RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 36, NUMBER 2 15 JULY 1987-I

Identification of underlayer components in the surface core-level spectra of W(111)

Kevin G. Purcell, Jacques Jupille,* Glyn P. Derby, and David A. King
Donnan Laboratories, Liverpool University, P.O. Box 147, Liverpool L69 3BX, United Kingdom

(Received 7 November 1986; revised manuscript received 20 April 1987)

Core-level photoemission spectra from a W(111) surface using synchrotron radiation are presented. These core-level spectra are shown to be composed of four components with the same peak shape: one from bulk atoms and three from different crystallographic sites in the selvedge. The selvedge peaks comprise a peak from the topmost surface atoms (shifted by -0.45 ± 0.01 eV) and two different underlayer sites (shifted by -0.30 ± 0.02 eV and -0.11 ± 0.002 eV from the bulk peak). This contrasts with a previous model, proposed by Wertheim, Citrin, and van der Veen, which used only two surface components: a broadened surface atom peak and one underlayer peak. The data presented can be fitted with three peaks, yielding good agreement with the peak energies obtained by these authors; however, we show that the four-peak model gives a better fit to the experimental spectra. The use of two underlayer peaks is in good agreement both with intuitive arguments based on the coordination number of atoms in the selvedge and with two previous theoretical calculations of the surface core-level shift. The values determined from the fitting parameters for the core-level line shape are also in good agreement with values calculated by other workers.

It has been known for some time that the core levels of atoms located at the metal surfaces are displaced in binding energy relative to the bulk core levels.[1-5] It has been proposed that each atom located in a different electronic environment at the metal surface can be associated with a particular core-level shift.[2,3] The magnitude of this shift is dependent upon the coordination number of the atom under consideration; a lower coordination number having a larger core-level shift. This is clearly demonstrated for the surface atoms of W(110) and W(100). The more densely packed W(110) surface [six nearest neighbors (NN) and four next-nearest (NNN) neighbors] exhibits a smaller shift of -0.30 eV (Refs. 2 and 6) than the more open W(100) surface, the surface atoms of which have four NN and five NNN and exhibit a shift of 0.35 eV.[7,8] The absence of next-nearest neighbors (and next-next-nearest neighbors), can have a pronounced effect on the magnitude of the surface core-level shifts (SCLS).[9,10] For example, the coordination of the underlayer atoms on the W(100) surface differ by only one next-nearest neighbor from that of the bulk, yet they exhibit a surprisingly large shift of -0.14 eV.[2,7,8] However, there have been reported some experimental results which run counter to that expected from this rule.[11,12] For tantalum the surface atoms on the (111) face have a lower coordination (four NN and three NNN) than those on the (100) face (six NN and four NNN), but the $4f_{7/2}$ core levels from surface atoms on the Ta(100) surface have been reported[13] to have a larger surface core-level shift than those on the Ta(111) surface.[11] The published decompositions of core-level spectra for Ta(111) and W(111) surfaces[8,13,14] also illustrate a discrepancy between the values obtained experimentally and the expectation on the basis of the above model.

The surfaces of body-centered-cubic (111) metals contain three groups of surface and subsurface atoms whose coordination number, up to the next-nearest neighbor, differs from that of the bulk. The atoms in the bulk have eight nearest neighbors and six next-nearest neighbors. At the surface there are atoms of three different coordinations: (i) surface atoms (four NN and three NNN), (ii) first-underlayer atoms (seven NN and three NNN), and (iii) second-underlyer atoms (seven NN and six NNN).

Calculations of the SCLS spectra for the W(111) surface by Rosengren,[10] using a semiempirical bond-breaking model, predict a shift of -0.24 eV for the first underlayer atoms and -0.07 eV for the second underlayer atoms, assuming a shift of -0.43 eV for the surface atoms. Other calculations by Spanjaard *et al.*, using a tight-binding model, give very similar results:[2] The surface atoms experiencing a shift of -0.43 eV relative to the bulk, with the first- and second-underlayer atoms displaying a shift of -0.20 and -0.10 eV, respectively. Similar values for the core-level shift can also be obtained using the Tomanek, Kumar, Holloway, and Bennemann bond-breaking model.[9] However, in the previous work on W(111) and Ta(111) surfaces[8,13,14] the experimental data have been fitted using a model with only three peaks: a bulk peak, a surface peak, and an underlayer peak. The surface peak for tungsten (tantalum) was found to be shifted by -0.43 eV ($+0.39$ eV) relative to the bulk peak, with the underlayer peak being shifted by -0.14 eV ($+0.11$ eV). This discrepancy between the theoretical expectations and the published experimental results stimulated us to look again at the core-level shifts at the W(111) surface.

