PHYSICAL REVIEW B VOLUME 53, NUMBER 8 15 FEBRUARY 1996-II

Core level and valence-band studies of the (111)2×2 surfaces of InSb and InAs

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(Received 20 September 1995)

The valence and core electronic surface states on the (111)2×2 surfaces of InSb and InAs have been studied by angle-resolved photoelectron spectroscopy. Similarities in data show that the vacancy-buckling model, which is known to describe the InSb(111)2×2 surface, also applies to InAs(111)2×2. Three surface valence bands are identified and their dispersions are mapped along symmetry directions in the surface Brillouin zone. The In $4d$ core levels show one surface shifted component while no surface shifted components of the Sb $4d$ or As $3d$ core levels could be resolved.

I. INTRODUCTION

A general feature of the (111) face of the III-V semiconductors seems to be that a 2×2 reconstruction can be produced by preparing the surface with sputtering and annealing.[1–17] It was early proposed that this reconstruction is geometrically described by the removal of one surface cation per 2×2 unit mesh.[1] A first confirmation of this vacancy model was provided by analysis of low-energy electron diffraction (LEED) data from GaAs(111)2×2.[2] A relaxation of the surface anions towards the missing Ga site was also invoked, which gives a bonding configuration almost planar at the Ga sites and a pyramidal arrangement at the As sites, similar to the geometry of the (110) surface. The same vacancy-buckling model also proved valid for the (111)2×2 surfaces of InSb and GaSb, which were studied by grazing-incidence x-ray diffraction,[3,4] and for GaP, which was examined with LEED.[5] Later, scanning tunneling microscopy (STM) images of empty surface states confirmed the vacancy-buckling geometry for GaAs(111)2×2.[6] On the theoretical side, the vacancy-buckling rearrangement was shown to be strongly exothermic for GaAs(111)2×2,[18] but also an As-rich 2×2 reconstruction was predicted to be stable.[19] This As-trimer geometry was also observed by STM on GaAs(111)2×2 under As-rich conditions.[7] The vacancy-buckling model has also been supported by comparison of the calculated surface electronic bands[20,21] with angle-resolved[8] and angle-integrated[9] photoelectron spectroscopy data from GaAs(111)2×2.

Previous photoelectron spectroscopy investigations of the electronic structure on this family of surfaces is very limited.[8–13] As a test of the generality of the reconstruction on sputtered and annealed (111) surfaces of III-V compounds we present a thorough investigation of the valence and core electronic structure of the previously unexplored InAs(111)2×2 and a surface that has proven to be vacancy buckled, InSb(111)2×2.[3] Since InSb and InAs are electronically very similar materials and core and valence electronic surface states are sensitive to the atomic surface configuration it is possible to test the validity of the vacancy-buckling model on InAs(111)2×2 by comparison of such data from these surfaces. From the great similarities in surface electronic structure we conclude that the vacancy-buckling model also applies to the InAs(111)2×2 surface. The present study also provides experimental information that can serve for characterizing the interplay between atomic geometry, surface composition, and the electron structure at compound semiconductor surfaces.

II. EXPERIMENT

The measurements were carried out in a VG (Vacuum Generators Ltd.) ADES 400 system at Chalmers University of Technology using the Ne I and He I resonance lines and in a modified VSW (Vacuum Science Workshop Ltd.) photoelectron spectrometer using synchrotron light from the MAX storage ring in Lund. The analysis chamber at MAX-lab is connected with a dedicated III-V molecular-beam epitaxy (MBE) system. Both analyzers have an angular resolution of ~2° and the detection angle is changed by rotation in the plane of incidence. Spectra were excited with 45° incidence angle and electrons were collected in the plane of incidence on the opposite side of the surface normal with respect to the incident light. The energy resolution was 0.1 eV. The azimuthal orientation was checked by LEED. The base pressure in both analytical systems was $\sim 1\times10^{-10}$ Torr.

The samples were 1×1 cm^2 pieces of polished p-type InSb(111) ($p=2\times10^{13}$ cm^{-3}) and n-type InAs(111) ($n=9\times10^{16}$ cm^{-3}) wafers (MCP Electronic Materials Ltd., England). The surfaces were cleaned by repeated cycles of 500-eV Ar$^+$ sputtering and annealing until sharp 2×2 LEED patterns with low background were obtained. The InAs(111)2×2 surface was also grown by MBE and showed the same photoemission spectra.

