Surface reconstruction and adsorbate geometry by surface core level spectroscopy

Autor(en): **Lecante, J. / Guillot, C.**

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SURFACE RECONSTRUCTION AND ADSORBATE GEOMETRY BY SURFACE CORE LEVEL SPECTROSCOPY

J. Lecante and C. Guillot
CEN.Saclay, Service de Physique des Atomes et des Surfaces,
91191-Gif-sur-Yvette Cédex (France) and LURE (Orsay), France.

Abstract. Previous studies on surface core level shifts have shown the interest of the core level spectroscopy as a very sensitive probe of surface layers. A brief review of the experimentally measured core level shifts is given and also a survey of a theoretical model using the tight binding approximation. Several applications of this new technique are presented concerning clean surface reconstruction and chemisorption studies.

INTRODUCTION

Recent photoemission experiments on 5d transition metal surfaces have shown that the binding energy of core levels is modified by the presence of a surface. The shift between core level of surface atoms and bulk atoms may amount to few tenths of an eV.

The first experimental evidence was obtained on polycristalline gold by Citrin et al. /1/. They observed on an X-ray photoemission spectrum of 4f levels recorded at grazing emission angle, a shoulder on the low-binding energy side of the peaks. They assigned this shoulder to photoemission from a surface layer.

One year later, an experiment performed with the synchrotron radiation of the ACO storage ring of LURE, allowed us to unambiguously distinguish between surface and bulk 4f levels of a (110) face of tungsten /2/. Core level spectra are now being obtained with better energy resolution than classical XPS experiments by using the tunability of the synchrotron radiation. With a low enough photon energy it becomes easy to get some core level spectra with an overall resolution (photon monochromator + electron analyzer) in the 100 meV range. With such a resolution it is possible to observe core level chemical shifts less than 100 meV provided that the natural width of the line is not too high.

This is the case for the 4f levels of 5d serie transition metal. So many experiments have been performed on the elements of this series.

In this paper, after a brief summary of the experimental results obtained up to now on these metals, we present a survey of a microscopic theory used to explain and calculate the surface shifts. In the last section some examples are given showing the interest of this new surface core level spectroscopy to study various surface problems such as reconstruction of clean surfaces and adsorbate geometry.

EXPERIMENTAL EVIDENCE OF SURFACE CORE LEVEL SHIFTS

The figure 1 shows different 4f 7/2 level spectra obtained with the synchrotron radiation of ACO for the 4f 7/2 levels of a clean (110) face of tungsten /2/. These spectra are recorded along the surface normal and the photon energy is 70 eV. The electron analyzer of the cylindrical type has an angular resolution of ± 1° and the overall energy resolution (photon monochromator + electron analyzer) is about 120 meV for $\hbar\omega$ = 70 eV. Figure 1a represents the clean surface spectrum obtain for an angle of incidence of the light of 70° which corresponds mainly to a p polarization. On this figure we clearly resolve two peaks separated by 300 meV. The experimental full widths at half maximum (FWHM) of the two peaks is about 250 meV. The effects of s polarization and of surface contaminants (hydrogen or oxygen) demonstrate that the low-binding energy peak is due to surface atoms. The binding energy of the bulk (measured relatively to the Fermi level) is 31.5 eV in agreement with XPS measurements.

The photon energy dependence of the surface 4f levels has been investigated in the 50-150 eV energy range for normal emission. The

