Model-Independent Structure Determination of the InSb(111)2×2 Surface with Use of Synchrotron X-Ray Diffraction

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We have measured accurate x-ray crystallographic data from the InSb(111)2×2 reconstructed surface using synchrotron radiation from the DORIS storage ring at DESY. We have analyzed these independently of all models and find a structure with seven atoms in the unit cell, implying that one site is unoccupied. The bonding configuration is reasonable for a III-V semiconductor surface, and is topologically identical (in projection) to the "vacancy-buckling" model proposed for the GaAs(111)2×2 surface. The differences between the InSb and GaAs structures are significant and reflect chemical trends in the periodic table.

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Orbital rehybridization is currently considered to be a major determinant of the atomic geometry in compound-semiconductor surfaces. The III-V(110) surfaces, well understood from low-energy electron-diffraction (LEED) studies,[1] buckle under this influence to reduce the bond angles at the surface group-V element and increase those at the group-III element, demonstrating *p*-type and sp^2-type bonding tendencies, respectively.[2] A buckling model has also been proposed by Haneman[3] to allow similar rehybridization in the reconstructed GaAs(111)2×2 surface, but Chadi[4] has shown that the buckled arrangement is unstable to the removal of one surface Ga atom. The vacancy so-formed has been identified in a recent LEED structure analysis of GaAs(111),[5] which shows dramatic in-plane buckling of the remaining seven atoms in the surface unit cell. Because glancing-incidence x-ray diffraction is highly sensitive to in-plane surface structures,[6] it is well-suited to this problem, and so we applied it to the InSb(111)2×2 reconstructed surface and determined the atomic arrangement. Our analysis includes no prior knowledge of these models and derives directly a seven-atom structure of the projected unit cell. We are able even to identify the atom types and conclude that it is an In atom missing, implicating "vacancy buckling" in InSb(111) also.

Precisely cut, oriented, and polished InSb crystals were cleaned in 2×10^{-10} mbar by repeated cycles of sputtering with 500-eV Ar^+ ions and annealing at 420 °C for several hours. The (111) surface gave a sharp 2×2 LEED pattern, while the ($\bar{1}\bar{1}\bar{1}$) surface was 3×3; the latter is discussed elsewhere and not considered further here.[7] Valence-band energy distribu-

tions curves were recorded at $h\nu = 30$ eV with use of synchrotron light from the storage ring DORIS at Deutsches Elektronen-Synchrotron in Hamburg; these were found to be much more sensitive to surface contamination than conventional Auger spectra, and showed the surface to be clean. The sample was then transferred in UHV to a small, ion-pumped diffraction cell with a 360° beryllium window and was mounted on a diffractometer on the adjacent beam line.

The white synchrotron beam was vertically monochromated by parallel Ge(111) crystals and filtered by total reflection from a horizontal flat Au-coated mirrror. The diffraction took place in the horizontal plane of an air table which was tilted with respect to the beam to control the angle of incidence on the sample. The natural vertical collimation of the source and the horizontal geometry thus confined the entire range of incident x rays to within ±0.005° of the critical angle for InSb (determined to be 0.236°) throughout the experiment. In-plane collimation was provided by 1-mm slits before and after the sample which kept the sensitive area of the diffractometer within the sample borders. The wavelength ($\lambda = 1.119$ Å) was chosen short to minimize polarization effects in the outermost reflections.

Half-order surface Bragg reflections were collected with a position-sensitive detector set vertical to accept a 4° range of exit angles. Scans of the azimuthal angle ω were integrated and background subtracted for every reflection. Rod profiles, accumulated in the position-sensitive detector, were flat except for a sharp edge and slight enhancement at the critical angle of exit from the surface; we therefore concluded that the dif-

fraction arose from a single plane of atoms and used the total intensity under each rod measured. Thirty-eight intensities were reduced to sixteen by symmetry equivalence; the reproducibility gave us their uncertainty. The values were corrected for polarization $(\cos^2 2\theta)$, Lorentz factor $[(\sin 2\theta)^{-1}]$, and variation of active sample area $[(\sin 2\theta)^{-1}]$. Structure-factor amplitudes were derived and are listed in Table I. The maximum count rate was 30 $\sec^{-1}$ under "parasitic" running conditions (5 GeV, 40 mA). A standard reflection was measured repeatedly over the 33 h of data collection and seen to remain constant, suggesting that surface deterioration was small. A second set of data, in which the ambient cell pressure was higher, was found to have exponential loss of intensity, with a half-life of 23 h; after rescaling, these data were in good agreement.