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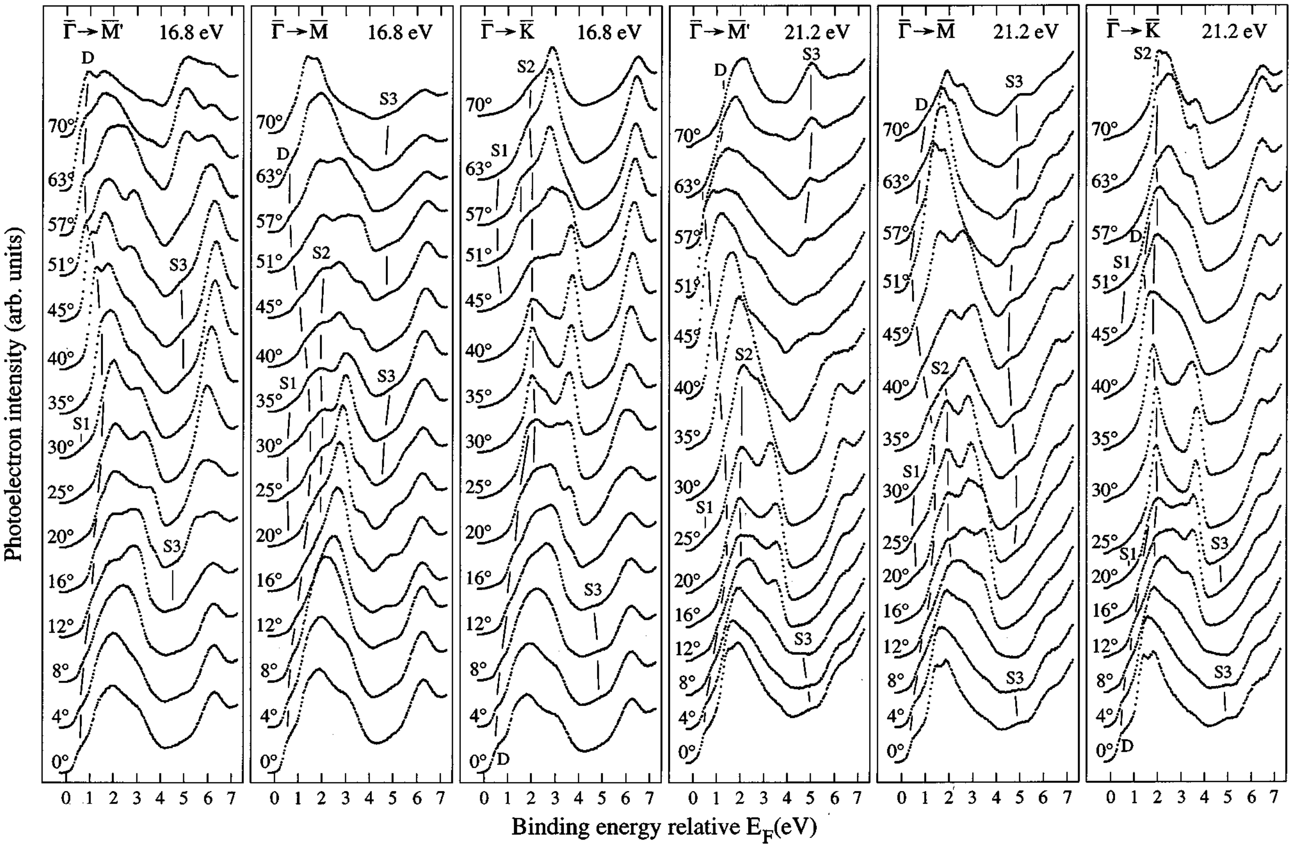

FIG. 1. Photoemission spectra of the InSb(111)2×2 valence band excited with 16.8- and 21.2-eV photons at different emission angles in three azimuths.

