

High-resolution core-level study of hexagonal WC(0001)

K. L. Håkansson, H. I. P. Johansson, and L. I. Johansson

Department of Physics and Measurement Technology, Linköping University, S-581 83 Linköping, Sweden

(Received 6 July 1993; revised manuscript received 27 September 1993)

Results from a high-resolution core-level-photoemission investigation of the (0001) surface of a WC single crystal using synchrotron radiation are reported. Surface-shifted components were identified in both the C 1s and the W 4f levels. A surface C 1s core-level shift of -0.66 eV and a surface W 4f core-level shift of -0.38 eV were determined using a curve-fitting procedure. When using a thermochemical model and accounting only for the loss of coordination at the surface a shift of -0.62 eV was predicted for the carbon level and -0.39 eV for the tungsten level. Oxygen exposures were made for aiding in the assignment of surface-shifted features but also for investigating the initial oxidation behavior. Two chemically shifted W 4f components, having shifts of $+0.29$ and $+0.66$ eV, could be identified after oxygen exposures in the 30–300-L range.

I. INTRODUCTION

Surface core-level shifts in the carbon and nitrogen 1s levels have recently been revealed in investigations of different surfaces of VC, ZrC, TiC, and TiN,^{1–3} while no surface shift could be observed in their metal levels. These transition-metal carbides and nitrides crystallize in the sodium chloride structure,⁴ which means that the (100) surface, which is the one that has been studied most extensively, exposes a mixed surface layer. Observation of surface core-level shifts in the nonmetal 1s level but not in the metal levels of these cubic carbides was, therefore, somewhat surprising, although plausible explanations exist.^{1–3} A study of another carbide crystal was, therefore, conducted for the primary purpose of revealing surface shifts in both metal and nonmetal levels.

In this investigation, high-resolution core-level studies of WC(0001) using synchrotron radiation have been performed. One reason for choosing WC was that the W 4f levels, which are expected to have small intrinsic linewidths, are located at a low binding energy so a good experimental energy resolution could be obtained. This should increase the possibility to observe a shift in the metal levels, particularly since this (0001) surface is polar and believed to be metal terminated.⁵ The results presented below for the clean surface show that surface-shifted levels are observed both in the C 1s and W 4f spectra. Effects of oxygen exposures, made for the purpose of aiding in the identification of surface-shifted levels and for studying initial oxidation, are also presented.

II. EXPERIMENTAL DETAILS

The experiments were performed at beam line 22 at the synchrotron radiation facility MAX laboratory in Lund, Sweden. The beam line utilized is equipped with a modified SX 700 monochromator and a large hemispherical electron analyzer from Scienta.⁶ A total instrumental broadening of about 0.2 eV was typically chosen in the high-resolution studies of the C 1s level and better than 0.1 eV for the W 4f level. Normal emission and an in-

cidence angle of 40° was normally chosen as the experimental geometry in the core-level studies reported below. The electron analyzer accepts a cone of angular width $\pm 8^\circ$.

The characterization and *in situ* cleaning procedure of this crystal, which has a simple hexagonal lattice with a two-atom basis, has been described in detail earlier.⁵ The same procedure was followed this time, gentle anneals in oxygen to remove possible carbon in form of graphite at the surface and thereafter high-temperature flashes to remove the oxygen. This cleaning procedure produced a clean and well-ordered 1×1 surface as checked by LEED (low-energy electron diffraction) and photoelectron spectroscopy.

Oxygen exposures were also made and the exposures are given below as the total pressure read at the ion gauge times the exposure time ($1 \text{ L} = 10^{-6} \text{ Torr s}$). The base pressure in the spectrometer was $5 \times 10^{-11} \text{ Torr}$.