The experiments were performed on the Synchrotron Radiation Source at Daresbury in a Vacuum Generators Angular Dispersive Electron Spectrometer 400 ultrahigh-vacuum photoelectron spectrometer attached to a toroidal grating monochromator, providing monochromatic vacuum-ultraviolet radiation, photon energies between 70 and 80 eV being used for this work. The base pressure of the system was better than 2×10^{-10} Torr, with a working pressure of less than 3×10^{-10} Torr. An angle resolving analyzer (4° half-width) was used to collect the electrons emitted normal to the surface. The light was incident at 70° to the surface normal. The total resolution of the system, monochromator, and analyzer, was estimated to be 0.16 eV from the Fermi edge; this value is in good agreement with the calculated resolution for the system.

The tungsten crystal was cleaned by repeated heating to 1800 K in 10^{-6} Torr oxygen and flashing in vacuum to 2400 K. The surface was considered clean when no further increase in the amplitude of the surface peak, relative to the bulk, could be seen in the core-level spectra. The spectra were taken as multiple scans (160 s per scan), the crystal being flashed to 2500 K before the start of each scan to minimize surface contamination. The crystal temperature during a scan was between 350 and 500 K.

The spectra were analyzed by least-squares fitting with a group of peaks defined by a set of parameters; the best fit is found by varying these parameters. In this case, the parameters capable of being adjusted were the energy position, the amplitude, the width, and asymmetry of the peaks, two parameters representing a linear background, and the width of the Gaussian peak, convolved with the spectrum to represent the instrument response. All of these parameters could either be fixed at a constant value or constrained to vary within a given range.

The line-shape parameters of the $4f_{7/2}$ core level were determined by fitting the isolated bulk peak in a spectrum taken from a heavily oxidized W(111) surface (see Fig. 1). This surface was prepared by repeated heating of the crystal to 1800 K in 10^{-6} Torr oxygen. The spectrum shows the bulk peak completely separated from the surface peaks; all the selvedge peaks have been chemically shifted by $\simeq +1.3$ eV relative to the clean surface peak, due to the charge transfer from the oxygen atoms. This value agrees well with the shift measured for tungsten atoms at an oxide surface (1.24 eV) prepared under similar conditions by Morar *et al.*[12] During this fit the energy position, amplitude, width, asymmetry of the peak, and background parameters were all allowed to vary; the Gaussian width was fixed at 0.16 eV. It was found that the bulk peak was well fitted by a single Doniach-Sunjic peak[15] located at 31.38 ± 0.1 eV below the Fermi level, in agreement with our previous work.[7] The best-fit line-shape parameters for this peak were a Lorentzian width (full width at half maximum) 0.15 eV and asymmetry parameter 0.05. For our four-peak model we assume that

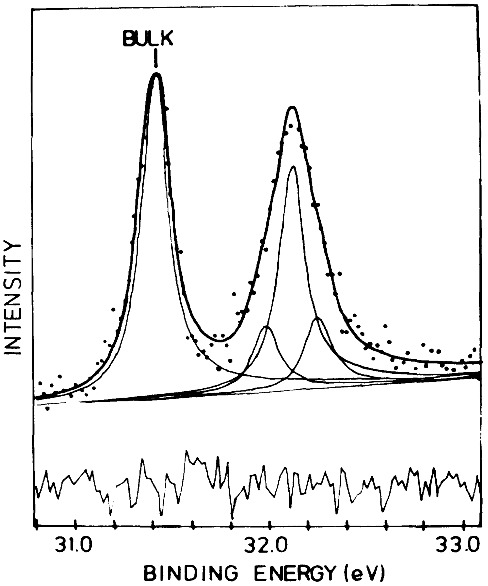

FIG. 1. $4f_{7/2}$ core-level spectrum from a heavily oxidized W(111) surface. The bulk peak is well separated from the oxidized surface peaks.

