High-resolution core-level study of ZrC(100) and its reaction with oxygen

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Results from a high-resolution core-level photoemission investigation of the (100) surface of a $ZrC_{0.92}$ single crystal using synchrotron radiation are reported. A surface-shifted component was identified in the C 1s level while no shifted component could be observed in the Zr 3d level. A surface C 1s core-level shift of -0.23 eV was 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 -0.07 eV was predicted for the carbon level. Oxygen exposures were made for investigating the initial oxidation behavior and also for aiding in the assignment of surface-shifted features.

I. INTRODUCTION

Surface core-level shifts in the C 1s level were recently revealed[1] in an investigation of two different surfaces of VC while no surface shift could be observed in the V 2p level. Since most transition-metal carbides and nitrides crystallize in the sodium chloride structure[2] their (100) surfaces are expected to expose a mixed surface layer and therefore it should, in principle, be possible to observe surface-shifted core levels both in the metal and the nonmetal levels. No surface core-level shifts have, however, been observed in investigations[1,3] of the metal levels on (100) surfaces of VC, TaC, and HfC while a surface shift has been detected[4] in the Hf 4f level on HfN(100). A calculation of the surface electronic properties of TiC(100) (Ref. 5) predicted no surface core-level shift in the C 1s level but a small shift in the Ti s levels. These findings motivated further investigations of the occurrence of surface-shifted nonmetal and metal levels on carbide surfaces.

In this investigation, high-resolution core-level studies of ZrC(100) using synchrotron radiation have been performed. One reason for chosing ZrC was that the Zr 3d level is expected to have a considerably smaller intrinsic linewidth than the previously investigated V 2p level, and also smaller than, for example, the Ti 2p and Nb 3d levels.[6,7] Besides this, the Zr 3d level is located at a lower binding energy which means that a lower photon energy can be used and a better experimental energy resolution can be obtained. This should increase the possibility of observing a shift in the metal level. Oxygen exposures were made for the purpose of aiding in the identification of surface-shifted levels and also for studying effects of initial oxidation.

II. EXPERIMENTAL DETAILS

The experiments were performed at the synchrotron radiation facility MAX Laboratory in Lund, Sweden. The beamline utilized is equipped with a modified SX 700 monochromator and a large hemispherical electron analyzer from Scienta.[8,9] Both the photon-energy resolution and the resolution of the electron analyzer depend on the operating parameters. A total instrumental broadening of about 0.2 eV was typically chosen in the high-resolution studies of the C 1s level. Normal emission and an incidence 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 $\pm 8°$.

The growth of the $ZrC_{0.92}$ single crystal is described elsewhere.[10] The surface was cleaned *in situ* by flash heatings to about 1600 °C. This cleaning procedure produced a clean and well-ordered 1×1 surface as checked by 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 L$=10^{-6}$ Torr s). The base pressure in the spectrometer was 5×10^{-11} Torr.

III. RESULTS AND DISCUSSION

C 1s spectra recorded at three different photon energies, 315, 330, and 345 eV, from the ZrC(100) surface are shown by the dots in Fig. 1. The two spectra recorded at photon energies of 315 and 330 eV are seen to be broader than the one recorded at 345 eV. Since the total instrumental energy resolution was decreasing with increasing photon energy this indicates that two components are needed in order to model the recorded spectra. A curve-fitting procedure[11] was applied and the results are shown by the solid lines through the data points in Fig. 1. The two fitted components are shown by the solid curves below the recorded spectra and the third solid line shows the integrated background which has been subtracted in order to compensate for inelastically scattered electrons. The spectrum recorded at 345 eV is expected to be the least surface sensitive of those shown in Fig. 1 due to the kinetic-energy dependence of the electron mean free path.[12] The intensity ratio between the two fitted components thus indicate that the component at lower binding energy is surface related and the one at higher binding energies is bulk related. A spectrum recorded at 375 eV also confirmed this although it is not shown in Fig. 1.