III. RESULTS AND DISCUSSION

C 1s spectra recorded at two different photon energies, 360 and 390 eV, from the WC(0001) surface are shown by the dots in Fig. 1. A surface-shifted C 1s level is clearly discernible. A curve-fitting procedure⁷ was applied and the results are shown by the solid lines through the data points in Fig. 1. The fitted components are shown by the solid curves below the recorded spectra. An integrated background has been used in the fitting procedure to compensate for inelastically scattered electrons. To obtain good fits it was necessary to include, also, a third component, although very weak, which is further discussed below, but first we concentrate on the two strong features. The spectrum recorded at 360 eV is expected to be the most surface sensitive of those shown due to the kinetic-energy dependence of the electron mean free path.⁸ The intensity ratio between the two stronger components thus indicates that the component at higher binding energy (labeled *B*) is bulk related and the one at lower binding energy (labeled *S*) is surface related. Spectra recorded at both lower and higher photon energies

also confirmed this, although they are not shown in Fig. 1. Using all these C 1s spectra a surface core-level shift of -0.66 eV was extracted and the spread in the extracted shift was less than ± 0.02 eV. The binding energy of the bulk component was determined to be $283.5 (\pm 0.1)$ eV relative the experimental Fermi level. Symmetric peaks with a Lorentzian FWHM (full width at half maximum) of 0.36 eV were used as fitting parameters for both the bulk and surface C 1s level. These parameters were found to give good fits of the C 1s spectra when keeping the instrumental broadening similar to what was used in the earlier experiments on VC, ZrC, and TiC.¹⁻³ Concerning the third peak, i.e., the one with low intensity and shifted to even smaller binding energy, we are convinced that it is due to contamination. It is known to be more difficult to prepare and maintain a clean WC(0001) surface⁵ than the earlier studied (100) surfaces of the cubic transition-metal carbides. The spectra shown in Fig. 1 were recorded within an hour after a high-temperature flash, i.e., when the surface was as clean as we could possibly obtain it. The intensity of this peak was observed to increase with time. When the surface was left over night, this feature (which exhibits a shift of -1.10 eV) increased and became a visible shoulder while the strong surface-shifted peak decreased somewhat in intensity and moved slightly towards the bulk peak. No O 1s peak

could, however, be observed in the photoelectron spectrum although the most likely contaminant is some form of carbonoxide. In the case of TiC(100) a second shifted component was also observed.³ In that case, however, the peak intensity was found to depend on the annealing temperature and it was interpreted to be due to carbon segregated to the surface during the cleaning procedure since it increased with increasing annealing temperature. In this case the second shifted peak does not show such a behavior, i.e., it does not increase with increasing annealing temperature. It should be noticed that the surface-to-bulk intensity ratio of this peak varies in the way expected for a surface-related feature, i.e., it exhibits a maximum when the photon energy is chosen to give maximum surface sensitivity.

When we then turn to the spin-split W 4f doublet levels we find surface-shifted components in this case also; see Fig. 2 where spectra recorded at photon energies of 100 and 150 eV are shown. Since the 100-eV spectrum is expected to be the most surface sensitive these two spectra indicate that the doublet shifted to lower binding energy is the surface-related feature. Also in this case spectra have been recorded using both higher and lower photon energies, giving further support of this assignment. The curve-fitting procedure resulted in a surface core-level shift of $-0.38 (\pm 0.01)$ eV. The binding energy of

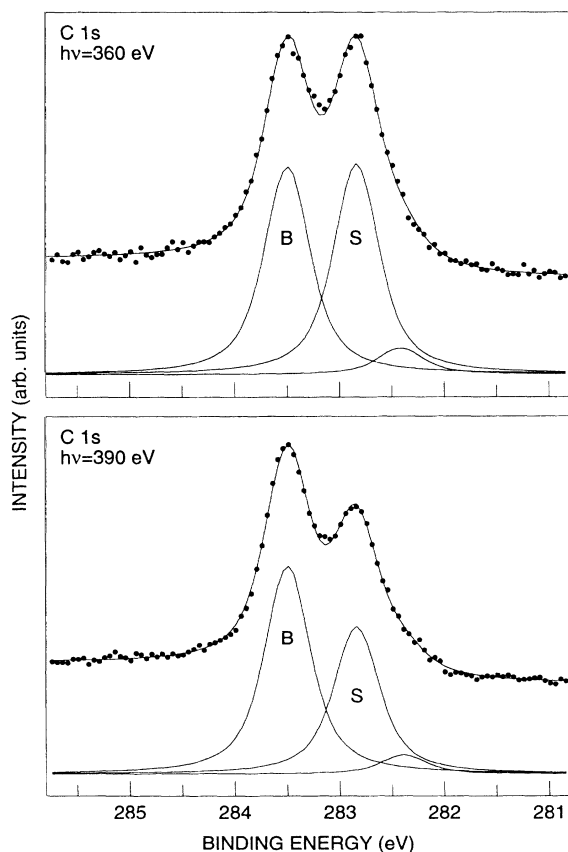


FIG. 1. C 1s core-level spectra, recorded from the WC(0001) surface at two different photon energies, are shown by the dots. The solid lines show the results of a curve-fitting procedure (see text for details).