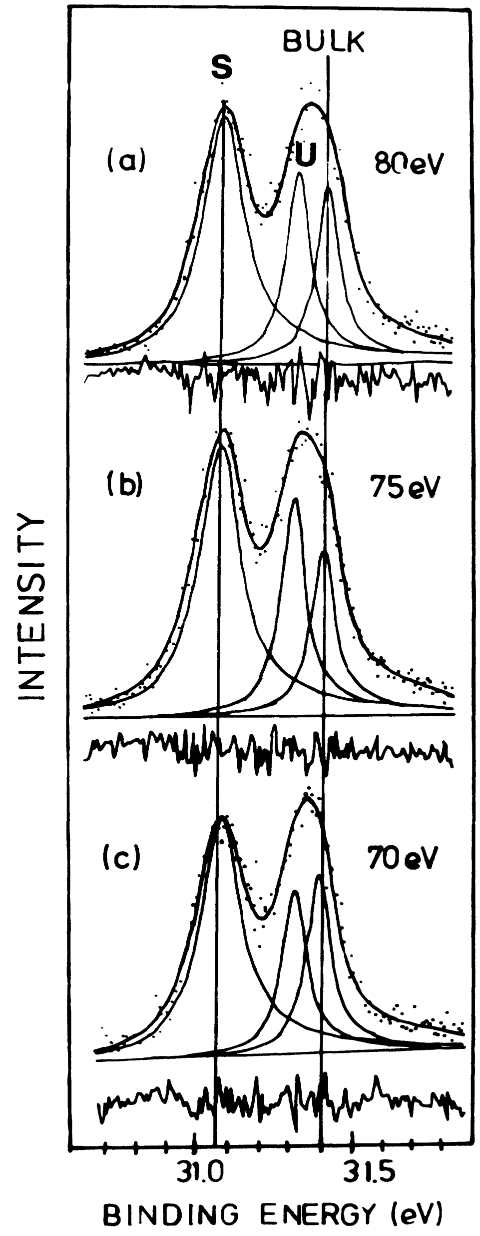

FIG. 2. W(111) $4f_{7/2}$ clean surface core-level spectra, taken at three different photon energies, decomposed into three peaks.

the $4f_{7/2}$ core levels of the surface atoms have the same Lorentzian width as those in the bulk.

The clean surface $4f_{7/2}$ core-level spectra, shown in Fig. 2, have been recorded at three different photon energies (70, 75, and 80 eV). The energies were chosen to maximize both surface sensitivity and monochromator throughput. The surface sensitivity varies due to both changes in escape depth and photoelectron diffraction effects,[6,16] so the components of spectra recorded at different photon energies have different amplitudes ratios. These changes in amplitude of the surface and underlayer peaks aid the fitting process, because the core-level spectrum changes its shape when measured at different photon energies. A given model, comprising a set of peak positions and line shapes, must be able to fit all the spectra at different photon energies to be considered an accurate description of the core level. This is a stringent requirement, considerably reducing the possibility of obtaining a good fit from an incorrect model.

In order to reproduce the results obtained by van der Veen and co-workers[8,11,14] we first attempted to fit the spectra using three peaks. Wertheim, Citrin, and van der Veen[8] found that the core-level spectra were well fitted using a surface peak that was somewhat broader than the other peaks. The program we used to fit the data was unable to convolve the surface peaks with a different Gaussian from the bulk; as a consequence, we fitted the spectra using two Doniach-Sunjic line shapes with different Lorentzian widths, convolving the sum with a Gaussian. This resulted in a surface peak with Lorentzian width 0.19 eV and a bulk peak with Lorentzian width 0.11 eV, both peaks having an asymmetry parameter 0.06. The energy positions of the selvedge peaks were -0.42 ± 0.02 and -0.11 ± 0.02 eV for the surface peak and underlayer peak, respectively, with respect to the bulk peak binding energy, in very close agreement with the results of Wertheim *et al.*[8] (see Table I). The Gaussian had a width of 0.21 eV. However, on the low-binding-energy side of the spectra the residuals indicate nonrandom deviations of the fit from the experimental data, showing that the experimental data points decrease in amplitude more rapidly than can be accounted for with a single wide surface peak. This is taken as evidence that the surface peak is, in fact, composed of more than one component.