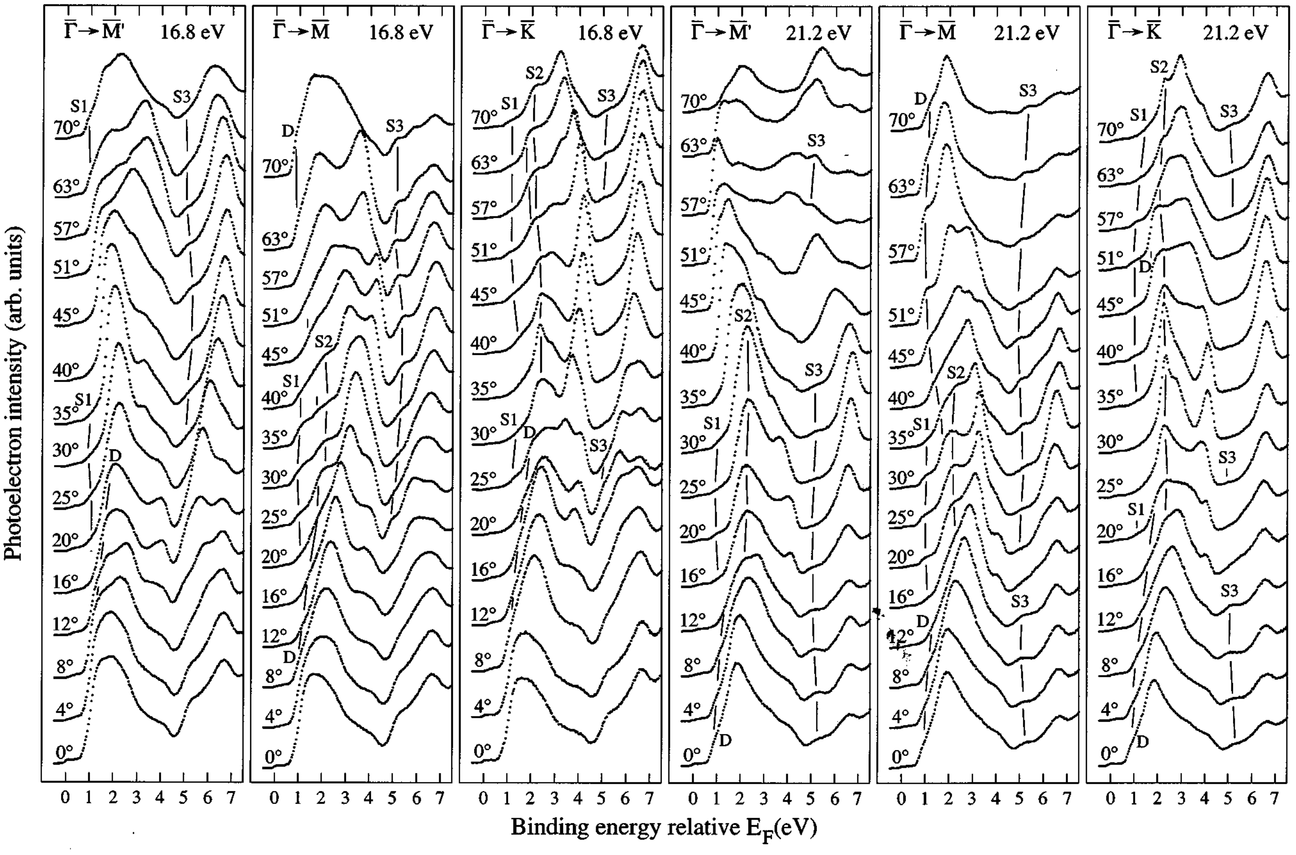

FIG. 2. Same as in Fig. 1, but for InAs(111)2×2.

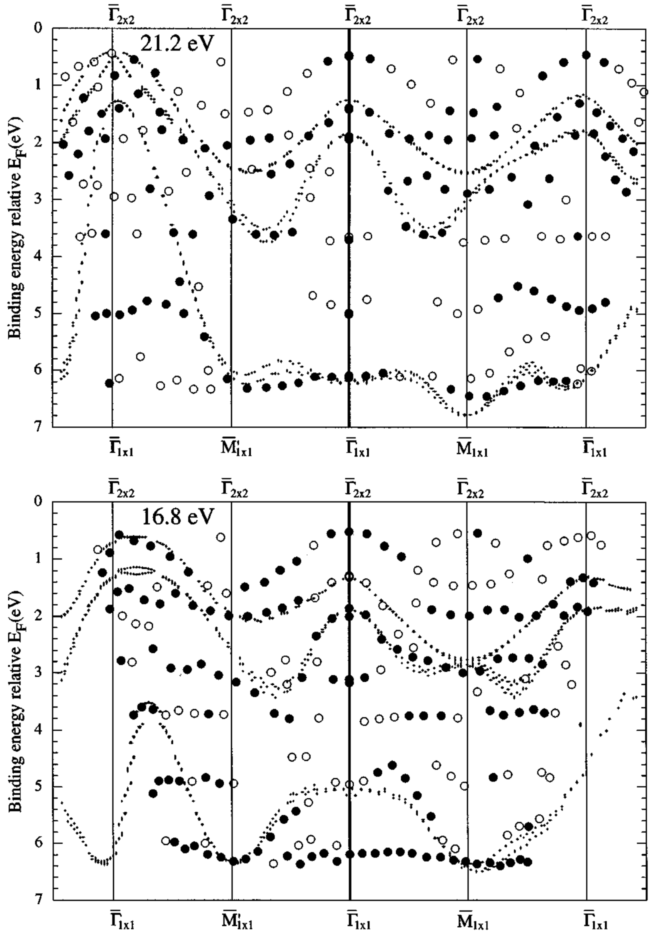

FIG. 3. Structure plots of all spectral features in the $\overline{\Gamma M'}$ and $\overline{\Gamma M}$ azimuthal series for two photon energies measured from InSb(111)2×2. Filled and open circles represent well-defined and weak structures, respectively. Theoretical structure plots of direct bulk interband transitions are indicated with dots. The $\bar{\Gamma}$ corresponding to normal emission is marked by a heavy line.

III. RESULTS AND ANALYSIS

Valence-band spectra from InSb and InAs were measured along the three azimuths $\overline{\Gamma M'}$, $\overline{\Gamma M}$, and $\overline{\Gamma K}$ in the surface Brillouin zone (SBZ) with different photon energies (the SBZ geometry is shown as an inset in Fig. 6). Figures 1 and 2 show spectral series obtained with 16.8- and 21.2-eV photons from the two samples. The first step in analyzing these data was to determine the peak positions in all spectra and plot them in "structure plots," i.e., with binding energy relative the Fermi level (E_F) versus the surface projection of the crystal momentum $\hbar k_\parallel$. For a single-crystal surface with lateral periodicity the latter quantity is, within a surface reciprocal vector, conserved in the photoemission process and is given by $k_\parallel$ $(\text{Å}^{-1}) = 0.512\sqrt{E_{\text{kin}}\ (\text{eV})}\sin\theta$, where E_{kin} is the measured kinetic energy and θ is the detection angle relative to the surface normal. Examples of structure plots are shown in Fig. 3.