Using these four C $1s$ spectra a surface core-level shift of -0.23 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 $281.5(\pm 0.1)$ eV relative to the experimental Fermi level. The C $1s$ level is thus located around 1 eV closer to the Fermi level in ZrC than in VC where a binding energy of 282.5 eV was reported.[1]

A Lorentzian full width at half maximum of 0.32 eV and an asymmetry parameter of 0.02 were used as fitting parameters for both the bulk and surface C $1s$ level. These parameters were obtained when trying to find values giving good fits of the C $1s$ spectra while keeping the instrumental (Gaussian) broadening similar to what was used in the earlier experiments on VC.[1] The Lorentzian width needed for the C $1s$ level in ZrC was then around 0.1 eV larger than in VC. Fits were also made using other parameters but they all resulted in the same surface shift and also in very similar surface to bulk intensity ratios.
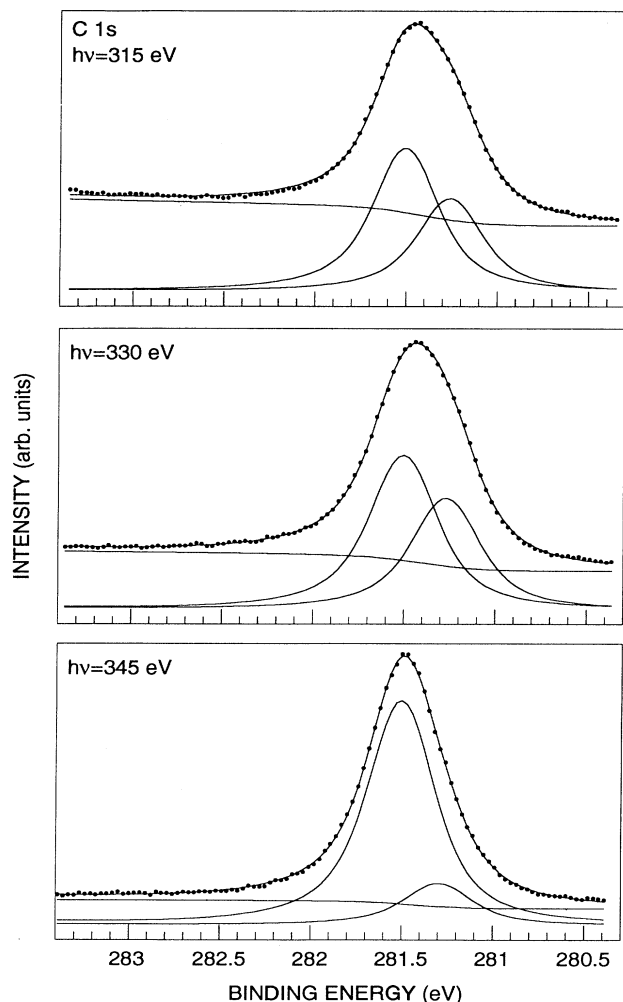
Zr $3d$ spectra were recorded at different photon energies, between 215 and 245 eV, in an effort to reveal surface-shifted levels. No shifted component could, however, be observed using this method and therefore we tried a different procedure. Since the surface sensitivity increases with increasing electron emission angle a comparison of spectra recorded at normal emission and at a large emission angle should reveal the occurrence of surface-shifted components. Normalized and background subtracted Zr $3d_{5/2}$ spectra recorded at two different emission angles, 0° and 50°, using a photon energy of 245 eV, are shown in Fig. 2. The structureless dotted curve shows the difference spectrum and indicates that no shifted component can be revealed in the Zr $3d$ level using this procedure. The solid line through the data points in the 0° spectrum shows a fit using a single component. The parameters used are a Gaussian width of 0.21 eV, a Lorentzian width of 0.29 eV and an asymmetry parameter of 0.09. The fit is, however, not really satisfactory and attempts to fit these spectra, by using two components, were also made but the quality of the fits were just marginally improved. We have to conclude, therefore, that no shifted component can be identified. This has been the case for the metal levels also in earlier studies on (100) surfaces of monocarbides of group-IV and -V transition metals,[1,3] i.e., of VC, TaC, and HfC.

