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Surface-shifted N 1*s* and C 1*s* levels on the (100) surface of TiN and TiC

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A high-resolution core-level-photoemission investigation of the (100) surface of TiN and TiC is reported. A surface-shifted component is revealed in both the N 1*s* level on TiN and in the C 1*s* level on TiC. Using a curve-fitting procedure a surface shift of -0.57 eV is extracted for the N 1*s* component on TiN and a shift of -0.26 eV for the C 1*s* component on TiC. No surface-shifted Ti 2*p* level could be revealed on either TiN or TiC. These results do not agree with earlier calculated results for TiC which predicted no surface shift in the C 1*s* level but a small positive shift in the Ti *s* levels. Using a thermochemical model and accounting only for the loss of coordination at the surface, a shift of -0.07 eV is estimated both for the N 1*s* level in TiN and for the C 1*s* level in TiC.

I. INTRODUCTION

This investigation is primarily aimed at elucidating the existence of surface core-level shifts in the C 1*s* and N 1*s* levels on the (100) surfaces of TiC and TiN. One motivation for these studies was that while surface-shifted C 1*s* levels recently have been revealed on other carbide surfaces,[1,2] no such results have so far been reported concerning the N 1*s* level on nitride surfaces. Another reason was that calculated results[3] for TiC(100) using the fully linearized augmented-plane-wave method (FLAPW) predicted no surface core-level shift in the C 1*s* level but a surface shift of about $+0.05$ eV for the Ti *s* levels. The absence of a surface core-level shift in the C 1*s* level on TiC was used to argue[3,4] that no overall shift in the electrostatic potential for the surface atoms could be expected on TiC nor on TiN since the ionicity of TiN is known to be similar to that of TiC. This cast doubts on earlier interpretations[5,6] of, for example, a surface state observed on TiN(100) and interpreted as a Tamm state, i.e., a state originating from a shift in the surface-layer potential large enough to pull a surface state out of a bulk band. High-resolution core-level studies of TiC and TiN could possibly resolve this issue, since the presence of surface-shifted C 1*s* and N 1*s* levels would imply the possibility of an overall electrostatic shift in the surface-layer potential. The results presented below clearly show the presence of a surface-shifted component in both the C 1*s* level on TiC and in the N 1*s* level on TiN. No surface shift could, however, be detected in the Ti 2*p* level on these surfaces.

II. EXPERIMENT

The experiments were performed at beamline 22 at the MAX I storage ring in Lund, Sweden. This beamline[7] is equipped with a modified SX700 monochromator and a large hemispherical electron analyzer from Scienta. A total instrumental energy resolution (photon plus analyzer) ranging from about 0.2 eV at the carbon edge to about 0.4 eV at the titanium edge was typically chosen in these experiments. Normal electron emission and a photon incidence angle of 40° was selected as the experimental geometry. The electron analyzer has acceptance angles of approximately ±8° in the horizontal direction and ±1° in the vertical direction. The TiC and TiN crystals[8] were cleaned *in situ,* initially by a 5-min Ar^+ ion sputtering and then by repeated flash heatings, as was used earlier.[9,10] The cleanliness of the surfaces was checked by monitoring the core levels of likely contaminants (O, C, and S) and by measurements of the valence-band region. No oxygen or sulfur could be detected on the TiC surface but carbon segregation could be observed at high flashing temperatures. Flashings of this surface were, therefore, carried out at the lowest temperature found to produce a well ordered surface. No sulfur or carbon was detected on the TiN surface but oxygen buildup could be observed after about 1 h. This surface is known to be extremely reactive towards oxygen[10] and was, therefore, flashed every hour. The base pressure of the system used was $<1\times10^{-10}$ torr. Distinct 1×1 low-energy electron-diffraction patterns with sharp diffraction spots and a low background intensity were obtained after cleaning.