To sort out the origin of different contributions in terms of bulk and surface related emission, the next step was to identify bulk interband transitions. For this purpose theoretical structure plots of vertical bulk interband transitions were calculated,[22] using initial bands obtained with a linear combination of atomic orbitals (LCAO) scheme and final bands in the crystals approximated by broadened (0.5-eV) free-electron parabolas. The LCAO parameters were obtained by fitting energies at critical points to those given in Ref. 23. The inner potentials, i.e., the bottoms of the free-electron parabolas, were to fit the experimental dispersions chosen to be 7 and 8 eV below the valence-band maximum (VBM) for InSb and InAs, respectively. Results of such theoretical structure plot calculations are shown by dots in Fig. 3. The calculated plots only include transitions where the same bulk reciprocal vector defines the final-state energy and the component of the final Bloch state that matches with a wave in vacuum, thereby determining the emission angle. In the following discussion, these transitions are referred to as "primary transitions." With this method almost all clear peaks with photon energy-dependent binding energies (i.e., dispersion with $k_\perp$) could be identified as bulk transitions (see Fig. 3). This approach also enabled the distinction between the $\overline{\Gamma M}$ ("backbond") and $\overline{\Gamma M'}$ ("counter-backbond") azimuths.

There are other structures that we also associate with bulk states even though they cannot be identified with the above method. High initial density of states (DOS) in combination with weak transitions to lifetime broadened final states will in general give rise to features in spectra with binding energies independent of photon energy. In the present data the stationary structures at 3.7 (4.2) and 6.2 (6.6) eV relative E_F for InSb (InAs) coincide in energy with the high DOS regions at Σ_{min} and the bottom of the third band. Since corresponding structures are seen at these energies in spectra from the (111) surfaces of InSb and InAs, they are assigned as bulk derived.[24–26] In addition, a shoulderlike feature (see Figs. 1 and 2), denoted D, with a dispersion following the 1×1 SBZ independently of photon energy (see Figs. 4 and 5) is also ascribed to bulk states. It disperses from 0.4 (0.9) eV at $\bar{\Gamma}_{1\times1}$ to 1.5 (1.8) eV relative E_F at $\bar{M}'_{1\times1}$ and $\bar{M}_{1\times1}$ for InSb (InAs) and further down when approaching $\bar{K}_{1\times1}$. As above, this assignment is partly based on the fact that the same dispersing structures are observed from the corresponding (111)2×2 surfaces[24] and from InSb(111)3×3.[25] The bulk origin of D is also suggested by its periodicity. Unlike a surface state, which should disperse with the periodicity of the 2×2 SBZ, this structure follows the upper edge of the surface projection of bulk bands, which has the symmetry of the ideal surface. This can be seen in Figs. 4 and 5, where, among other structures, points labeled D are plotted together with projections of bulk bands onto the surface. The $k_\parallel$ dispersion is a direct evidence that D reflects direct interband transitions in the band structure. As pointed out above, only primary transitions were needed to describe the majority of bulk features with $k_\perp$ dispersion. In the case of structure D, however, also transitions where different bulk reciprocal vectors enter the expressions for final-state energy and emission angle or transitions with a surface umklapp involved, i.e., diffraction of the photoelectron by a surface reciprocal vector and/or excitations to final bands deviating from the free electron parabolas, must contribute. From our LCAO band-structure calculations it is clear the D originates from regions of high initial DOS. Since these transitions occur over a wide