In order to estimate the expected core-level shifts, a thermochemical model,[13] which expresses the total shift as a sum of partial shifts, can be used. The partial shift originating from the loss of coordination, which often is considered to be the dominating one,[13,14] 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) is changed to atoms of a $Z+1$ element, and the studied compound. When using tabulated values[15] a difference in cohesive energy between ZrN and ZrC of -0.41 eV is obtained. If the surface atoms at the (100) surface of a bulk truncated crystal is assumed to

FIG. 1. C $1s$ core-level spectra, recorded from the ZrC(100) surface at three different photon energies, are shown by the dotted curves. The solid lines show the results of a curve-fitting procedure (see text for details).
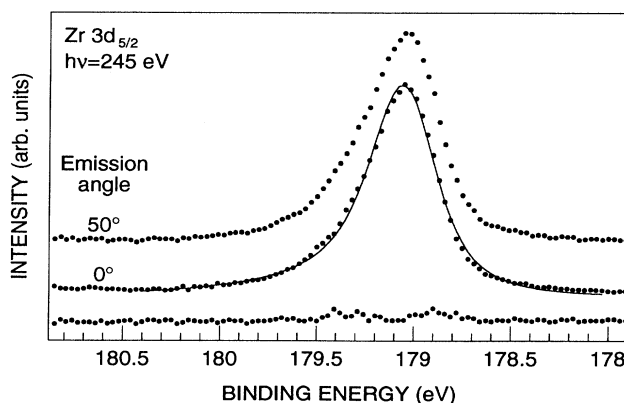

FIG. 2. Zr $3d_{5/2}$ core-level spectra recorded at two different emission angles. The solid line in the 0° spectrum shows a fit using a single component and the bottom dotted curve shows the difference spectrum between the two recorded core-level spectra.

lose one of its six nearest neighbors (a total loss of coordination corresponds to an effective concentration parameter equal to one), then a shift towards lower binding energy of 0.07 eV is expected for the carbon level. For zirconium levels a positive shift of 0.05 eV is obtained since the difference in cohesive energy between NbC and ZrC is +0.33 eV. The predicted direction of the shift is thus correct for the C $1s$ level but the estimated size is much smaller than what is observed experimentally. In the case of VC(100),[1] the model predicted a negative shift of about 0.1 eV for the C $1s$ level while a shift of -0.33 eV was determined experimentally. The model accounts only for the loss of coordination for the surface atoms at a bulk truncated crystal and other effects may be present. Low-energy electron diffraction studies of the (100) surface of TaC,[3,16] HfC,[3] and VN (Ref. 17) have shown a rippled reconstruction in the surface layer, with the nonmetal atoms displaced outwards and the metal atoms inwards. If ZrC and VC are terminated with a similar rippled surface, which we believe they are, the surface core-level shifts should be affected. Since the carbon atoms at the surface will be located further away from the nearest neighbors (which all are metal atoms) than if the termination was just a truncated crystal, a larger shift in the C $1s$ level towards lower binding energy may well be anticipated. The metal atoms closest to the surface, on the contrary, experience a surrounding that is more similar to bulk atoms and may be expected to be less affected. The rippled termination of the (100) surface may thus provide an explanation to the discrepancy between the experimental core-level shifts and the shifts predicted by the thermochemical model.

The effects on the C $1s$ and Zr $3d$ core levels upon oxygen exposures were also investigated and the results are shown in Fig. 3, where all spectra are raw data without background subtraction. The growth of the O $1s$ signal upon different exposures is illustrated in Fig. 3(a) while