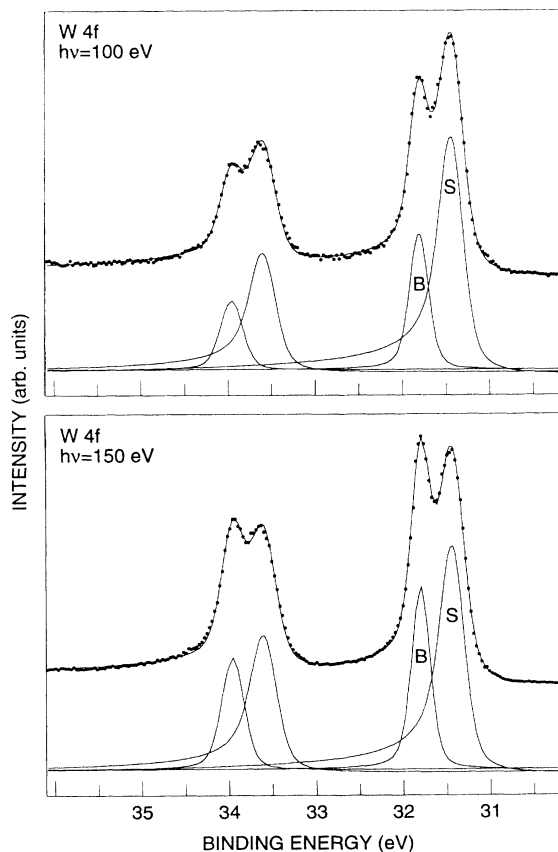


FIG. 2. W 4f core-level spectra, recorded from the WC(0001) surface at two different photon energies, are shown by the dots. The solid lines show the results of a curve-fitting procedure (see text for details).

the bulk $4f_{7/2}$ level was determined to be 31.8 eV, relative the experimental Fermi level, and for the spin-orbit split a value of 2.16 eV was obtained. This means that the binding energy for the bulk W $4f$ level is 0.4 eV higher than in pure tungsten while the spin-orbit split is the same.⁹ For pure tungsten it has previously been shown^{10,11} that different fitting parameters should be used, both for the $4f_{7/2}$ and $4f_{5/2}$ levels and for the bulk and the surface component, respectively. Since the valley between the bulk and the surface component, in Fig. 2, is seen to be much less pronounced for the $4f_{5/2}$ levels it is clear that also in our case the $4f_{5/2}$ levels are broader than the $4f_{7/2}$ levels. When fitting these spectra¹² it became obvious that the surface component must be broader but also more asymmetric than the bulk component. In the fits shown in Fig. 2 the asymmetry parameter has been chosen to be 0.16 for the surface component and 0.02 for the bulk component. The difference in asymmetry is considerably larger than in the case of W(110),¹¹ but this difference was found to be needed in order to obtain reasonable fits over the photon energy range investigated, 80–190 eV. One can speculate that this large difference may indicate that the assigned surface peak actually consists of two surface-shifted levels with an energy separation so small that they are not resolvable in this experiment. Lorentzian widths of 0.08 and 0.13 eV for the bulk and surface components, and Gaussian widths for the $4f_{7/2}$ and $4f_{5/2}$ components of, respectively, 0.20 and 0.25 eV for the bulk and 0.23 and 0.25 eV for the surface components were used to produce¹² the fits shown in Fig. 2. These Gaussian widths are larger than the instrumental broadening, which means that other broadening effects may be present. Before considering why surface-shifted levels are observed both in the W $4f$ and C $1s$ levels on this polar surface, which is expected to be metal terminated,^{5,13} we make an estimate of the surface shift expected for, respectively, tungsten and carbon termination.