III. RESULTS AND DISCUSSION

High-resolution N 1*s* spectra recorded from TiN(100) using three different photon energies are shown by the dotted curves in Fig. 1. Two features are clearly resolved in these spectra and their relative intensities show pronounced variations when changing the kinetic energy of the photoelectrons. In the 440-eV spectrum the low-binding-energy feature is seen to be the dominating structure while the high-binding-energy feature is dominating in the 470-eV spectrum. This energy dependence[11] allows us to conclude that the high-binding-energy feature is the bulk peak while the low-binding-energy feature is a surface-shifted component. In order to extract the shift of the surface component, a curve-fitting procedure was utilized.[12] The results of this fitting procedure are shown by the solid curves through the data points in Fig. 1 and the two fitted components are shown by the two solid curves displayed below each recorded spectrum. The same Gaussian width and asymmetry parameter were selected for the two components in the fitting procedure. When allowing the Gaussian width to vary from 0.36 to 0.41 eV, when fitting spectra recorded at photon energies between 430 and 500 eV, best fits were obtained using an asymmetry parameter of zero and Lorentzian widths of 0.40 and 0.36 eV for the bulk and surface components. A surface core-level shift of $-0.57(\pm 0.02)$ eV was extracted, where the value in parentheses specifies the maximum deviation obtained. Concerning the fitting parameters, it should be noted that the Gaussian and Lorentzian widths have not been determined independently. The reported values represent the results of a fitting procedure in which the total instrumental energy resolution (photon plus analyzer) was assumed to be the Gaussian width. The Lorentzian width values obtained may, therefore, include other contributions apart from lifetime-broadening effects. This simple procedure was selected because the surface core-level shift value extracted was found to be insensitive to changes in these width parameters and other approaches tried gave fits of similar quality.

High-resolution C 1*s* spectra recorded from TiC(100) using three different photon energies are shown by the dotted curves in Fig. 2. The 330-eV spectrum shows that at least two components are present in this case also. From this and the 350-eV and 380-eV spectra, it is evident that one surface-shifted component is located at lower binding energy than the bulk component. However, when fitting these spectra and keeping the fitting parameters similar to those which have been used previously for the C 1*s* level on other carbide surfaces,[1,2] we found that we had to use three components. The third component (labeled *S*2 in Fig. 2), is seen to be fairly weak at all three energies and is located at a larger binding energy than the bulk component. When fitting spectra recorded between 330 and 380 eV and allowing the Gaussian width to vary from 0.23 to 0.27 eV, best fits were obtained when selecting an asymmetry parameter value of 0.04 and Lorentzian widths of 0.26 eV for the bulk component, 0.20 eV for component *S*1, and 0.40 eV for component *S*2. Shifts of, respectively, $-0.26(\pm 0.02)$ and $+0.43(\pm 0.04)$ eV were extracted for component *S*1 and *S*2. Judging from Fig. 2 alone, it appears that component *S*2 might be redundant, i.e., that fits of similar quality could be obtained by increasing the asymmetry parameter and using only two components. However, when flash heating the TiC crystal to a slightly higher temperature, the third component was observed to increase in intensity and after several of these flashings a weak shoulder could actually be observed on the high-binding-energy side of the bulk peak. Therefore, we interpret this component to originate from carbon segregated to the surface while component *S*1 is interpreted as originating from carbon in the carbide surface layer. The *B* and *S*1 components were not found to be affected by

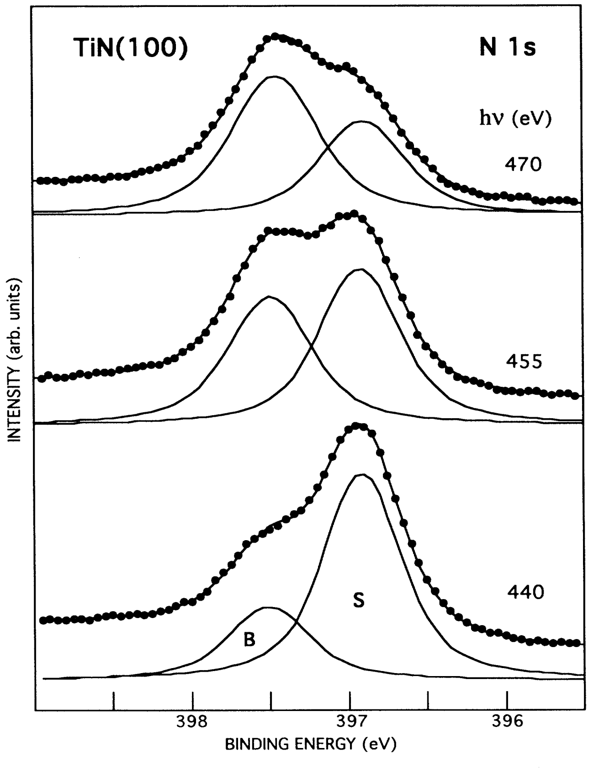

FIG. 1. N 1*s* photoemission spectra from TiN(100) recorded at three different photon energies (dotted curves). The results of a curve-fitting procedure are shown by the solid curves through the data points. The two solid curves below each recorded spectrum show the two fitted components.

