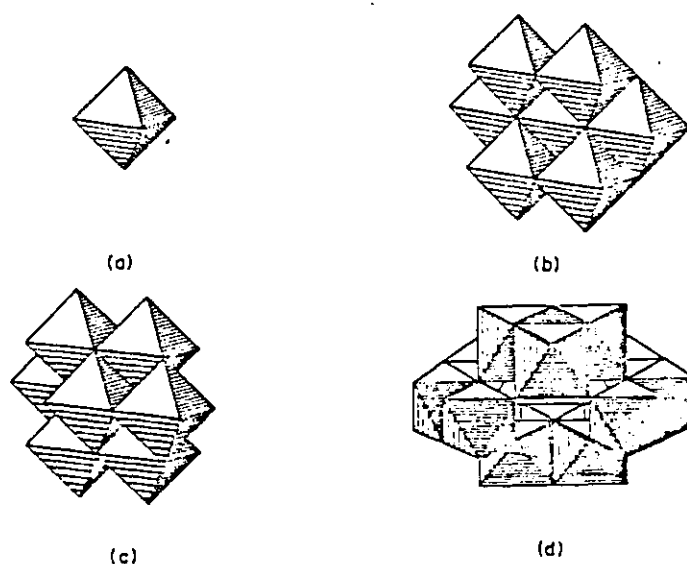


Fig. 9.1. Diagrammatic representation of structures developed from octahedral units (from Cotton and Wilkinson, 1972).

A LEED study by Usami, S. et al (1977) of the oxidation of a NbO(100) surface indicated that an amorphous surface layer forms after an exposure of about $20 \times 10^{19} \text{ O.m}^{-2}$. This shows that the structure based upon these octahedra are not well organised. Pantel, R. et al also noted featureless LEED patterns from the Nb(100), Nb(110) and Nb(111) surfaces for exposures above about $15 \times 10^{19} \text{ O.m}^{-2}$. Reider, K.H. (1980) noted the similarity in the SIMS spectra of an oxidised Nb(110) surface and a bulk Nb₂O₅ crystal. This evidence supports the duplex layer suggested in this work, in which Nb₂O₅ occupies the outermost layer. Reider, K.H. (1980) also observed the formation of a featureless LEED pattern after an exposure of more than $20 \times 10^{19} \text{ O.m}^{-2}$. All of these results show that

Nb_2O_5 layer lacks any long range order.

The shift in the O 1s binding energies by 0.1 eV on all three Spns has already been described (chapter 7) and its similarity with two other systems noted. It is believed that it is due to the setting up of an electric field across the oxide layer caused by chemisorbed anions. Such a field has been proposed by Fehler, F.P. and Mott, N.F. (1970) as being the driving force for the formation of thin oxide films on metals at low temperatures. At low temperatures thermal diffusion alone is not sufficient to explain the rates of oxidation, and a field assisted mechanism was invoked. That such fields seem to be observed during the oxidation of niobium, as well as on Mg and Cr (chapter 7), supports this particular mechanism.

Gross oxidation, at room temperature, produces further oxidation of the underlying Nb to Nb_2O_5 . It is likely that this very thin layer of Nb_2O_5 is the maximum oxide thickness formed on niobium at room temperature and at reduced oxygen pressure. An increase in both these parameters is required to form much thicker layers, i.e. the 2 - 3 nm passivation oxide layer on atmosphere exposed niobium foil.

In conclusion, it can be noted that a duplex layer composed of two metal oxidation states is formed and needs to be accounted for in models of metal oxidation. The duplex layer has been observed in the case of niobium owing to the favourable spectral parameters and the use of XPS difference spectra.

However, it is possible that the formation of a duplex layer during metal oxidation in the very thin film regime, is a common phenomena which has generally been overlooked.

FUTURE WORK

The present work has shown the usefulness of electron spectroscopy in the study of low temperature oxidation. Future work along similar lines applied to the nearest neighbours of niobium in the periodic table would prove useful. The elements molybdenum and tantalum have been studied by other surface techniques suggesting that some similarities do exist between these elements and niobium. In particular it would be interesting to determine whether lower oxides are formed on these elements. Both elements are suited to study by the methods followed in this thesis. Tantalum may prove most rewarding as the Ta 4f levels can be studied using HeII radiation, allowing core level studies at very high resolution.

A temperature dependent oxidation study of niobium would illuminate the hypothesis that formation of the second NbO layer occurs by thermally activated place exchange. In addition, low temperature adsorption of oxygen onto the NbO double layer could produce larger potential gradients across the oxide film.

All of the above studies would benefit from the use of orientated single crystal specimens. The overlap between various stages in the oxidation would be reduced, such that a clearer understanding of the reaction of oxygen with clean metal surfaces could emerge.

APPENDIX

The present section tabulates the basic experimental data obtained in the XPS study of the oxidation of niobium. This data includes peak areas, positions, widths and asymmetries, as well as oxide layer thickness. Data for the high temperature NbO surface and the gross oxidation Nb₂O₅ surface is also included.