A thermochemical model,^{14,15} which accounts for the final-state screening of the core hole, has previously been used quite successfully to estimate core-level shifts for metals and compounds. The total shift can, in this model, be expressed as a sum of partial shifts and the partial shift originating from the loss of coordination is often considered to be the dominating one.^{14,15} This partial shift is given as the product of an effective concentration parameter and a difference in cohesive energies. This difference is taken between a compound, where the atoms of the element investigated (a Z element) are changed to atoms of a $Z + 1$ element and the studied compound. No tabulated values of cohesive energies for the compounds of interest in the hexagonal form could, however, be found. Therefore, recently tabulated cohesive energy values¹⁶ for these compounds in the sodium chloride structure had to be used as an approximation. The additional uncertainty introduced by this should be small if the difference in cohesive energy between the hexagonal and sodium chloride phases is similar (or very small) for the different carbides. Using these tabulated values¹⁶ a difference in cohesive energy between WN and WC of -1.24 eV is obtained. If the surface atoms at the (0001)

surface of a bulk truncated crystal are assumed to lose half of their six nearest neighbors (a total loss of coordination corresponds to an effective concentration parameter equal to 1), then a shift towards lower binding energy of 0.62 eV is expected for the carbon level. For the tungsten levels a negative shift of 0.39 eV is obtained since the difference in cohesive energy between ReC and WC is -0.78 eV. Thus the direction and size of the shifts are for both the C $1s$ and the W $4f$ levels, predicted very well by this model. In earlier core-level experiments on transition-metal carbides and nitrides^{1–3} the model estimated the correct direction but a smaller size of the shift for the nonmetal levels. For the metal levels small shifts were predicted but could not be observed experimentally. The differences, particularly for the nonmetal levels, were suggested to depend on the rippled reconstruction observed^{17,18} on (100) surfaces of carbides and nitrides. Such a reconstruction is not expected for the polar WC(0001) surface, where every second layer consists of tungsten and every second of carbon. Relaxation effects have, however, been observed¹⁹ on polar carbide surfaces, which are believed to be metal terminated.¹³ Since surface shifts were observed both in the carbon and tungsten levels this surface is most probably terminated with both carbon and tungsten areas, areas separated by steps in the surface. It seems very unlikely that carbon in a layer underneath a surface tungsten layer can give rise to a shift in the C $1s$ level of the magnitude observed. Effects observed upon oxygen exposures also support the interpretation that carbon-terminated areas exist on the surface.

In order to illustrate the effects upon oxygen exposures core-level and valence-band spectra recorded on the clean surface and after an oxygen dose of 30 L are shown in Figs. 3–5. The O $1s$ spectra in Fig. 3 show that no oxygen signal can be detected on the clean surface but that a strong O $1s$ peak appears after an exposure of 30 L. A similar observation is made in the valence-band spectra shown in Fig. 4. For the clean surface the valence-band spectrum is dominated by contribution from W $5d$ states,⁵ located between 0 and 6 eV. The weak broad structure located around 12 eV originates from C $2s$ states. After an exposure of 30 L a strong O $2p$ signal appears at about 6 eV and also a weak O $2s$ signal at about 22 eV. The structure located around 12 eV is seen to be slightly narrower in the 30-L spectrum, which may indicate the presence of some CO on the surface.^{2,20} Effects upon oxygen exposures on the C $1s$ and W $4f$ core levels are shown in Fig. 5. These results support the earlier assignment made, of the bulk component at higher binding energy and the surface-shifted component at lower binding energy, both in the case of C $1s$ and W $4f$. In the C $1s$ spectrum the surface-shifted component and the earlier discussed contaminant peak are both seen to become strongly attenuated after oxygen exposure. This sensitivity is interpreted to indicate that carbon-terminated areas do exist on the surface. If carbon should exist only in layers underneath a surface tungsten layer this high sensitivity to oxygen adsorption would not be expected. The W $4f$ spectra in Fig. 5 show that the surface-shifted doublet becomes strongly attenuated in the 30-L spectrum