The clean surface spectra were decomposed into four peaks all having the same line shape, as illustrated in Fig. 3. The bulk-peak-energy position and the linewidth and asymmetry were fixed to the values determined from the isolated bulk peak. The energy positions and amplitudes

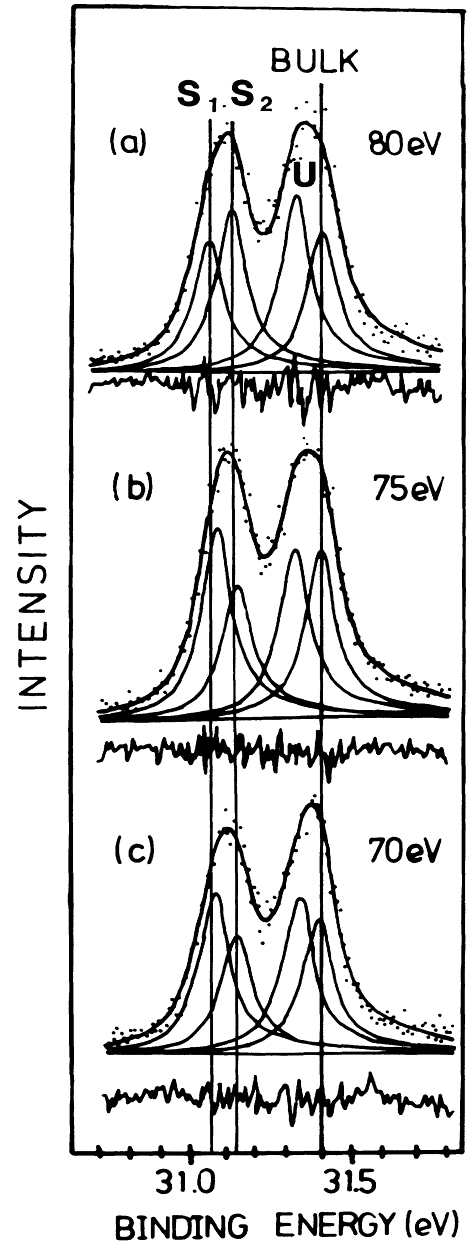

FIG. 3. Clean surface W(111) $4f_{7/2}$ spectra fitted with four peaks all having the same line shape. Note, the nonrandom deviations in the residuals are almost completely eliminated (cf. Fig. 2).

TABLE I. Three- and four-peak models for decomposition of W(111) surface core-level shift spectra. Values are expressed in units of eV.

	Wertheim *et al.* (Ref. 8)	This work (two surface peaks)	This work (three surface peaks)
Surface	-0.43 ± 0.01	-0.42 ± 0.02	-0.46 ± 0.03
Underlayer	-0.11 ± 0.01	-0.11 ± 0.02	
First underlayer			-0.36 ± 0.03
Second underlayer			-0.11 ± 0.02

of the surface and subsurface peaks were left unconstrained. Nonrandom deviations in the residuals are almost completely eliminated indicating a good fit between experiment and model. The three surface components, labeled S_1, S_2, and U are shifted by -0.45 ± 0.01, -0.30 ± 0.02, and -0.12 ± 0.01 eV, respectively, relative to the bulk peak (see Table I).

Although the improvement in the quality of the fit for the four-peak model compared to the three-peak model is not proof that the data are composed of four peaks, it is a convincing argument that this is the case. To select between the two models one should examine their physical basis, in addition to the quality of the fit obtained.

As we have already shown in the introduction, using empirical coordination number arguments and on the basis of two different theoretical calculations, we would expect four peaks for an adequate fit. The results we obtain from our fitting procedure agree well with the values derived from two different calculations. This in itself is good evidence for the core level being composed of four peaks.

Another point in favor of our model comes from constraining all the peaks to have the same line-shape parameters, whereas the three-peak model requires the surface peak to have a different width from that in the bulk. Although this results in a reduction in the number of parameters for the three-peak model compared to the four-peak model, it requires an explanation for the increase in the width of the surface peak. Wertheim *et al.*[8] speculated that this excess width originated from an increase in the phonon broadening of the photoemission line from the surface atoms. On this basis, one should also expect the underlayer peak width to differ from that in the bulk. Consequently, for reasons of consistency, the fitting procedure should be performed with the width of the underlayer peak unconstrained. In previous work, however, the underlayer peak has always been given a fixed width equal to the width of the bulk peak. If one includes the width of the underlayer peak as a variable parameter, the three-peak model would have the same number of parameters as the four-peak model, removing one reason to choose the three-peak model in preference to the four-peak model.