The results are presented in the following order:

1. Nb 3d (total)
2. Nb 3d (oxide)
3. Nb 3d (metal)
4. Nb 3d (surface plasmon)
5. Nb Auger
6. O 1s
7. O Auger
8. O 1s characteristics
9. O Auger characteristics
10. NbO and Nb₂O₅ surface data
11. Oxide thickness

Intensities for the emission features are presented in arbitrary units, internally consistent from one feature and specimen to another. Binding and kinetic energies are referred to the spectrometer calibration such that the Au 4f_{7/2} binding energy is 83.8 eV.

1. Nb 3d (Total) Intensities

Exposure (x 10 ¹⁹ 0.m ⁻²)	Specimen 1	Specimen 2	Specimen 3
0.0	10.85	8.39	10.04
0.36	9.99	8.22	-
0.72	10.37	8.02	10.08
1.44	9.68	7.86	9.52
2.16	-	7.79	9.50
3.6	9.01	7.56	-
5.8	-	7.91	-
7.2	-	7.62	-
14.4	-	7.35	8.30
21.6	-	7.27	-
36.0	9.14	-	-
72.0	8.54	7.10	-
720.0	8.11	7.15	8.60

2. Nb 3d (Oxide) Intensities

Exposure (x 10 ¹⁹ o.m ⁻²)	Specimen 1	Specimen 2	Specimen 3
0.36	2.04	0.84	-
0.72	3.01	1.55	1.41
1.44	3.81	2.57	1.76
2.16	-	2.76	2.71
3.6	4.40	3.21	-
5.8	-	3.52	-
7.2	-	3.17	-
14.4	-	3.76	3.72
21.6	-	3.34	-
36.0	4.03	-	-
72.0	3.66	3.66	-
720.0	4.04	3.82	4.04

3. Nb 3d (Metal) Intensities

Exposure (x 10 ¹⁹ O.m ⁻²)	Specimen 1	Specimen 2	Specimen 3
0	10.85	8.39	10.05
0.36	7.90	7.38	-
0.72	7.48	6.47	10.08
1.44	5.78	5.29	9.52
2.16	-	5.03	9.50
3.6	4.61	4.33	-
5.8	-	4.39	-
7.2	-	4.44	-
14.4	-	3.59	8.30
21.6	-	3.93	-
36.0	4.936	-	-
72.0	4.88	3.44	-
720.0	4.07	3.33	8.60

4. Nb Auger Intensities

Exposure ($\times 10^{19}$ $\text{O}\cdot\text{m}^{-2}$)	Specimen 2	Specimen 3
0	2.21	3.34
0.36	2.03	-
0.72	1.83	2.28
1.44	1.66	2.29
2.16	1.65	2.10
3.6	1.82	-
5.8	1.50	-
7.2	1.89	-
14.4	1.46	-
21.6	1.50	-
36.0	-	-
72.0	1.42	-
720.0	1.39	1.62

5. Nb 3d (Surface Plasmon) Intensities

Exposure ($\times 10^{19}$ O.m^{-2})	Specimen 1	Specimen 2	Specimen 3
0	0.094	0.064	0.078
0.36	0.064	0.060	-
0.72	0.044	0.038	0.041
1.44	0.014	0.016	0.024
2.16	-	0.085	0.015
3.6	0.00	0.00	-
-	-	-	-
14.4	-	-	0.00

6. O 1s Intensities

Exposure ($\times 10^{19} \text{ O.m}^{-2}$)	Specimen 1	Specimen 2	Specimen 3
0.36	0.70	0.37	-
0.72	0.96	0.64	0.50
1.44	1.15	0.92	0.78
2.16	-	0.99	0.94
3.6	1.39	1.25	-
5.8	-	1.39	-
7.2	-	1.43	-
14.4	-	1.42	1.49
21.6	-	1.44	-
36.0	1.77	-	-
72.0	1.81	1.50	1.51
720.0	1.90	1.54	1.64

7. O Auger Intensities

Exposure ($\times 10^{19}$ O.m ⁻²)	Specimen 1	Specimen 2	Specimen 3
0.36	0.67	0.40	-
0.72	0.73	0.56	0.39
1.44	0.91	0.82	0.58
2.16	-	0.84	0.78
3.6	1.05	1.03	-
5.8	-	-	-
7.2	-	1.12	-
14.4	-	1.19	1.11
21.6	-	1.12	-
36.0	1.35	-	-
72.0	-	1.17	1.18
720.0	1.29	1.18	1.22