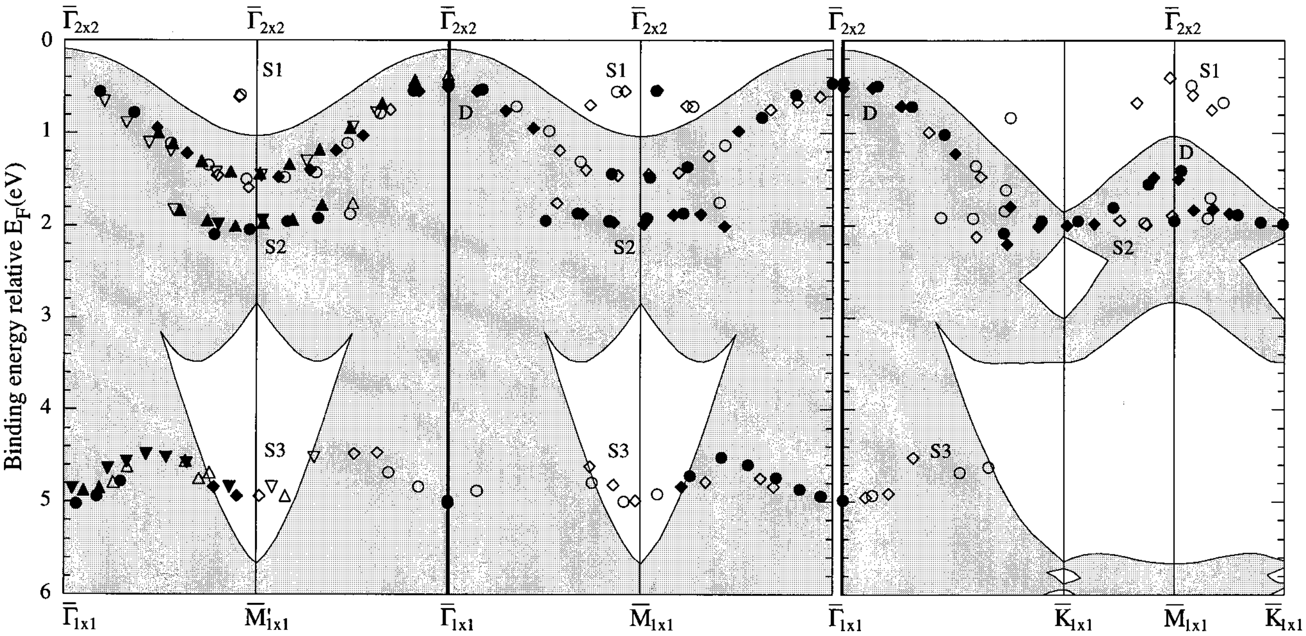

FIG. 4. Structure plot of surface related features $S1-S3$ in spectra from InSb(111)2×2. The bulk related structure D is also included. The different symbols represent different photon energies: 16.8 eV (◇), 20.0 eV (△), 21.2 eV (○), and 24.0 eV (▽). Filled symbols indicate well-defined structures and open symbols are used for weaker structures. The shadowed area is the projection of bulk bands onto the 1×1 SBZ. The $\bar{\Gamma}$ corresponding to normal emission is marked by a heavy line.

photon energy range (see Figs. 4 and 5) final-state energy broadening must be of importance.

To find out whether the structures not identified as bulk excitations are surface induced, two criteria characterizing surface bands were tested: (a) the peak positions in a structure plot must be independent of photon energy and (b) surface related features should disperse with the surface periodicity, i.e., 2×2 in the present case. Apart from these criteria the most direct way in which a surface band may reveal its identity is if it happens to be located in a gap of the bulk band projection represented in the reduced 2×2 SBZ. In the present cases no structures were, however, seen in such areas. (Note that in Figs. 4 and 5 the bulk state projections are not folded to the 2×2 SBZ.) Also useful in the analysis is the

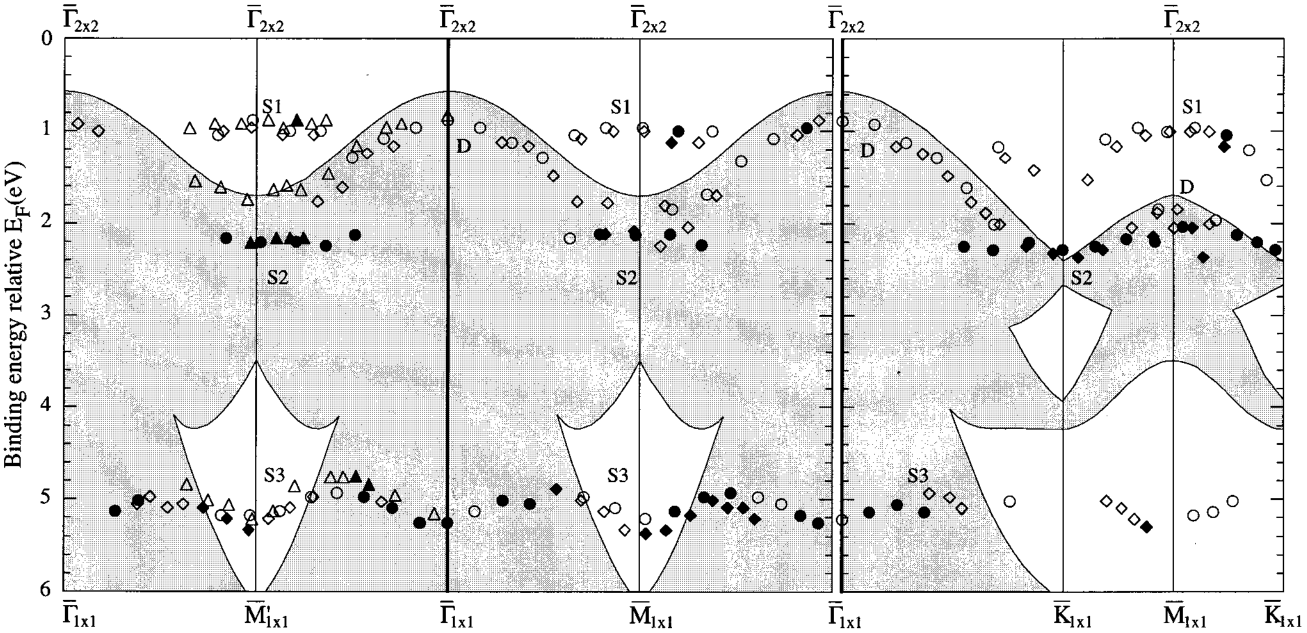

FIG. 5. Same as in Fig. 4, but for InAs(111)2×2.