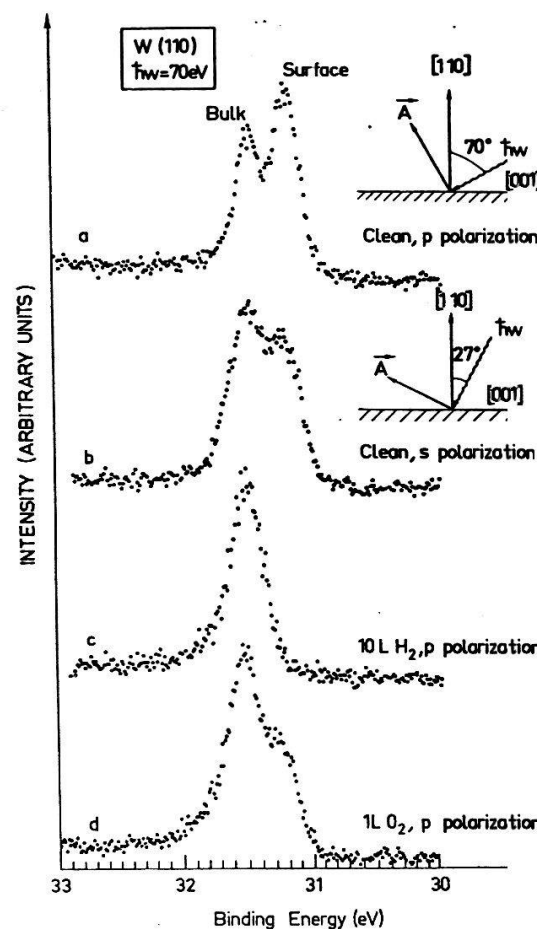

FIGURE 1 − W4f 7/2 spectra of (110) face. Curve a, clean surface, p polarization; curve b, s polarization; curve c, 10 L. H_2 exposure, p polarization; curve d, 1L. O_2 exposure, p polarization.

relative variation of surface and volume peak intensity as a function of $\hbar\omega$ is mainly due to final state effects, namely scattering of the photoelectrons.

Similarly final state effects can be observed on peak intensity variation with polar or azimuthal angle. These final state effects may be, as in LEED, but with greater sensitivity and specificity, used to extract structural informations on the clean surface. Thus some problems of clean surface reconstruction may be studied by this method.

The figure 2 shows 4f 7/2 spectrum obtained on the less dense W(100) surface. The photon energy is now 78 eV which gives the surface peak more intense relatively to the bulk one. The separation in bulk and surface contribution is not so obvious as for the (110) face. The bulk emission
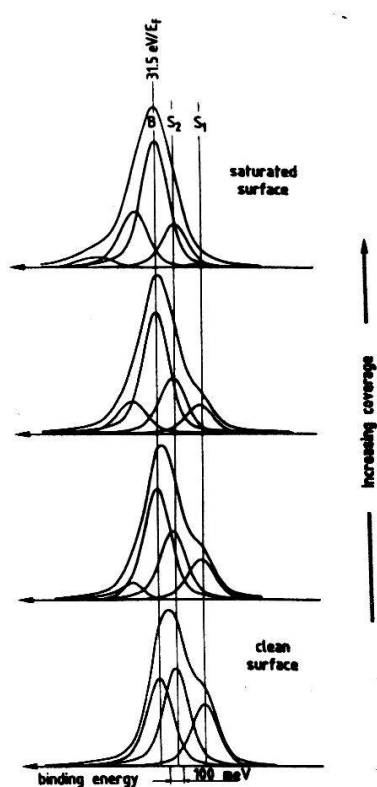
FIGURE 2 - W4f 7/2 spectrum for clean (100) face. The photon energy is 78 eV. The photoelectrons are collected at the normal.

FIGURE 3 - W4f 7/2 spectra for increasing coverage of carbon monoxide on (100) face.

corresponds to the peak which is unchanged when CO is adsorbed on the surface (fig. 3). For the clean surface (fig. 3a) the lowest binding energy peak S_1 is assigned to surface atoms. When we substract the two peaks (S_1 + B) from experimental spectra, we obtain a third peak S_2 which has the same shape and FWHM than the other peaks. The peak S_2 is attributed to the atoms of the first underlayer. This interpretation is supported by theoretical calculations and also by the low sensitivity of this level to pollution : on figure 3, at the CO saturation S_1 has almost disappeared whereas S_2 is still intense /3/.

The presence of two surface peaks on W(100) is not surprising since this face is fairly open and the atoms of the first underlayer are thus significantly perturbed by the surface and even though the second (100) plane atoms have their full shell of first nearest neighbours, their core
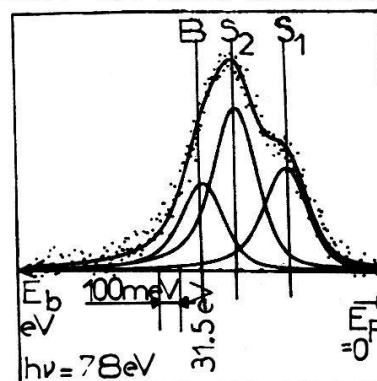
levels can nevertheless be shifted due to the strong modification of surface
atom environments.

