# High-resolution core-level studies of $VC_{0.80}$ surfaces

K. L. Håkansson and L. I. Johansson

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

M. Hammar and M. Göthelid

*Department of Material Science, Royal Institute of Technology, S-100 44 Stockholm, Sweden*

(Received 26 June 1992; revised manuscript received 14 December 1992)

High-resolution core-level-photoemission investigations of the (100), (111)-1×1, and (111)-8×1 surfaces of $VC_{0.80}$ using synchrotron radiation are reported. Surface-shifted C 1s levels were observed on all three surfaces while surface-shifted V 2p levels could not be identified on any of the surfaces. The surface core-level shifts were extracted using a curve-fitting procedure. For the major surface-shifted component which was identified on all three surfaces, a shift of −0.33(±0.02) eV was determined. For the (111)-8×1 surface a second shifted component having a shift of +0.44(±0.02) eV was identified.

## I. INTRODUCTION

The surface properties of refractory compounds have attracted considerable attention mainly because of the large variety of applications possible for these materials[1] but also because of the unusual combination of bonding properties that these compounds possess.[2] Experimental and theoretical investigations of the electronic structure of nitride and carbide surfaces have revealed surface states but different interpretations of their origin have been proposed. The surface states observed in experiments on TiN(100) and ZrN(100) were interpreted as originating from Tamm surface states,[3,4] i.e., from a shift in the surface-layer potential large enough to pull a surface state out of a bulk band. Calculated results[5,6] for TiC(100) using the full linearized-augmented-plane-wave method put this interpretation in doubt however, and it was proposed that the surface states observed did not originate from an overall electrostatic shift in the surface-layer potential. Instead, it was proposed that the extended valence states sample a less attractive potential in the surface vacuum region, due to charge rearrangement on the vacuum side of the surface layer, while the more localized core levels are little affected. The calculation predicted no surface core-level shift in the C 1s level and a surface-induced shift of about 50 meV towards a larger binding energy for the Ti s levels. The absence of a core-level shift in the C 1s level was argued to indicate that one could not expect an overall shift in the electrostatic potential for the surface atoms in TiN either since the ionicity of TiN is known to be similar to that of TiC. If surface-shifted C 1s levels could be observed or not was therefore a point of primary interest in these investigations of the two carbide surfaces.

In this investigation high-resolution core-level studies of the (100) and (111) surfaces of vanadium carbide are reported. The main objectives were (1) to reveal surface-shifted C 1s and V 2p levels, if any, (2) to investigate differences between the (100) and (111) crystal faces which are expected to have terminating layers of different compositions and, (3) to try to reveal differences in the terminating layer between the unreconstructed and reconstructed (111) surface. Transition-metal carbides often crystallize in the sodium chloride structure.[1] The (100) surface is then expected to expose a mixed surface layer while the polar (111) surface is believed to be metal terminated.[7,8] For vanadium carbide the (111) surface forms a metastable 1×1 structure on argon-ion bombardment and annealings not exceeding a temperature of about 900 °C. When the annealing temperature is raised above 1000 °C the surface reconstructs and a three-domain 8×1 low-energy electron diffraction (LEED) pattern is observed. Recent LEED (Ref. 9) and scanning tunneling microscopy (STM) (Ref. 10) investigations have indicated metal termination both for the unreconstructed and reconstructed (111) surfaces. The presence of smaller $(\sqrt{3} \times \sqrt{3})R\,30°$ areas were revealed in the STM investigation of the reconstructed surface, areas that were believed to be carbon terminated.

## 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.[11,12] 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 and 0.4 eV was chosen in the high-resolution studies of the C 1s and V 2p levels, respectively. 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 has acceptance angles of approximately ±8° in the horizontal and ±1° in the vertical directions.