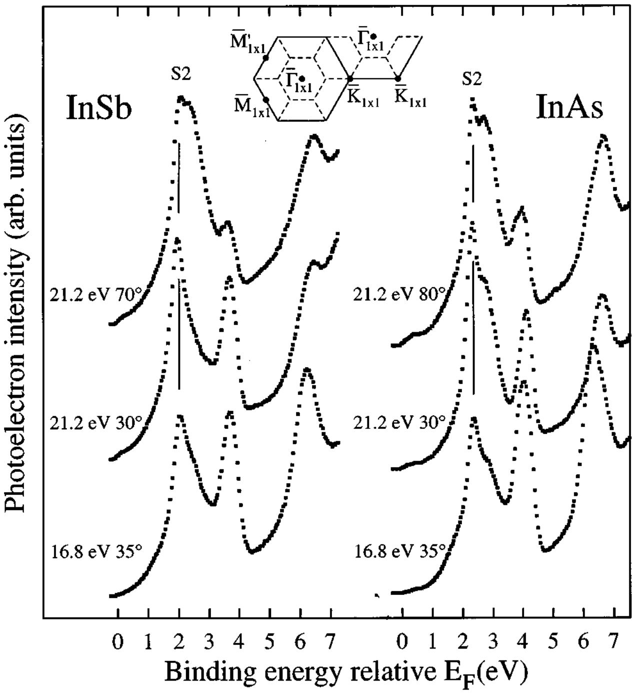

FIG. 6. Valence-band spectra recorded at the $\bar{K}_{1\times1}$ points shown in the SBZ inset above. Broken lines in the inset indicate the 2×2 SBZ boundaries.

fact that due to time-reversal invariance, the $\overline{\Gamma M}$ and $\overline{\Gamma M'}$ azimuths are in a structure plot equivalent for surface bands, but not for primary bulk transitions. With these methods three possible surface bands for each (111)2×2 surface were identified, as displayed in Figs. 4 and 5. These bands are denoted $S1$, $S2$, and $S3$. Because of the similarities in the dispersions of these bands they will be discussed in parallel for the two materials.

The $S1$ band appears as a weak shoulder in the spectra, coinciding in energy with the bulk band edge D (see Figs. 1 and 2). It disperses downward from 0.5 (0.9) eV relative E_F at $\bar{\Gamma}_{2\times2}$ with a bandwidth of at least 0.2 (0.2) eV for InSb (InAs). The quantification of the dispersion of $S1$ is based on spectral features located in the gap of the bulk band projection onto the 1×1 SBZ. In these 2×2 SBZ's the contribution from regions in the band structure giving rise to D should be less since bulk state emission only can enter via surface umklapp. The surface band $S2$ is detected at 2.0 (2.2) eV for InSb (InAs) with no resolvable dispersion except a weak tendency to reduced binding energy when reaching the SBZ boundaries. It is detected at all photon energies, but is never identified near normal emission, which is probably due to partly overlapping bulk features. Emission from $S2$ gives rise to clear peaks in spectra (see Figs. 1 and 2) and, as seen in Fig. 6, it is the dominant peak at the $\bar{K}_{1\times1}$ symmetry points near the gap in the projection of bulk bands. The fact that $S2$ appears as a sharp structure at the same binding energy and $k_{\parallel}$ for different photon energies is taken as clear support for its surface origin. The assignment of $S3$ as due to states localized to the surface is also quite clear. It shows 2×2 periodicity in the $\overline{M'\Gamma M}$ azimuth (see Figs. 4 and 5) as it disperses for InSb (InAs) from 4.9 (5.3) eV at $\bar{\Gamma}_{2\times2}$ to 4.5 (4.9) eV at $\bar{M}_{2\times2}$ and ~4.6 (~5.0) eV at $\bar{K}_{2\times2}$.