Figure 1(a) shows the pair-correlation (Patterson) function calculated from the observed structure factors in Table I,

$$P(x,y) = \sum_{hk} |F_{hk}^{obs}|^2 \cos 2\pi (hx + ky).$$

There are three clear nonorigin peaks that must correspond to interatomic vectors in the surface structure. The bulk structure projected into the (111) plane is a

honeycomb arrangement of atoms, in which the repeating unit is a covalently bonded hexagon, shown as open circles in Fig. 1(b). If the hexagon is placed in a 2×2 unit cell, interatomic vectors are the open circles shown in Fig. 1(c). If the hexagon is distorted so as to conserve bond length, as the closed circles in Fig. 1(b) indicate, the peaks in the pair-correlation function move to the positions indicated in Fig. 1(c), which are exactly those observed in Fig. 1(a). This distorted hexagon is the only simple arrangement of atoms with $3m$ symmetry that agrees with the Patterson function.

A structure-factor calculation was then performed with these six atoms in the 2×2 unit cell at coordinates (x_j, y_j) and form factors $f_j(q_{hk})$,

$$|F_{hk}^{calc}| \exp(i\alpha_{hk}^{calc})$$
$$= \sum_j f_j(q_{hk}) \exp[2\pi i (hx_j + ky_j)]. \qquad (1)$$

When a comparison of the $|F_{hk}^{calc}|$ with the observed F_{hk}^{obs} (Table I) is made, however, the agreement is poor. The mean-square residual is $\chi^2 = 125$, indicating that a typical calculated amplitude is more than ten standard deviations away from the observed value. Missing parts of the structure are revealed in Fig. 2 by a map of the difference electron density,
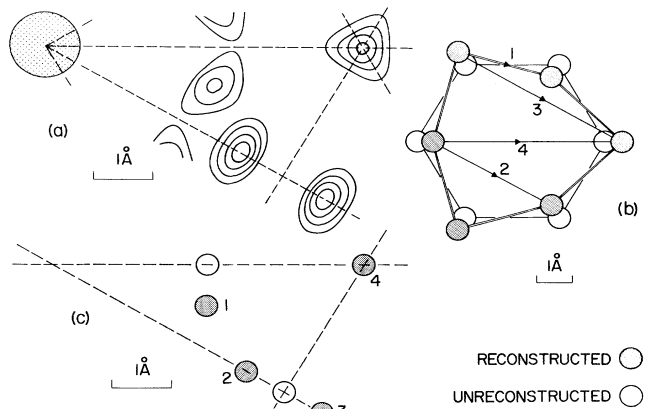
$$\Delta\rho(x,y) = \sum_{hk} (F_{hk}^{obs} - |F_{hk}^{calc}|) \exp\{i[\alpha_{hk}^{calc} - 2\pi(hx + ky)]\}. \qquad (2)$$

A single peak, well above the noise level of the map, indicates the discrepancy: a seventh atom sitting on one of the threefold axes is required to complete the structure. The seven-atom structure has a residual of $\chi^2 = 25$ which drops to 2.1 when the positions of the atoms are least-squares refined (consistent with the symmetry) and a

TABLE I. Observed and calculated surface structure factors for InSb(111)2×2. The indices (h,k) used to label the reflections refer to the hexagonal coordinate frame defined in Fig. 2. The superscript 6 refers to the values calculated for the six-atom model derived directly from the Patterson function after adjustment of a scale factor only. The superscript 7 refers to the final four-parameter model.

h	k	F_{hk}^{obs}	$F_{hk}^{calc\,6}$	$F_{hk}^{calc\,7}$
1/2	0	3.5 ± 0.2	9.0	4.0
1/2	1/2	6.2 ± 0.5	9.4	6.4
1	1/2	21.1 ± 0.4	10.0	21.0
3/2	0	32.1 ± 0.6	30.0	31.6
3/2	1/2	8.6 ± 0.5	3.1	9.0
3/2	1	7.6 ± 0.5	13.8	8.0
3/2	3/2	9.3 ± 1.0	11.3	11.6
2	1/2	18.5 ± 0.9	15.9	19.0
2	3/2	17.5 ± 0.8	9.3	17.3
5/2	0	26.2 ± 1.1	14.6	22.0
5/2	1/2	16.6 ± 1.0	5.2	17.5
5/2	1	29.4 ± 1.2	26.5	29.2
5/2	3/2	14.1 ± 0.8	9.0	14.7
3	1/2	3.8 ± 2.6	4.1	2.6
7/2	0	8.9 ± 2.2	12.2	9.1
7/2	1/2	12.8 ± 2.0	12.6	13.7