The growth of the $VC_{0.80}$ single crystal is described elsewhere.[13] Both the (100) and (111) surfaces were cleaned *in situ*. The (100) surface was cleaned by flash heatings to about 1100 °C while the (111) surface was bombarded by $Ar^+$ ions and annealed to 800 °C for a few minutes to produce the 1×1 surface and to 1150 °C to produce the 8×1 surface. These cleaning procedures[9,10,14−16] produced clean and well-ordered sur-

    

faces as checked by LEED and photoelectron spectrosco-py.

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 $5 \times 10^{-11}$ torr.

## III. RESULTS AND DISCUSSION

High-resolution C 1s spectra recorded at three different photon energies, 330, 360, and 390 eV, from the (100) sur-face are shown by the dotted curves in Fig. 1. The shape of these curves clearly indicates that a surface-shifted component is needed in order to model the recorded spectra. The result of a curve-fitting procedure[17] is shown by the solid line through the data points in the figure and the two fitted components are shown by the solid curves below. In order to compensate for inelasti-cally scattered electrons an integrated background has been subtracted which is shown by the solid line below the recorded spectra. Since the electron mean free path is expected to exhibit a minimum around a kinetic energy of about 40 eV (Ref. 18) and then to increase monotoni-cally with increasing kinetic energy the spectrum record-ed at 390 eV, which corresponds to a kinetic energy for the photoelectrons of approximately 100 eV, is expected to be the most bulk sensitive of those shown in Fig. 1.
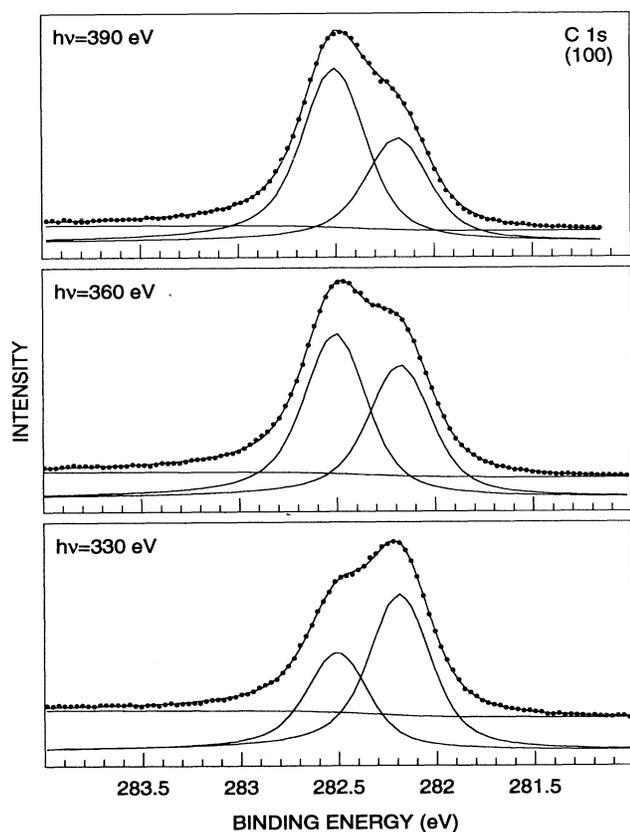


FIG. 1. C 1s core-level spectra recorded from the (100) sur-face at three different photon energies.

The intensity ratio between the two extracted com-ponents indicates, therefore, that the peak at lower bind-ing energy corresponds to the surface-shifted component and the one at higher binding energy to the bulk com-ponent. Spectra were actually recorded at different pho-ton energies between 300 and 470 eV and when using the fits from all those spectra a surface core-level shift of $-0.33$ eV was obtained. These high-resolution spectra of the C 1s level clearly show the presence of a surface-shifted component on the (100) surface. In earlier photo-emission investigations of VC(100) a surface state was ob-served,[15,16] but the nature of this surface state could not be determined. It could be of either the Tamm or the Shockley type, i.e., it could arise either from a shift in the potential at the surface or to the existence of hybridiza-tion band gaps. The presence of a surface shift of $-0.33$ eV in the C 1s level indicates, however, that the surface state may actually be of the Tamm type.