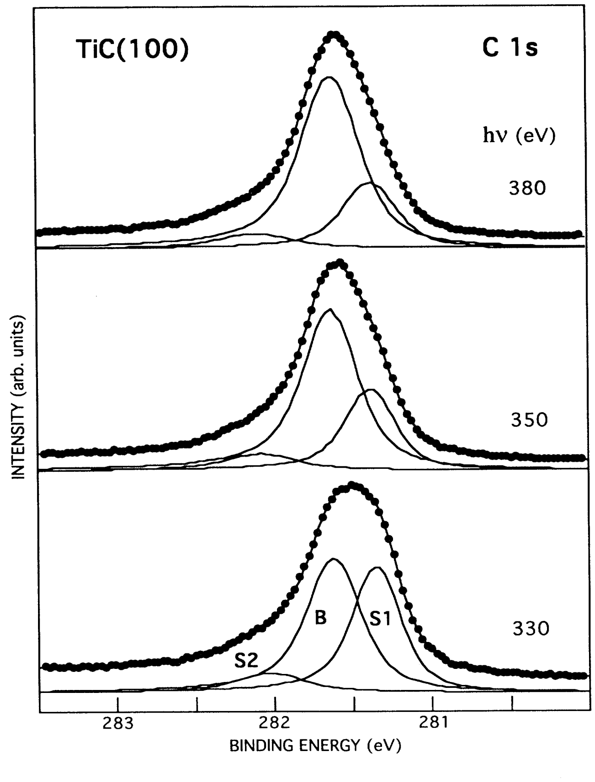

FIG. 2. C 1*s* photoemission spectra from TiC(100) recorded at three different photon energies (dotted curves). The results of a curve-fitting procedure are shown by the solid curves through the data points. The three solid curves below each recorded spectrum show the fitted components.

the higher temperature flashings. The spectra presented in Fig. 2 represents our best effort to eliminate this third component but the curve-fitting procedure showed it still to be there but with an intensity of about 10% of the bulk peak. Since we could not monitor the sample temperature well enough during the experiment to perform a systematic study of this component with temperature, this had to be left as an issue for future studies. This time we just tried to minimize its influence by performing flashings at successively higher temperatures until a good low-energy electron-diffraction (LEED) pattern was observed, which resulted in the spectra presented in Fig. 2. For the present investigation, though, observation of component $S1$ is important, since it shows the presence of a surface-shifted C 1s component on TiC(100).

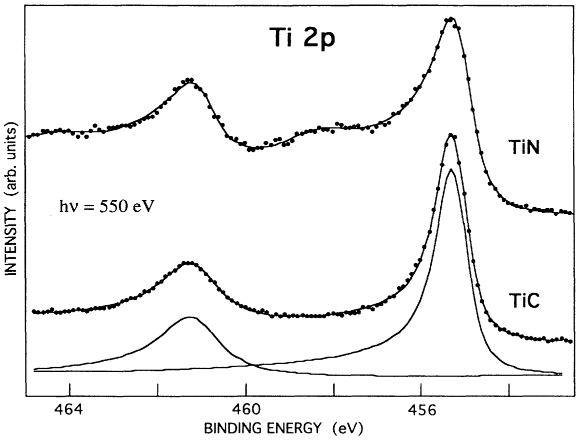

FIG. 3. Ti 2p photoemission spectra recorded from TiC(100) (lower dotted curve) and TiN(100) (upper dotted curve) using a photon energy of 550 eV. The solid curves through the data points show the results of a curve-fitting procedure. The two solid curves below the TiC spectrum show the fitted components. In the TiN spectrum additional broad structures shifted about +3.1 eV from the main 2p levels are visible and, therefore, four peaks were used when fitting this spectrum.