SURVEY OF THE MICROSCOPIC THEORY (limited to the d-series)

The reduced coordination number of atoms on the surface results in
a narrowing of the valence band. The displacement of the center of the local
density of valence d states at the surface is induced by a small charge
transfer. The shift is calculated in the tight binding approximation and must
correspond to a quasi neutrality of the surface plane /4/. The main results
are : the shift increases with the number of broken bonds, and it changes
sign near the middle of the d-series (between Ta and W). This behaviour can
be understood using the following simple argument given on figure 4 : the
presence of broken bonds at the surface leads
to a narrowing of the density of states.
Therefore to recover a quasi-neutrality
of the surface plane, it is necessary to
shift upwards the center of the band if
E_F is above the middle of the band (fig. 4a
case of a more than half-filled d-band metal
such as W). This displacement is almost
rigidly followed by the core levels.

FIGURE 4 - The dashed (full)
line represents the bulk (sur-
face) density of states. The
hatched area gives the lack
(a) or excess (b) of electrons

The opposite conclusion holds when
E_F is below the middle of the band : case
of Ta, the surface atom 4f level is shifted
to higher binding energy relative to the
bulk value. Figure 5 shows the opposite
(relative to W) shift of the surface peaks
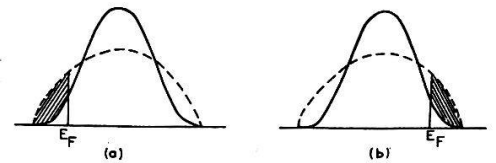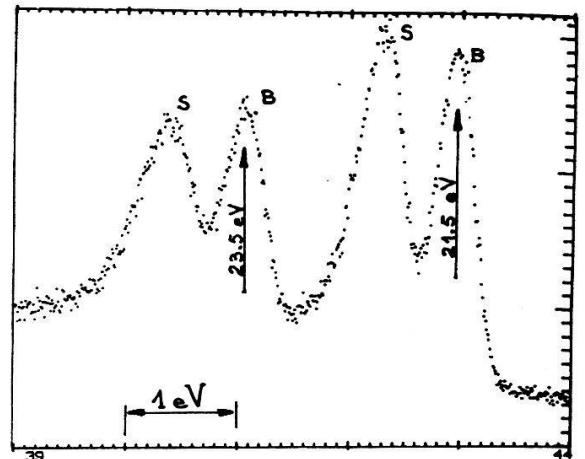for the 4f levels of a (100) face of
tantalum.

FIGURE 5 - Ta 4f 7/2 and 4f 5/2
for clean (100) face. The photon
energy is 65 eV.

SOME APPLICATIONS OF SURFACE CORE LEVEL SPECTROSCOPY

1 - Oxygen adsorption on W(110) -

The above theory can be extended to calculate the core level shift
due to chemisorption and to compare them with experimental values.

Figure 6 shows W (110) 4f 7/2 spectra for clean
surface and for two different exposures to oxygen. The
3.2 Langmuir exposure corresponds to the completion of
the P(2 x 1) LEED pattern. The early stages of adsorp-
tion (0 to 1 L.) are characterized by two new peaks
A and B which appear on the left side of the clean
surface peak (towards higher binding energy) (fig.
6b). These two new peaks increase simultaneously
from the beginning of the adsorption up to an
exposure of 0.4 L. Then the peak A decreases whereas
peak B increases monotically up to 10 L. Peak A is
correlated with isolated oxygen atoms adsorbed on
W(110). Peak B is correlated with the formation of
the P(2 x 1) LEED pattern.

The clean surface peak is strongly depressed
by oxygen adsorption and disappears for exposures
greater than 3 L. The total area under the
different peaks observed from the clean surface
spectrum up to the 10 L. oxygen exposure
spectrum is constant.

FIGURE 6 - W 4f 7/2 spectra
for clean (110) surface and
for oxygen exposure of 0.4 L.
One scale division = 0.2 eV.