A Lorentzian (lifetime) full width at half maximum (FWHM) of 0.19 eV and an asymmetry parameter of 0.04 were used as fitting parameters for both the bulk and sur-face C 1s level. These parameters were obtained when trying to find values giving good fits of the C 1s levels on all three surfaces investigated. The binding energy of the bulk component was determined to be 282.5($\pm$0.1) eV. The Gaussian (instrumental) FWHM used was 0.23 eV for the 330-eV spectra, 0.25 eV for the 360-eV spectra, and 0.27 eV for the 390-eV spectra. The scattering in the extracted core-level shifts did not exceed $\pm$0.02 eV for any of the investigated surfaces.

C 1s spectra recorded from the (111)-8$\times$1 surface us-ing the same three photon energies as for the (100) sur-faces are shown by the dotted curves in Fig. 2. These spectra clearly indicate that a weaker surface component, shifted towards higher binding energy, is needed besides the major surface component, shifted towards lower bind-ing energy, in order to model the recorded spectra. When using the fits from spectra recorded at different en-ergies between 300 and 450 eV, surface shifts of $-0.32$ and $+0.44$ eV were obtained.

The corresponding C 1s spectra from the (111)-1$\times$1 surface are shown by the dotted curves in Fig. 3. In this case, spectra were recorded only at four different ener-gies. The relative intensity of the surface-shifted com-ponents are seen to be smaller and except for the 360-eV spectrum it was found to be necessary to use only one surface component, shifted to lower binding energy, to produce good fits. For this component a shift of $-0.33$ eV was extracted. Two surface components are, howev-er, included in the fits shown in Fig. 3 but it is seen that the component shifted towards larger binding energy is of significant magnitude only in the 360-eV spectrum. The shift of this weak component is found to be the same as on the 8$\times$1 surface. Surface-shifted C 1s components are thus observed both on the unreconstructed and recon-structed (111) surface but before discussing the differences observed we turn to the V 2p levels.

Normalized and background subtracted V $2p_{3/2}$ spec-tra recorded from the (111)-1$\times$1 and -8$\times$1 surfaces using a photon energy of 600 eV are shown in Fig. 4. The difference spectrum is shown by the bottom curve and it

does not show any features on top of the noise. The same result was also obtained when using the V $2p_{3/2}$ spectrum recorded from the (100) surface instead of one of these curves. When trying to fit these V $2p_{3/2}$ spectra with a single component a peak with a Lorentzian width of 0.7 eV and an asymmetry parameter of about 0.2 is obtained. This width is, however, much larger than the width of around 0.2 eV which has been determined for the V $2p_{3/2}$ level in pure vanadium.[19] Efforts were made, therefore, to fit a surface-shifted level using the width measured on pure vanadium and a different asymmetry parameter but peaks then become too narrow to obtain reasonable fits. No good fit of a surface-shifted component could be obtained either when varying the width and asymmetry parameters.

Oxygen exposures were made in a further effort to identify surface-shifted levels. The effects on the C 1s and V $2p_{3/2}$ core levels of the (111)-8×1 surface after an oxygen exposure of 100 L (1 L=$10^{-6}$ torr s) are shown in Figs. 5(a) and 5(b), respectively. The clean spectrum is, in both cases, shown by the bottom curve while the upper curve shows the spectrum recorded after oxygen exposure. Both core levels are clearly affected by the exposure. In the C 1s spectrum the two features that were previously suggested to be surface related are clearly attenuated after exposure compared to the bulk peak, giv-



FIG. 3. C 1s core-level spectra recorded from the (111)-1×1 surface at three different photon energies.

ing further support to the assignments made. The strongest surface-shifted component is also found to be shifted towards the Fermi level after exposure. In the V $2p_{3/2}$ spectrum, on the other hand, an oxide-related structure has started to appear on the high binding-energy side which prevents us from distinguishing any surface-shifted