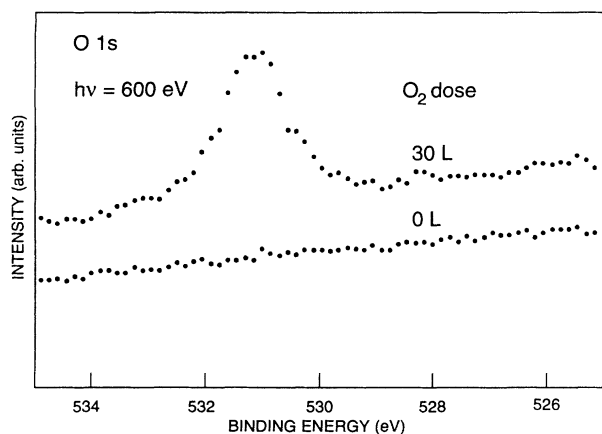


FIG. 3. O 1s core-level spectra recorded from the clean surface and after an oxygen dose of 30 L.

but moreover that chemically shifted $4f$ peaks, shifted to larger binding energy, appear after the oxygen exposure. The curve-fitting procedure was utilized to extract the chemical shifts. In this case only the $4f_{7/2}$ components were used in order to get a reasonable number of components to fit. When using the same fitting parameters for the oxygen-derived structures as used previously for the surface-shifted component, the results shown in Fig. 6 were obtained. Two additional components, shifted to larger binding energy and labeled C1 and C2 in Fig. 6, were found to be needed in order to obtain reasonable fits. Chemical shifts of +0.29 and +0.66 eV were extracted for the C1 and C2 components. For the surface component (labeled S) the shift was found to decrease to -0.29 eV after the oxygen exposures. The chemically shifted components should correspond to either chemisorption or oxidation states. The appearance of additional $4f$ peaks at 0.4–1.3 eV larger binding energy than the bulk peak was revealed upon adsorption of oxygen in a previous study⁹ of tungsten surfaces. Three chemically shifted W $4f$ levels were observed in investigations of ox-

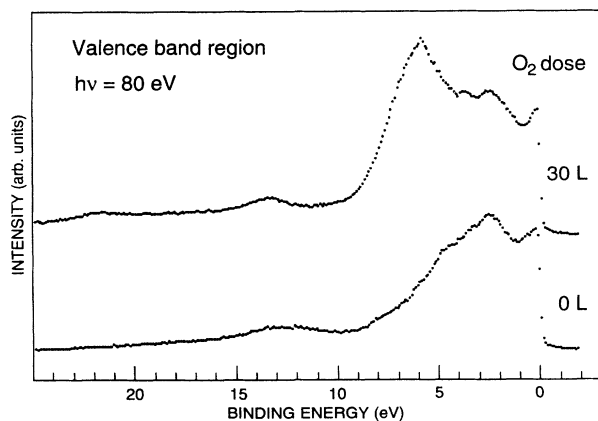


FIG. 4. Valence-band spectra recorded from the clean surface and after an oxygen dose of 30 L.

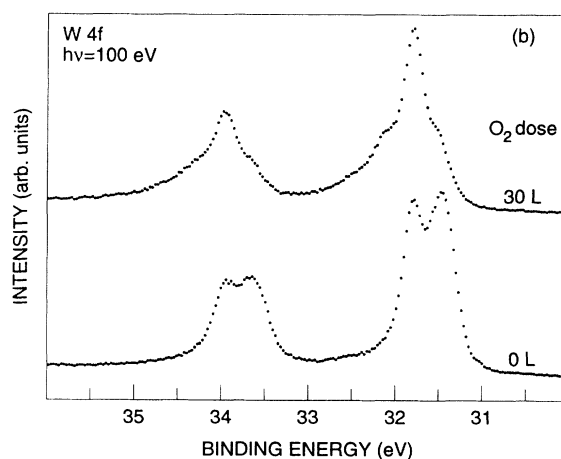
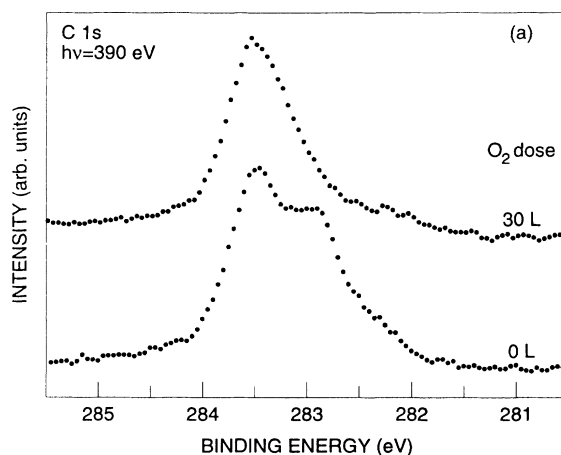