the effects on the Zr $3d$ levels are shown in Fig. 3(b). For the clean surface the binding energy of the Zr $3d_{5/2}$ level was determined to be $179.05(\pm 0.05)$ eV and the spin-orbit split to be 2.40 eV. In pure Zr metal,[18,19] the spin-orbit split is the same but the Zr $3d_{5/2}$ level is located at 178.7 eV. Oxidation studies of pure Zr metal[18,19] have revealed suboxide formation during the initial stages, at exposures below about 10 L, and ZrO_2 growth at larger exposures. ZrO_2 growth was identified by the appearance of a chemically shifted Zr $3d$ component, shifted by $+4.2$ eV. The formation of suboxides was identified by the appearance of an intermediately shifted Zr $3d$ component having a chemical shift of between $+1$ and $+2$ eV. In the latest study it was suggested[18] that two different suboxides are formed since the position of the intermediately shifted Zr $3d$ component is seen to appear at the high-binding-energy side of the clean $3d$ doublet. The position of this shifted component appears to shift towards larger binding energy when increasing the exposure up to 30 L. At larger exposures a Zr $3d$ component, shifted by about $+2.7$ eV, and interpreted to originate from ZrO_2, appears in the spectrum. It is clear from these observations that different types of zirconium oxides are formed during the initial stages also on ZrC(100), although the shifts both for ZrO_2 and the suboxides are smaller than on pure Zr. The effects on the C $1s$ level are shown in Fig. 3(c). At the smallest exposures the surface-shifted C $1s$ level (the shoulder at the low binding-energy side in the clean spectrum) is seen to shift away from the bulk level and decrease in intensity. This is as expected and supports our earlier assignment. The C $1s$ level appearing around 283 eV and most pronounced at the intermediate exposures is more difficult to understand. Formation of suboxide complexes also involving carbon and giving rise to a larger chemical shift in the C $1s$ level than in the Zr $3d$ level seems unlikely to us. Dis-
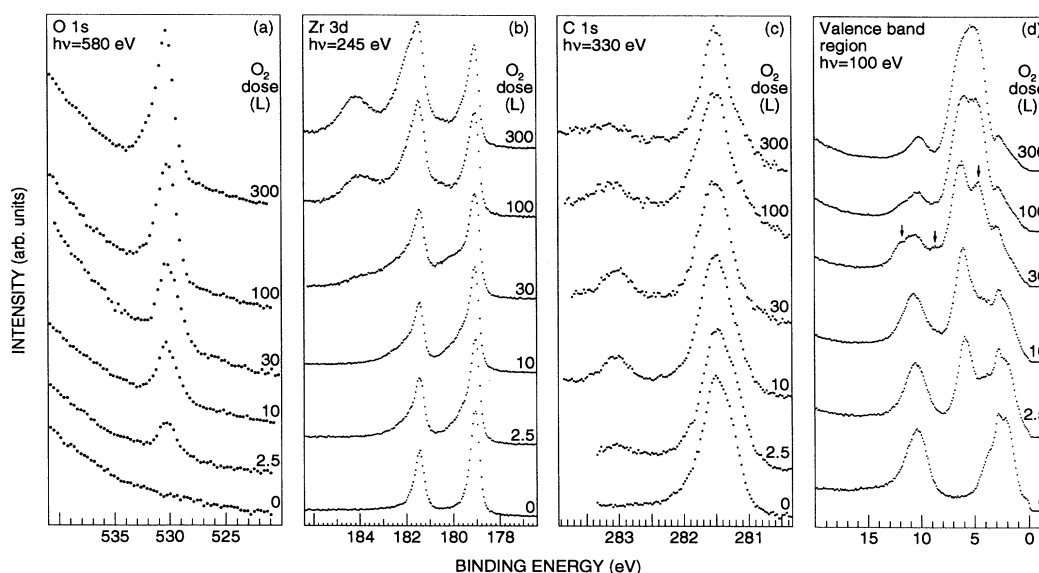

FIG. 3. (a) O $1s$, (b) Zr $3d$, (c) C $1s$, and (d) valence-band spectra recorded from the clean surface and after different oxygen exposures.