FIG. 2. C 1s core-level spectra recorded from the (111)-8×1 surface at three different photon energies.
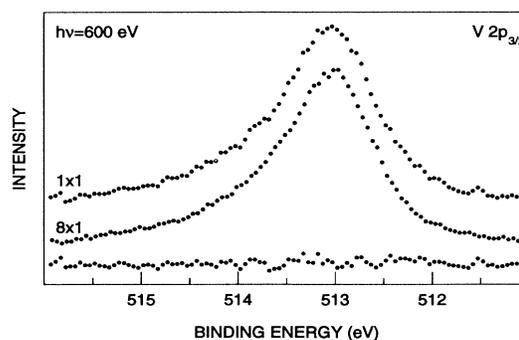


FIG. 4. V $2p_{3/2}$ core-level spectra recorded from the (111)-8×1 and (111)-1×1 surface using a photon energy of 600 eV. The difference spectrum between the two core-level spectra is shown by the bottom dotted curve.

component. The conclusion for the V $2p_{3/2}$ levels must therefore be that we cannot identify any surface-shifted levels for any of the surfaces investigated. If this is due to the absence of surface-shifted V $2p_{3/2}$ levels or an inability to reveal them, because a higher energy resolution is required, the best we could make at 600-eV photon energy was about 0.40 eV, or because the intrinsic width of the levels is too large, is not, however, clear. It has been observed earlier[20] that the metal $4f$ levels in HfC and TaC become broader when the number of carbon vacancies increases. This was suggested to be caused by the fact that the number of distinguishable metal sites, corresponding to metal atoms surrounded by different numbers of carbon atoms, increased with increasing number of carbon vacancies since all the nearest neighbors to a metal atom are carbon atoms. This may possibly explain the quite broad V $2p_{3/2}$ level observed in this experiment since the crystals contained as much as 20% vacancies on the carbon sites. The effects from the vacancies in the carbon lattice on the width of the carbon levels is expected to be much smaller since the nearest neighbors to a carbon atom are all metal atoms and since all carbon atoms are expected to be surrounded by the same number of metal atoms. The bulk binding energy of V $2p_{3/2}$ was determined to be 512.9($\pm$0.2) eV, from fits using a single



FIG. 5. (a) C $1s$ and (b) V $2p_{3/2}$ spectra recorded from the clean (111)-8$\times$1 surface and after an oxygen exposure of 100 L.

component.

A thermochemical model,[21] which expresses the total shift as a sum of partial shifts, can be used to make an estimate of the surface core-level shifts expected. When accounting only for the loss of coordination at the surface and using tabulated values of the cohesive energy,[22] negative shifts, i.e., shifts towards smaller binding energies, are obtained both for the carbon level and for the vanadium level. For the (100) surface the estimated shift is about $-0.1$ eV for the C $1s$ level and $-0.2$ eV for the V $2p$ level. The model thus predicts the correct sign but a smaller size of the shift than what is observed for the major C $1s$ component.