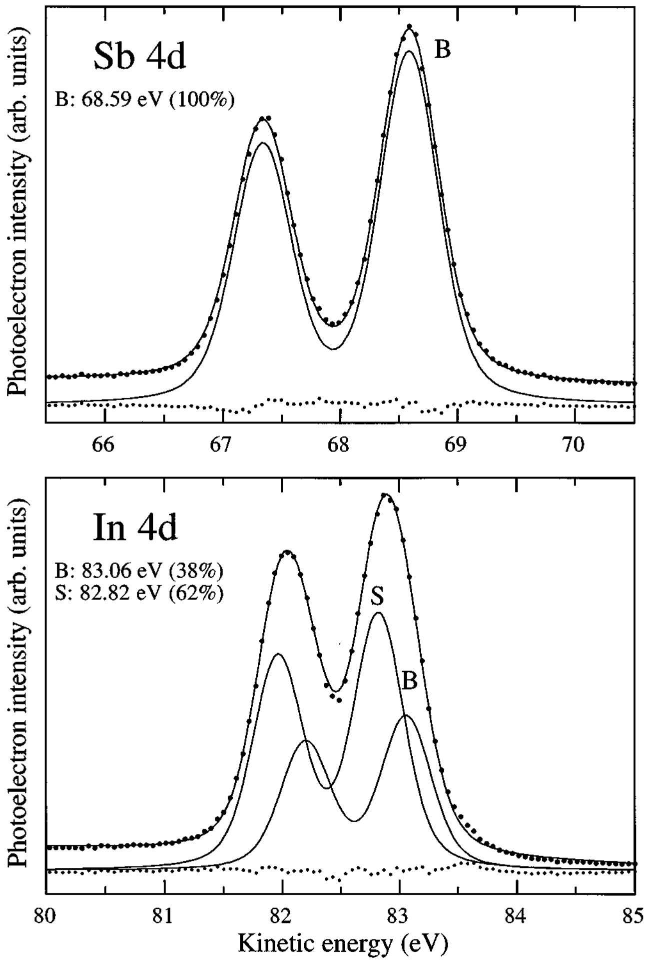

FIG. 7. Core level spectra from the InSb(111)2×2 surface excited with 105-eV photons in normal emission. Data points are presented together with fitted curves. Also shown is the decomposition into bulk (B) and surface (S) contributions and the residual. The fitting parameters for the Sb $4d$ (In $4d$) core level are $\Delta E_{\mathrm{Gauss}}=0.48$ eV (0.41 eV), $\Delta E_{\mathrm{Lor}}=0.20$ eV (0.175 eV), $\Delta E_{s\text{-}o}=1.25$ eV (0.855 eV), and branching ratio 1.36 (1.20). E_F was measured at 100.36 eV.

The presence of a surface band with the qualitative behavior of $S1$ is expected according to a self-consistent calculation on the GaAs(111)2×2 surface with a vacancy-buckled geometry.[19] Similar results were obtained for the same surface from empirical tight-binding calculations, according to which this surface band is derived from As p orbitals in the surface plane.[18,20] This surface band has also been detected by angle-resolved photoelectron spectroscopy (ARPES) on GaAs(111)2×2.[8] In the case of GaAs(111)2×2 another two surface bands were identified within 3 eV below the VBM.[8] This is to be compared with only one band in the present study of InSb(111)2×2 and InAs(111)2×2. No surface band analogous to $S3$ was detected for GaAs(111)2×2,[8] while a surface band probably corresponding to $S3$ was identified in an ARPES study of InSb(111)2×2 in the $\overline{\Gamma M}$ azimuth.[10]

Surface sensitive core level spectra are shown in Figs. 7 and 8 for InSb and InAs. These spectra were analyzed by using linear background functions and spin-orbit split Voigt functions in a fitting process to determine the number of components, their binding energies, and relative intensities.

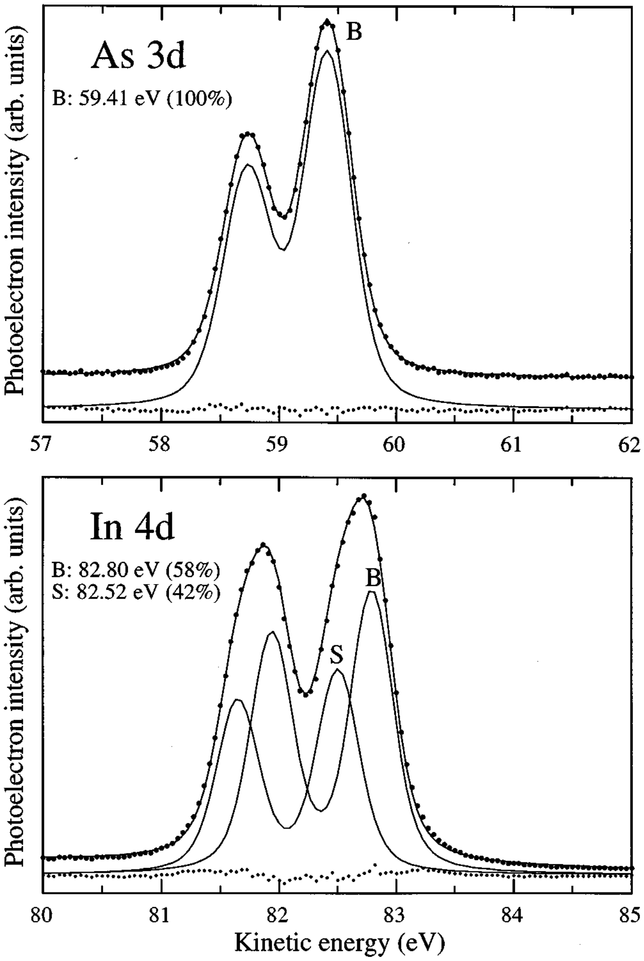

FIG. 8. Same as in Fig. 7, but for InAs(111)2×2. The fitting parameters for the As 3d (In 4d) core level area $\Delta E_{\mathrm{Gauss}}$=0.40 eV (0.33 eV), ΔE_{Lor}=0.16 eV (0.175 eV), $\Delta E_{s\text{-}o}$=0.68 eV (0.855 eV), and branching ratio 1.52 (1.18). E_F was measured at 100.28 eV.