FIG. 5. (a) C 1s and (b) W $4f$ core-level spectra recorded from the clean surface and after an oxygen dose of 30 L.

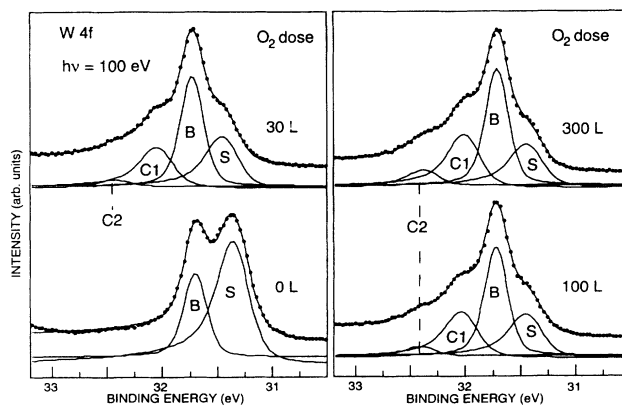


FIG. 6. The dots show W $4f_{7/2}$ spectra recorded from the clean surface and after oxygen exposures of 30, 100, and 300 L. The solid line through the data points shows the results of a curve-fitting procedure. The curves below each spectrum show the fitted bulk (B), surface-shifted (S), and chemically shifted (C1 and C2) components.

dized tungsten films^{21,22} and were shown to be associated with specific formal oxidation states. For the +2 oxidation state a chemical shift of 0.61–0.73 eV to larger binding energy was determined. Based on these earlier results^{9,21,22} the C1 component observed is interpreted to originate from a chemisorption state while the C2 component corresponds well to the +2 oxidation state. Upon increasing the exposure both these components were found to increase in relative intensity, with a larger rate, for the C2 component as seen in Fig. 6. In the valence band and O 1s spectra the only changes observed at the larger exposures, compared to the 30-L spectra, were a gradual increase in the oxygen-related features. These results tend to indicate that the carbon at the surface disappears upon oxygen exposures, probably by CO formation and desorption as was suggested to be the case for ZrC(100).² The surface saturates gradually, as in the case of pure tungsten,⁹ and chemisorption and oxidation states are formed as indicated by the chemically shifted W 4f components and the appearance of a single O 1s peak. A more detailed study of the initial oxidation behavior of this surface could unfortunately not be performed due to experimental circumstances.

IV. SUMMARY

A high-resolution core-level-photoemission investigation of hexagonal WC(0001) utilizing synchrotron radiation has been reported. Surface-shifted components both in the C 1s and W 4f level could be identified. The surface shifts extracted for the C 1s and W 4f component were –0.66 and –0.39 eV, respectively. The shifts predicted using a thermochemical model and assuming perfect bulk termination were in good agreement with the observed core-level shifts, although cohesive energies from compounds in the NaCl structure had to be used. Upon oxygen exposures the surface-shifted W 4f components were found to shift slightly and to be strongly attenuated. Two chemically shifted W 4f components, having shifts of +0.29 and +0.66 eV, appeared upon oxygen exposures and were found to increase in relative intensity with increasing exposure.

ACKNOWLEDGMENTS

The authors would like to thank the staff at the MAX laboratory for their assistance during the experiments and the Swedish Natural Science Research Council for their financial support.

¹K. L. Håkansson, L. I. Johansson, M. Hammar, and M. Göthelid, *Phys. Rev. B* **47**, 10 769 (1993).

²K. L. Håkansson, H. I. P. Johansson, and L. I. Johansson, *Phys. Rev. B* **48**, 2623 (1993).

³L. I. Johansson, H. I. P. Johansson, and K. L. Håkansson, *Phys. Rev. B* **48**, 14 520 (1993).