8. O 1s Peak Characteristicsi) Specimen 1

Exposure (x 10^{19} O.m ⁻²)	BE (eV)	FWHM (eV)	LHS (eV)	RHS (eV)	ASY
0.36	530.7	2.15	0.9	1.25	1.39
0.72	530.75	2.35	1.0	1.35	1.35
1.44	530.95	2.3	1.0	1.3	1.3
3.6	530.95	2.15	0.95	1.20	1.26
36.0	530.95	2.1	0.95	1.15	1.21
72.0	530.95	2.05	0.95	1.1	1.16
720.0	530.85	1.95	0.95	1.05	1.17

ii) Specimen 2

Exposure (x 10^{19} O.m ⁻²)	BE (eV)	FWHM (eV)	LHS (eV)	RHS (eV)	ASY
0.36	530.65	1.9	0.85	1.05	1.24
0.72	530.65	2.05	0.9	1.15	1.28
1.44	530.7	2.25	0.95	1.30	1.37
2.16	530.7	2.2	0.95	1.25	1.32
3.6	530.85	2.2	1.0	1.2	1.20
5.8	530.8	2.1	0.95	1.1	1.16
7.2	530.85	2.05	0.95	1.1	1.12
14.4	530.85	2.0	0.9	1.1	1.22
21.6	530.9	2.0	0.9	1.1	1.22
72.0	530.9	1.95	0.9	1.05	1.17
720.0	530.85	2.00	0.85	1.05	1.35

8. O 1s Peak Characteristics (continued)iii) Specimen 3

Exposure (x 10 ¹⁹ o.m ⁻²)	BE (eV)	FWHM (eV)	LHS (eV)	RHS (eV)	ASY
0	530.65	1.8	0.75	1.05	1.40
0.72	530.7	1.85	0.85	1.0	1.18
1.44	530.75	2.05	1.1	0.95	1.16
2.16	530.8	2.3	1.0	1.3	1.30
14.4	530.7	2.1	0.95	1.15	1.21
72.0	530.7	2.0	0.9	1.1	1.22
720.0	530.8	1.95	0.9	1.05	1.17

9. Oxygen Auger Peak Characteristicsi) Specimen 1

Exposure ($\times 10^{19}$ O.m ⁻²)	KE (eV)	FWHM (eV)	LHS (eV)	RHS (eV)	ASY
0.36	513.25	3.4	1.2	2.2	1.83
0.72	513.0	4.1	1.35	2.75	1.65
1.44	512.75	4.2	1.7	2.5	1.47
3.6	512.3	4.0	1.75	2.25	1.29
36.0	512.2	4.1	1.85	2.35	1.27
720.0	512.2	4.1	1.85	2.25	1.22

ii) Specimen 2

Exposure ($\times 10^{19}$ O.m ⁻²)	KE (eV)	FWHM (eV)	LHS (eV)	RHS (eV)	ASY
0.36	513.7	3.0	1.15	1.85	1.61
0.72	513.45	3.4	1.25	2.15	1.72
1.44	513.05	4.0	1.55	2.15	1.39
2.16	512.85	4.0	1.85	2.15	1.16
3.6	512.5	4.2	1.9	2.1	1.11
7.2	512.45	4.1	1.9	2.1	1.11
14.2	512.5	4.1	1.7	2.4	1.41
21.6	512.45	4.0	1.7	2.2	1.22
72.0	512.45	4.0	1.75	2.25	1.29
720.0	512.25	4.0	1.9	2.1	1.11

9. Oxygen Auger Peak Characteristics (continued)iii) Specimen 3

Exposure (x 10 ¹⁹ O.m ⁻²)	KE (eV)	FWHM (eV)	LHS (eV)	RHS (eV)	ASY
0	513.7	-	-	-	-
0.72	513.7	3.0	1.2	1.8	1.5
1.44	513.55	3.6	1.2	2.4	2.0
2.16	513.1	3.9	1.5	2.4	1.6
14.4	512.4	4.0	1.9	2.1	1.11
72.0	512.3	3.9	1.95	1.95	1.0
720.0	512.35	3.9	1.8	2.1	1.17

10. NbO (high temperature stable) surface data

Feature	Intensity	BE/KE(eV)
Nb 3d (total)	11.2	-
Nb 3d (oxide)	1.97	-
Nb 3d (surface plasmon)	0.53	-
O 1s	0.95	530.75
O Auger	0.90	513.4

Nb₂O₅ (gross oxidation) surface data

Feature	Intensity	BE/KE(eV)
Nb 3d (total)	11.6	-
Nb 3d (oxide)	6.6	-
Nb 3d (surface plasmon)	0.0	-
O 1s	5.4	530.9
O Auger	3.2	511.9

11. Oxide thickness (nanometers)

Exposure ($\times 10^{19} \text{ O.m}^{-2}$)	Specimen 1	Specimen 2	Specimen 3
0.36	0.21	0.08	-
0.72	0.24	0.17	0.10
1.44	0.41	0.30	0.25
2.16	-	0.33	0.25
3.6	0.50	0.43	-
5.8	-	0.42	-
7.2	-	0.41	-
14.4	-	0.55	0.50
21.6	-	0.50	-
36.0	0.51	-	-
72.0	0.52	0.58	-
720.0	0.64	0.60	0.50

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