Surface-shifted C $1s$ levels were observed on both the (100) and the two (111) surfaces investigated. That the component shifted towards lower binding energy exhibits the same shift in all three cases is a bit surprising however since the termination of these surfaces is expected to be quite different. VC, as most of the group-IV and -V transition-metal carbides and nitrides, crystallizes in the sodium chloride structure. If perfect bulk termination is assumed, the (100) surface is expected to expose a mixed surface layer with equal concentration of metal and non-metal atoms while the polar (111) surface is believed to be metal terminated.[7,8] Low-energy electron diffraction studies of the (100) surface of TaC,[23,24] HfC,[24] and VN (Ref. 25) have, however, shown a rippled relaxation in the surface layer, with the nonmetal atoms displaced outwards and the metal atoms inwards. A recent investigation of the (111)-1$\times$1 surface of VC (Ref. 9) showed it to be terminated with a single vanadium layer and the spacing between this surface layer and the next carbon layer to be contracted 10% with respect to the spacing in the bulk. Metallic termination of the (111) surface has also been found in other carbides such as TiC,[8,26] NbC,[27,28] and TaC.[29] The reconstructed (111)-8$\times$1 surface, which appears when the annealing temperature is raised above 1000 °C, was found in a recent scanning tunneling microscopy study[10] to consist of a mixture of (8$\times$1) and smaller ($\sqrt{3}\times\sqrt{3}$)$R$ 30° reconstructed areas. The (8$\times$1) periodicity could be determined to be the result of a square lattice surface layer superimposed on the hexagonal substrate and it was deduced to consist of vanadium atoms. The ($\sqrt{3}\times\sqrt{3}$)$R$ 30° structure was found in small triangular areas between the three domains of the (8$\times$1) reconstruction and was believed to be carbon terminated. These ($\sqrt{3}\times\sqrt{3}$)$R$ 30° areas are believed to be too small, in general, to be observed by LEED. The major surface-shifted component observed in this investigation was in all three cases the one shifted towards lower binding energy. The origin of this component can be explained if the carbon atoms in the outermost layer for the (100) surface give rise to the same core-level shift as the carbon atoms in the layer beneath the topmost vanadium layer on the (111) surface. Then, the weaker component shifted towards larger binding energy on the (111)-8$\times$1 surface can be interpreted to originate from the smaller ($\sqrt{3}\times\sqrt{3}$)$R$ 30° areas. This component, although very weak, was also necessary to use in at least one of the (111)-1$\times$1 spectra. For the reconstructed surface a step was observed[10] between the ($\sqrt{3}\times\sqrt{3}$)$R$ 30° and the
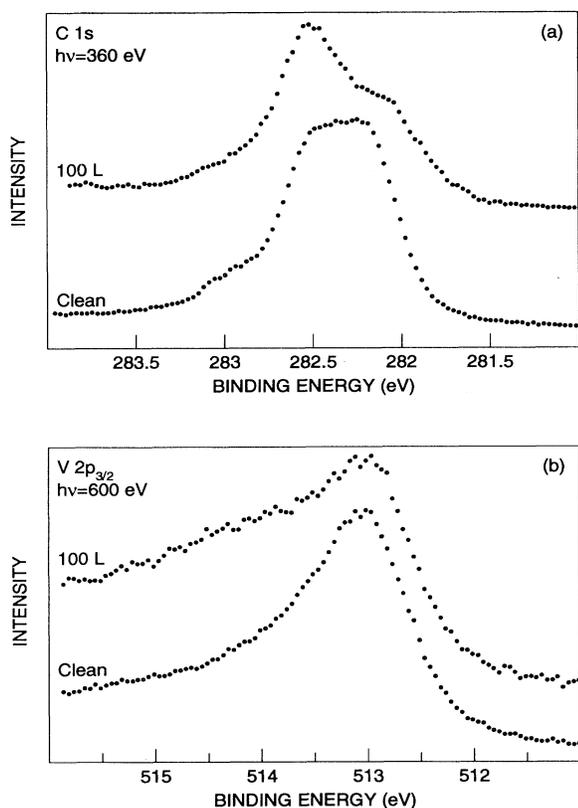
(8×1) areas with a height corresponding to the inter-layer distance. It is therefore tempting to suggest that the weak component shifted towards larger binding energy on the (111)-1×1 surface originates from carbon at steps in the surface which can be the start of the ($\sqrt{3} \times \sqrt{3}$)$R$ 30° reconstruction. Although we have no basis for the underlying assumption, i.e., that the carbon core-level shift for the atoms in the outermost layer of the (100) surface and for the atoms in the layer beneath the topmost vanadium layer on the (111) surface should be the same, this interpretation seems most plausible to us. Carbon termination of the (111) surface was considered unlikely since all previous investigations of carbide (111) surfaces indicate metal termination.[8-10,26-29] In a recent study[30] of TiC(100) we deliberately annealed the crystal to a considerably higher temperature than needed for producing an ordered surface with the purpose of pushing carbon out onto the surface, via diffusion. This resulted in a third carbon peak located at around 0.5 eV higher binding energy than the bulk peak which was located around 282.5 eV, i.e., the same as in VC. Therefore, carbon driven out onto the surface of these VC crystals is also expected to give rise to a carbon peak at higher binding energy while the major peaks we ascribed to surface-shifted peaks were shifted towards lower binding energy. Efforts to reveal differences in the carbon content in the surface layer between the different surfaces were made by measuring the V 2$p$ to C 1$s$ intensity ratio at different emission angles. Due to our experimental geometry, however, the peak intensities became so weak at large emission angles that we could not determine these ratios accurately enough to reveal any significant differences.