The chemisorption leads to a bonding between the oxygen atom and the
nearby tungten atoms in which the 5d electrons are involved. This implies
a small charge transfer of these 5d electrons towards oxygen. In the case
of a strongly localized bonding, this charge transfer should only occur for
W atoms that are directly bound to oxygen. These atoms lose electrons and
thus their 5d levels (and therefore their core levels) are shifted back to
larger binding energies. The tight binding calculation based on this
assumption reproduces very well the experimental observations. The presence
of peak B at the early stages of the adsorption confirm the existence of
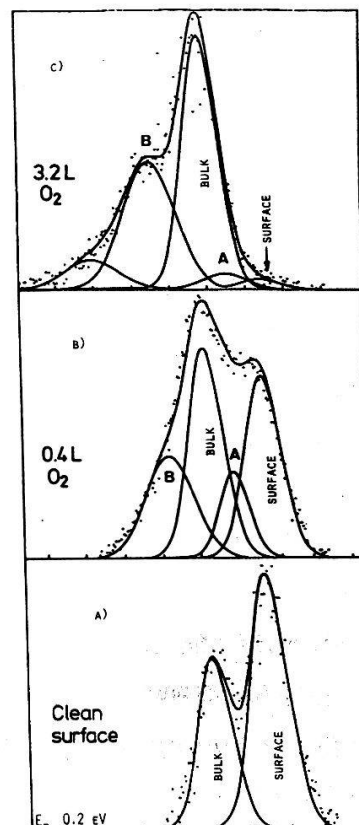P(2 x 1) oxygen islands at these stages.

2 - Hydrogen induced reconstruction of W(100) -

A small hydrogen adsorption induces a (C 2 x 2) reconstruction of the (100) face of tungsten. The hydrogen induced reconstructed surface is characterized by two new peaks S'_2 and S'_1 which are shifted relatively to S_2 and S_1 towards higher energy (fig. 7). For hydrogen exposure, beyond completion of reconstruction, up to the P(1 x 1) structure at saturation coverage, the surface atoms shift back to their initial positions by domains. Nevertheless the final peaks (S''_1, S''_2) are distinct from the initial ones (S_1, S_2) and this fact can be explained by a hydrogen-induced chemical shift.

The tight binding calculation assuming the coexistence of reconstructed and unreconstructed domains gives a fairly good agreement with the shifts of the 4f levels peaks experimentally observed. However we must point out that this calculation has been performed for clean surfaces. Therefore there is an uncertainty in the case of hydrogen-induced reconstruc-tion since then chemical shifts due to this adsorption should occur. This last point was confirmed by the recent experi-ments we have performed on the thermally induced reconstruction : the core level spectrum corresponding to the C(2 x 2) structure thus obtained is different to the spectrum exhibited by the hydrogen induced C(2 x 2) structure : the relative intensity of S_1 and S_2 peaks is strongly modified.

FIGURE 7 - W 4f 7/2 spectra for different hydrogen covera-ges :
a) clean surface
b) 0.3 L of hydrogen :C(2 x 2) LEED pattern
c) saturation coverage

CONCLUSION

We have presented here some experimental data showing the modifica-tion of W core level shifts either by the adsorption of oxygen or by the reconstruction of the surface layer. The theoretical interpretation (restric-
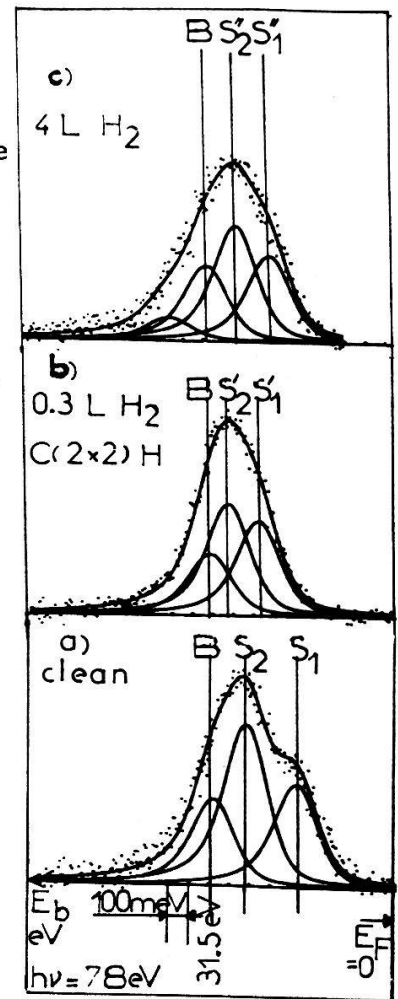
ted to the d-series) of these data, in spite of the simplicity of the model, gives a fair agreement with experiments. So such an interpretation allow us to assign a given core level peak to a given site location, which generalises the possibilities of ESCA to surface geometry determination.

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