Another more compelling argument against a broad surface peak arises from recent calculations of the core-level photoemission lineshape at the surface. Sebilleau *et al.*[16] have calculated the magnitude of the phonon broadening at a tungsten surface. They found that at 500 K the W (100) surface atoms experience a Gaussian broadening only 0.02 eV greater than the bulk (i.e., 0.15 eV at the surface, compared to 0.13 eV in the bulk). This is somewhat smaller than the additional Gaussian broadening of 0.12 eV obtained by Wertheim *et al.*[8] for fits from the W(100) and W(111) surfaces. In spectra with a relatively poor signal-to-noise ratio, such as ours, a 20-meV change in width of the surface peak cannot be accurately measured.

We have presented core-level spectra taken from a clean W(111) surface. These data have been fitted with a model consisting of three peaks: a broadened surface peak, an underlayer peak, and a bulk peak, obtaining values for the SCLS in good agreement with previous work.[13] We have also presented an alternative model, in which the spectra are fitted with four peaks with the same line shape. In this model, the peaks correspond to a surface peak and two different underlayer peaks. The three-peak model, using only two surface components, gave unsatisfactory results when used to fit the clean surface, but the values obtained for the surface core-level shifts were the same as those found by Wertheim, Citrin, and van der Veen. The four-peak model showed a considerably improved fit compared to the previous model. We have accounted for this extra peak in a simple and intuitive manner, using coordination number arguments. We also showed that our results are in good agreement both with two different theoretical calculations for the SCLS on this surface and a calculation of the width of the surface and bulk peaks.

This work was supported by the Science and Engineering Research Council (SERC). We wish to thank the SERC for financial support for one of us (K.G.P.). The assistance of Daniel Law, Frances Quinn, and Howard Padmore with the use of experimental equipment at Daresbury Laboratory is gratefully acknowledged. We are indebted to David Norman for a critical reading of an early draft of this paper.

---

*Permanent address: Laboratoire Maurice Letort, Boîte Postale 104, 54600 Villers-les-Nancy, France.

[1] P. H. Citrin, G. K. Wertheim, and Y. Baer, Phys. Rev. Lett. **41**, 1425 (1978).

[2] D. Spanjaard, C. Guilliot, M. C. Desjonqueres, G. Treglia, and J. Lecante, Surf. Sci. Rep. **5**, 1 (1985).

[3] P. H. Citrin, G. K. Wertheim, Phys. Rev. B **27**, 3176 (1983).

[4] D. E. Eastman, F. J. Himpsel, and J. F. van der Veen, J. Vac. Sci. Technol. **20**, 609 (1982).

[5] W. F. Egelhoff, Surf. Sci. Rep. **6**, 253 (1986).

[6] Tran Minh Duc, C. Guillot, Y. Lassailly, J. Lecante, Y. Jugnet, and J. C. Vendrine, Phys. Rev. Lett. **41**, 1425 (1978).

[7] J. Jupille, K. G. Purcell, and D. A. King, Solid State Commun. **58**, 273 (1985).

[8] G. K. Wertheim, P. H. Citrin, and J. F. van der Veen, Phys. Rev. B **30**, 4343 (1984).

[9] D. Tomanek, V. Kumar, S. Holloway, and K. H. Bennemann, Solid State Commun. **41**, 273 (1982).

[10] A. Rosengren, Phys. Rev. B **24**, 7393 (1981).

[11] J. F. van der Veen, D. E. Eastman, and F. J. Himpsel, Phys. Rev. B **25**, 4343 (1982).

[12] J. F. Morar, F. J. Himpsel, G. Hughes, J. L. Jordan, F. R. McFeely, and G. Hollinger, J. Vac. Sci. Technol. A **3**, 1477 (1985).

[13] C. Guillot, P. Roubin, J. Lecante, M. C. Desjonqueres, G. Treglia, D. Spanjaard, and Y. Jugnet, Phys. Rev. B **30**, 5487 (1984).

[14] J. F. van der Veen, D. E. Eastman, and F. J. Himpsel, Solid State Commun. **37**, 555 (1981).

[15] S. Doniach and M. Sunjic, J. Phys. C **3**, 285 (1970).

[16] D. Sebilleau, G. Treglia, M. C. Desjonqueres, C. Guillot, D. Chauveau, and D. Spanjaard (unpublished).