The surface-to-bulk intensity ratio extracted for the major surface-shifted component is plotted versus photon energy in Fig. 6. Differences between the different surfaces are clearly observed. The (100) and (111)-8×1 surfaces show ratios of comparable magnitude while the (111)-1×1 surface shows a much lower relative intensity of the surface component. In all three cases a maximum is obtained at a photon energy around 325–330 eV which corresponds to a kinetic energy for the photoelectrons of about 35–40 eV. The intensity ratios follow roughly the variation expected from the energy dependence of the electron mean free path.[18] However, for the (100) and (111)-8×1 surfaces fairly strong modulations are clearly observed which we attribute to photoelectron diffraction effects. Such effects have been observed earlier in several investigations on metals and semiconductors[31-37] and it has been pointed out that a simple intensity analysis of the surface-to-bulk ratio (neglecting diffraction effects) in such cases is not applicable for extracting information about the concentration of surface atoms. Since we observe variations in the surface-to-bulk intensity ratio of about a factor of 2 when changing the electron kinetic energy by 30 eV (see the value extracted between photon energies of 330 and 360 eV) our conclusion is that diffraction effects contribute so strongly that making an estimate of the concentrations of atoms in the outermost
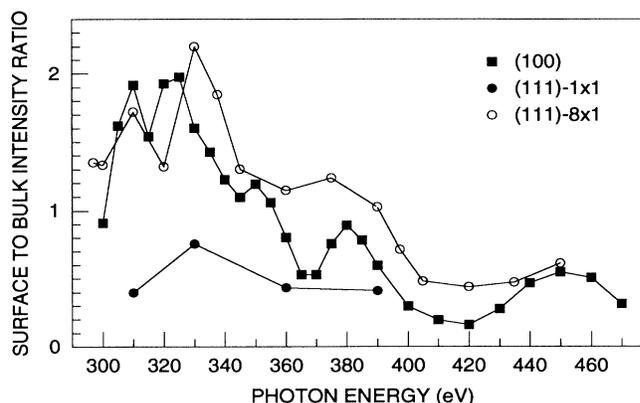


FIG. 6. Surface-to-bulk intensity ratio as a function of photon energy for the three different surfaces.

layers without including these effects is not meaningful.

The feature in the C 1$s$ spectrum that is characteristic for the (111)-8×1 surface, the component shifted towards higher binding energy, has a relative intensity of less than 20% of the bulk component and it shows a slightly different energy dependence. The surface-to-bulk intensity ratio for this component exhibits a maximum at a slightly larger photon energy, around 345–360 eV, compared to the major surface-shifted component. This also supports our interpretation that this feature originates from a different surface structure than the major component.

## IV. SUMMARY

A high-resolution photoemission investigation of the core levels in VC$_{0.80}$ utilizing synchrotron radiation has been reported. Surface-shifted C 1$s$ levels were revealed on all three surfaces studied, the (100), (111)-1×1, and (111)-8×1, but no surface-shifted V 2$p$ level could be identified on any of the surfaces. The extracted shift for the major surface C 1$s$ component was found to be the same for all three surfaces, −0.33 eV. Besides this component the (111)-8×1 surface exhibited a second shifted component having a shift of +0.44 eV. The origin of these shifted levels was discussed and an interpretation, based on observations made in other investigations of carbide surfaces, was proposed. Earlier interpretations of surface states on the (100) surface of carbides and nitrides was briefly discussed since the existence of a surface-shifted C 1$s$ level was revealed. Effects induced in the core-level spectra upon oxygen exposures were presented and utilized in the assignment of surface-shifted levels.