Calculated results predicted[3] a small positive shift in the Ti s levels on TiC(100). Since the Ti 3s level is fairly broad, however, we instead tried the narrower 2p levels on both TiC and TiN. A Ti 2p spectrum recorded from TiC using a photon energy of 550 eV is shown in Fig. 3 by the lower dotted curve. Since the two spin-split peaks observed have different lifetime widths, two components, displayed below the recorded spectrum, were used when fitting this spectrum. The solid curves through the data points show the result of the fitting procedure. The parameters producing this curve were an asymmetry parameter of 0.18, a Gaussian width of 0.47 eV, and Lorentzian widths of, respectively, 0.48 and 1.32 for the $2p_{3/2}$ and the $2p_{1/2}$ component. Spectra were recorded also at 500 and 520 eV and at an emission angle of 50° but no surface-shifted component could be identified on TiC. Since the total resolution at these energies was ≥ 0.4 eV, this means only that no surface shift of about that magnitude or larger could be identified on this surface. This was also the case for TiN, which is illustrated by the upper dotted curve in Fig. 3. The Ti 2p levels are, in this case, seen to be broader and have a larger asymmetry, and additional broad structures shifted about +3.1 eV from the main 2p levels can be observed. Four peaks were therefore used when fitting this spectrum and the result is shown by the solid line through the data points. Satellite structures in the Ti 2p spectrum of TiN have been observed earlier[13] and have been attributed to screening effects of the core hole by the conduction electrons. The nitride crystal used has a bulk composition of $TiN_{0.83}$ while the carbide crystal has a bulk composition of $TiC_{0.93}$. The larger amount of nonmetal vacancies in the nitride crystal can provide an explanation of the larger width[14] of the Ti 2p levels in TiN. That the additional structures observed on TiN were not oxygen induced was checked by performing oxygen exposures of both the TiC and TiN crystal. Oxide-related Ti 2p peaks then appeared, shifted about +2.0 eV from the main 2p levels.

The results on TiC agree with recent findings on VC and ZrC surfaces,[1,2] that a surface-shifted C 1s component with a negative shift can be observed but that no surface-shifted component can be revealed in the metal levels. Calculated results for TiC predicted[3] a surface shift of +0.05 eV in the Ti s levels, which, however, would be too small for us to observe, but predicted, moreover, no surface shift in the C 1s level. These results obviously do not match. One reason for this may be that only initial-state effects were considered in the calculation, since the surface shift was derived from the difference in the core-level energy eigenvalue of an atom at the surface and in the bulk. That final-state screening of the core hole needs to be included when estimating surface core-level shifts has been shown by the success of the thermochemical model.[15,16] This model predicted for VC and ZrC (Refs. 1 and 2) the same sign but a smaller size of the C 1s surface shift than that which was observed experimentally. In this model, the surface shift is expressed as a sum of partial shifts. The partial shift originating from the loss of coordination at the surface, which often gives the dominant contribution,[15,16] 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 compound under investigation. Using tabulated experimental cohesive energy values[17] gives a difference between TiN and TiC of -0.463 eV and between VC and TiC of -0.218 eV. Assuming bulk truncation of the (100) surface means that a surface atom has lost one of its six nearest neighbors, resulting in an effective concentration parameter of $\frac{1}{6}$. For TiC, shifts of about -0.07 and -0.04 eV are predicted for the C 1s and Ti 2p levels, respectively. When applying this model to TiN, the experimental[17] and calculated[18] cohesive-energy difference between, respectively, VN and TiN, and TiO and TiN, predict a shift of about -0.07 eV for both the Ti 2p and N 1s levels. The model thus predicts the same sign but a smaller size than the experimentally determined N 1s and C 1s surface shifts. A smaller size can, however, be understood if a rippled reconstruction such as the one observed on the (100) surface of TaC,[19] HfC,[20] and VN (Ref. 21) do exist also on the (100) surface of TiN and TiC.

IV. SUMMARY

In summary, the high-resolution core-level investigation carried out on the (100) surface of TiN and TiC clearly shows the presence of surface shifts in the nonmetal core levels. The surface shift extracted using a curve-fitting procedure was -0.57 eV for the N 1*s* level on TiN and -0.26 eV for the C 1*s* level on TiC. No surface-shifted Ti 2*p* levels could, however, be observed on either the nitride or the carbide crystal. These findings show that an overall electrostatic shift in the surface-layer potential may well exist, contrary to the implications of earlier calculated results.[3] A negative surface shift is predicted both for the N 1*s* level in TiN and for the C 1*s* level in TiC using a thermochemical model and tabulated cohesive energies.

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