⁴L. E. Toth, *Transition Metal Carbides and Nitrides* (Academic, New York, 1971).

⁵P. M. Stefan, M. L. Shek, I. Lindau, W. E. Spicer, L. I. Johansson, F. Herman, R. V. Kasowski, and G. Brogen, *Phys. Rev. B* **29**, 5423 (1984).

⁶J. N. Andersen, O. Björneholm, A. Sandell, R. Nyholm, J. Forsell, L. Thånell, A. Nilsson, and N. Mårtensson, *Synch. Radiat. News* **4**, 15 (1991).

⁷P. H. Mahowald, D. J. Friedman, G. P. Carey, K. A. Bertness, and J. J. Yeh, *J. Vac. Sci. Technol. A* **5**, 2982 (1987).

⁸M. P. Seah and W. A. Dench, *Surf. Interface Anal.* **1**, 2 (1979).

⁹J. F. van der Veen, F. J. Himpsel, and D. E. Eastman, *Phys. Rev. B* **25**, 7388 (1982).

¹⁰G. K. Wertheim and P. H. Citrin, *Phys. Rev. B* **38**, 7820 (1988).

¹¹D. M. Riffe, G. K. Wertheim, and P. H. Citrin, *Phys. Rev. Lett.* **63**, 1976 (1989).

¹²Two different approaches were tried which resulted in fits of similar quality over the photon energy range investigated. In one of the approaches the Gaussian broadening was kept the same for all four components and a Lorentzian width was selected for each component. Using this procedure Lorentzian widths for the 4f_{7/2} and 4f_{5/2} components of 0.07 and 0.14 eV for the bulk and of 0.15 and 0.20 eV for the surface components were found to produce good fits when a Gaussian broadening of 0.21 eV was used. In the other approach Lorentzian widths of 0.08 and 0.13 eV for the bulk and sur-

face components were used and a Gaussian width was selected for each component. In this case Gaussian widths of 0.20 and 0.25 eV for the bulk and 0.23 and 0.25 eV for the surface 4f_{7/2} and 4f_{5/2} components, respectively, were found to produce good fits over the photon energy range investigated. Asymmetry parameters of 0.02 for the bulk and 0.16 for the surface components were in both cases found to produce best fits. The same surface core-level shift was extracted using these two different procedures.

¹³M. Hammar, C. Törnevik, J. Rundgren, Y. Gauthier, S. A. Flodström, K. L. Håkansson, L. I. Johansson, and J. Häglund, *Phys. Rev. B* **45**, 6118 (1992), and references therein.

¹⁴B. Johansson and N. Mårtensson, *Phys. Rev. B* **21**, 4427 (1980).

¹⁵A. Nilsson, B. Eriksson, N. Mårtensson, J. N. Andersen, and J. Onsgaard, *Phys. Rev. B* **38**, 10 357 (1988).

¹⁶A. Fernández Guillermet, J. Häglund, and G. Grimvall, *Phys. Rev. B* **48**, 11 685 (1993).

¹⁷G. R. Gruzalski, D. M. Zehner, J. R. Noonan, H. L. Davis, R. A. Didio, and K. Müller, *J. Vac. Sci. Technol. A* **7**, 2054 (1989).

¹⁸Y. Gauthier, Y. Joly, J. Rundgren, L. I. Johansson, and P. Wincott, *Phys. Rev. B* **42**, 9328 (1990).

¹⁹J. Rundgren, Y. Gauthier, R. Baudoing-Savois, Y. Joly, and L. I. Johansson, *Phys. Rev. B* **45**, 4445 (1992).

²⁰G. Brodén, T. N. Rhodin, C. Bruckner, R. Benbow, and Z. Hurych, *Surf. Sci.* **59**, 593 (1976).

²¹J. F. Morar, F. J. Himpsel, G. Haughes, J. L. Jordan, F. R. McFeely, and G. Hollinger, *J. Vac. Sci. Technol. A* **3**, 1477 (1985).

²²F. J. Himpsel, J. F. Morar, F. R. McFeely, R. A. Pollak, and G. Hollinger, *Phys. Rev. B* **30**, 7236 (1984).