## ACKNOWLEDGMENTS

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

[2]K. Schwarz, CRC Crit. Rev. Solid State Mater. Sci. **13**, 211 (1987).

[3]J. E. Inglesfield, A. Callenås, and L. I. Johansson, Solid State Commun. **44**, 1321 (1982).

[4]A. Callenås and L. I. Johansson, Solid State Commun. **52**, 143 (1984).

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

[6]J. Redinger, P. Weinberger, E. Wimmer, A. Neckle, and A. J. Freeman, Phys. Rev. B **32**, 6993 (1985).

[7]C. Oshima, M. Aono, T. Tanaka, S. Kawai, S. Zaima, and Y. Shibata, Surf. Sci. **102**, 312 (1981).

[8]M. Aono, C. Oshima, S. Zaima, S. Otani, and Y. Ishizawa, Jpn. J. Appl. Phys. **20**, L829 (1981).

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

[10]M. 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).

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

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

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

[14]P. A. P. Lindberg, L. I. Johansson, and A. N. Christensen, Surf. Sci. **192**, 353 (1987).

[15]P. A. P. Lindberg and L. I. Johansson, Surf. Sci. **192**, 366 (1987).

[16]K. L. Håansson, L. I. Johansson, P. L. Wincott, and D. S. L. Law, Surf. Sci. **258**, 389 (1991).

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

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

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

[20]G. R. Gruzalski and D. M. Zehner, Phys. Rev. B **42**, 2768 (1990).

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

[22]J. Häglund, G. Grimvall, T. Jarlborg, and A. Fernández Guillermet, Phys. Rev. B **43**, 14 400 (1991).

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

[24]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).

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

[26]S. Zaima, Y. Shibata, H. Adachi, C. Oshima, S. Otani, M. Aono, and Y. Ishizawa, Surf. Sci. **157**, 380 (1985).

[27]I. Kojima, M. Orita, E. Miyazaki, and S. Otani, Surf. Sci. **160**, 153 (1985).

[28]K. Edamoto, T. Anazawa, E. Shiobara, H. Hatta, E. Miyazaki, H. Kato, and S. Otani, Phys. Rev. B **43**, 3871 (1991).

[29]S. L. Hulbert, C. C. Kao, R. F. Garrett, R. A. Bartynski, S. Yang, M. Weiner, E. Jensen, and D. M. Zehner, J. Vac. Sci. Technol. A **9**, 1919 (1991).

[30]L. I. Johansson, K. L. Håkansson, and H. I. P. Johansson (unpublished).

[31]Y. Jugnet, N. S. Prakash, L. Porte, Tran Minh Duc, T. T. A. Nguyen, R. Cinty, H. C. Poon, and G. Grenet, Phys. Rev. B **37**, 8066 (1988).

[32]R. A. Bartynski, D. Heskett, K. Garrison, G. Watson, D. M. Zehner, W. N. Mei, S. Y. Tong, and X. Pan, J. Vac. Sci. Technol. A **7**, 1931 (1989).

[33]R. Leckey, J. D. Riely, R. L. Johnson, L. Ley, and B. Ditchek, J. Vac. Sci. Technol. A **6**, 63 (1988).

[34]H. C. Poon, G. Grenet, S. Holmberg, Y. Jugnet, Tran Minh Duc, and R. Leckey, Phys. Rev. B **41**, 12 735 (1990).

[35]L. I. Johansson, K. L. Håkansson, P. L. Wincott, U. O. Karlsson, and A. N. Christensen, Phys. Rev. B **43**, 12 355 (1991).

[36]K. L. Håkansson, L. I. Johansson, and A. N. Christensen, Phys. Rev. B **46**, 1535 (1992).

[37]T. Miller, A. P. Shapiro, and T.-C. Chiang, Phys. Rev. B **31**, 7915 (1985).