The bulk components were identified by observing relative intensity variations between the components in spectra measured at different surface sensitivity conditions, set by the emission angle and photon energy. The obtained bulk binding energies were combined with literature values for core level–VBM separations[27,28] to determine the VBM positions in spectra. By this method the VBM energy was determined to be 0.10±0.05 eV below E_F for InSb and 0.57±0.05 eV below E_F for InAs. With a band gap of 0.36 (0.18) eV for InAs (InSb) this means that the conduction-band minimum of InAs is located below E_F, which is in fact also seen directly as shoulders close to E_F in the normal emission spectra of Fig. 2.[28]

As is the case for the As 3d core level from the sputtered and annealed GaAs(111)2×2,[11] the anion core levels on InSb(111)2×2 and InAs(111)2×2 are also described by a single component (see Figs. 7 and 8). The absence of surface shifted anion components seems therefore to be a general feature of the vacancy-buckled geometry. This is quite surprising given that in the reconstruction model a cation is removed in each 2×2 unit cell, thus changing the coordination number for 75% of the anions in the first double layer. It has been pointed out that atoms in this double layer rearrange to a local configuration similar to the (110) surface geometry.[2,18] However, for the (110) face of InSb, InAs, and GaAs the surface anion energy shifts are all around 0.3–0.4 eV.[27,29,30] The absence of a significantly shifted surface component in the present cases probably reflects cancellation of the various contributions to surface core level shifts (charge, transfer, Madelung potential, and final-state effects). A theoretical treatment of this issue would clearly be of great interest.

The In 4d spectra, comprising one surface component (see Figs. 7 and 8), are, on the other hand, easier to reconcile with the vacancy-buckling model. This surface component is ascribed to the threefold coordinated In atoms in the surface layer. With the surface component shifted 0.24 (0.28)±0.05 eV towards higher binding energy for InSb (InAs) these shifts are similar to those on the corresponding (110) surfaces, 0.22 (0.27) eV.[27,29] The Ga 3d core level of GaAs(111)2×2 was also fitted with one shifted surface component,[11] similar to that of the (110) surface.[30] The difference in relative intensity between the surface components in In 4d spectra from InSb and InAs is surprisingly large (62% of the total intensity for InSb and 42% for InAs) considering that spectra were recorded under the same experimental conditions. We tentatively attribute this difference to diffraction effects, which are known to be particularly strong in this energy region for In-based III-V compounds.

The similarity between the surface electronic structures of InSb(111)2×2 and InAs(111)2×2 is clear. The same structural model is therefore likely to apply to both surfaces. As pointed out above, there is experimental evidence that the InSb(111)2×2 is described by the vacancy-buckling model.[3] We therefore conclude that the same model also applies to the InAs(111)2×2 surface. A comparison of the surface electronic structure between InSb and InAs on the one hand, and GaAs on the other does not give the same clear result, even though they all show evidence to reconstruct the same way. As discussed above, the core levels are similar with respect to the number of components and energy shifts, while the resemblance in surface valence-band structure is not as good. Given the similarities observed in this study between InSb and InAs this difference is surprising. A possible explanation of the variance in the number of surface bands at lower binding energies (<3 eV) may lie in the data interpretation. In the present case we have identified a structure (D) as bulk derived, while a similar structure in data from GaAs was interpreted as surface states with an apparent 1×1 periodicity.[8]

IV. SUMMARY

The similarities in surface valence-band dispersions and surface sensitive core level spectra show that the InSb(111)2×2 and InAs(111)2×2 surfaces are subject to the same reconstruction. The spectral features in the valence-band data from InSb(111)2×2 and InAs(111)2×2 can be divided roughly into three categories: *primary* transitions with $k_\perp$ dispersion, which can be identified under the assumption of direct bulk interband transitions into parabolic final bands, other bulk related transitions without $k_\perp$ dispersion from regions of high initial DOS, and emission from surface-induced electronic states, which also lack dispersion with

$k_\perp$. The distinction between the two latter types of emission is not trivial and relies, in the present study, on comparisons of data from other (111) surfaces and on the requirement of 2×2 periodicity for surface-induced states.

The In $4d$ core levels are fitted by a bulk and a surface component, while only one component is needed for Sb $4d$ and As $3d$ core levels. The cation core level shape can be understood within the vacancy-buckling model. The absence of any surface shifted anion components is surprising with respect to this model and motivates a theoretical treatment of the surface core levels shifts from (111)2×2 surfaces.

ACKNOWLEDGMENTS

The MAX-lab staff is gratefully acknowledged for their assistance. This work was financially supported by the Swedish Natural Science Research Council.

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