sociative adsorption of oxygen[19] is expected on ZrC and this is actually also observed in recorded valence-band spectra at the smallest exposure, see Fig. 3(d). In the clean valence-band spectrum two main features are observed; the valence band arising from hybridized Zr $4d$ and C $2p$ states, distributed between 0 and 5 eV, and a C $2s$ peak, located around 10.5 eV. After the smallest oxygen exposure (2.5 L) an O $2p$ peak appears around 6 eV which indicates dissociative oxygen adsorption. After larger exposures new features are, however, seen to appear. In the 30-L spectrum a second O $2p$ derived structure is observed around 4.5 eV,[20] but also weaker structures around 11.5 and 8.5 eV, as shown by the arrows in Fig. 3(d). The energy positions of these latter two structures agree well with the positions expected for the σ- and π-derived molecular orbitals upon CO adsorption on transition metals.[21,22] At the largest exposure investigated these structures are, however, not present. These results therefore tend to indicate that carbon is pushed out on the surface by the smaller exposures. At the largest exposure, 300 L, this carbon seems to have been desorbed, probably by CO formation and desorption, since the carbon peak around 283 eV is seen to have a considerably smaller relative intensity and the structures observed around 11.5 and 8.5 eV in the valence-band spectrum at the intermediate exposures have disappeared.

IV. SUMMARY

A high-resolution core-level photoemission investigation of $ZrC_{0.92}(100)$ utilizing synchrotron radiation has been reported. A surface-shifted C $1s$ level was revealed but no shift in the Zr $3d$ level could be identified. The surface shift extracted for the C $1s$ component was -0.23 eV. The shifts predicted using a thermochemical model and assuming perfect bulk termination was -0.07 eV for the carbon level and $+0.05$ eV for the zirconium levels. The differences between the model and the experimental results were suggested to arise from a possible rippled reconstruction at the surface. Effects induced in the core-level spectra upon oxygen exposure were also presented. Initial suboxide formation and ZrO_2 growth at larger exposures could be identified from the recorded Zr $3d$ level. The C $1s$ spectra indicated that carbon seemed to be pushed out on the surface by small oxygen exposures and that at larger exposures this carbon was desorbed, probably by CO formation.

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

[2]L. E. Toth, Transition Metal Carbides and Nitrides (Academic, New York, 1971).

[3]G. 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).

[4]L. I. Johansson, K. L. Håkansson, P. L. Wincott, D. S. L. Law, and J. E. Inglesfield, Phys. Scr. **41**, 565 (1990).

[5]E. Wimmer, A. Neckel, and A. J. Freeman, Phys. Rev. B **31**, 2370 (1985).

[6]N. Mårtensson and R. Nyholm, Phys. Rev. B **24**, 7121 (1981).

[7]R. Nyholm, N. Mårtensson, A. Lebugle, and U. Axelsson, J. Phys. F **11**, 1727 (1981).

[8]R. Nyholm, S. Svensson, J. Nordgren, and S. A. Flodström, Nucl. Instrum. Methods Phys. Res. A **246**, 267 (1986).

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

[10]A. N. Christensen, J. Cryst. Growth **33**, 99 (1976).

[11]P. H. Mahowald, D. J. Friedman, G. P. Carey, K. A. Bert-

ness, and J. J. Yeh, J. Vac. Sci. Technol. A **5**, 2982 (1987).

[12]M. P. Seah and W. A. Dench, Surf. Interf. Anal. **1**, 2 (1979).

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

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

[15]A. Fernández Guillermet, J. Häglund, and G. Grimvall, Phys. Rev. B **45**, 11 557 (1992).

[16]J. R. Noonan, H. L. Davis, and G. R. Gruzalski, J. Vac. Sci. Technol. A **5**, 787 (1987).

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

[18]C. O. de Gonzalez and E. A. Garcia, Surf. Sci. **193**, 305 (1988).

[19]P. Sen, D. D. Sarma, R. C. Budhani, K. L. Chopra, and C. N. R. Rao, J. Phys. F **14**, 565 (1984).

[20]C. Oshima, S. Otani, M. Aono, S. Zaima, and Y. Shibata, Jpn. J. Appl. Phys. **22**, 930 (1983).

[21]D. Tomanek, R. Hauert, P. Oelhafen, R. Schlögl, and H.-J. Güntherodt, Surf. Sci. **160**, L493 (1985).

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