FIG. 1. (a) Repeating unit of the Patterson function calculated for the F_{hk}^{obs} in Table I. Positive contour levels above zero are shown. Dashed mirror lines surround the asymmetric repeating unit. The shaded circle is the origin peak that rises seventeen contour levels. (b) Distortion of a hexagonal arrangement of atoms taken from the projected unreconstructed InSb(111) surface. (c) Pair-correlation peaks 1 to 4 derived from vectors 1 to 4 in (b).
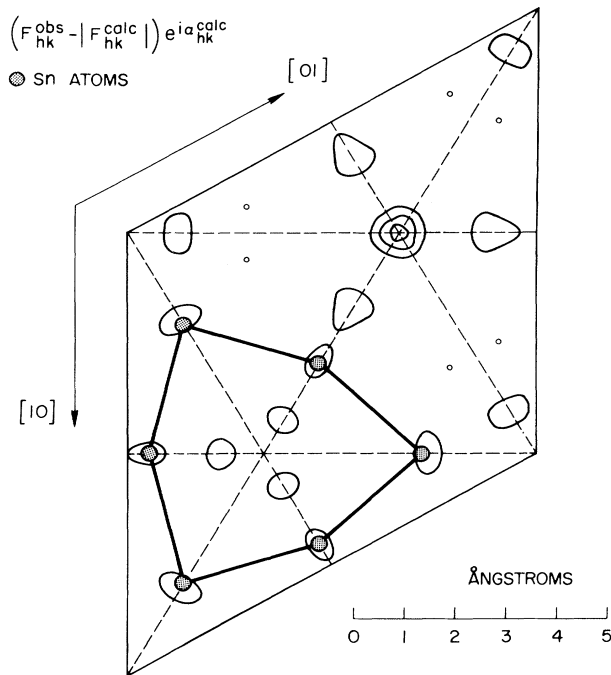
FIG. 2. Difference Fourier map of one InSb(111)2×2 unit cell. Positive contours above zero are shown. The hexagonal unit-cell vectors shown are used throughout the paper and defined as follows: $[1,0]_{hex} = [\frac{1}{2}, -\frac{1}{2}, 0]_{bulk}$ and $[0,1]_{hex} = [0,\frac{1}{2}, -\frac{1}{2}]_{bulk}$.

thermal-vibration parameter is included. At this stage the calculated amplitudes are only slightly outside the error bars of the observations. Repeating the difference-map calculation [Eqs. (1) and (2)] with the new calculated structure factors generates only noise. Furthermore, testing of models with one less or one more atom, even with allowance of parameter relaxation by least-squares refinement, always gives residuals in excess of 30.

The analysis above has not differentiated between the In $(Z = 49)$ and Sb $(Z = 51)$ atom types; form factors for Sn $(Z = 50)$ were used throughout the calculations. When the atomic number of the outer three atoms (symmetry equivalent) of the distorted hexagon is allowed to vary (with the others fixed at 50), the best agreement is for $Z_1 = 54.6$; for the inner three, $Z_2 = 48.5$; for the seventh atom on the threefold axis, $Z_3 = 50.3$. Clear assignments of $Z_1 = 51$ (Sb) and $Z_2 = 49$ (In) can be made, with a probable assignment of $Z_3 = 51$ (Sb). The last statement is strengthened by the observation that the assignment means every Sb has only In nearest neighbors in the plane and vice versa. Furthermore, since this structure has three In and four Sb atoms in the 2×2 unit cell, we are seeing the projection of a single layer of InSb with a vacant In site.
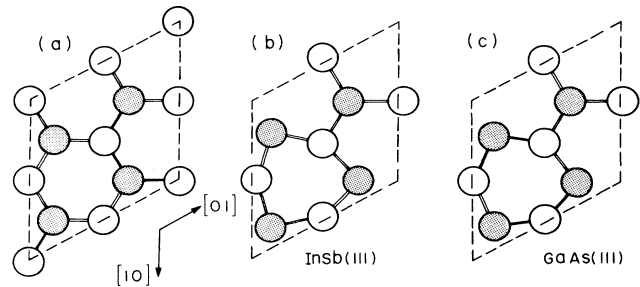

FIG. 3. Scale drawing of the projected atomic positions in (a) an unreconstructed III-V(111) surface, (b) InSb(111)2 ×2, (c) GaAs(111)2×2 (Ref. 5). Group-V atoms are shaded.

In our two-dimensional determination of the InSb structure we cannot say *which* layer reconstructs, but when we consider its remarkable similarity with the GaAs(111)2×2 structure determined by LEED,[5] we can be confident that it is the top layer. Drawn to scale in Fig. 3 are the InSb(111)2×2 reconstructed surface, the GaAs(111)2×2 surface (lattice-parameter adjusted), and an ideal unreconstructed InSb(111) surface. We have assigned bonds between the atoms as shown and connected the reconstructed layer to the bulk in exactly the same manner as GaAs, although the assignment with the layer rotated 180° (i.e., with a stacking fault between the first and second double layers) is strictly indistinguishable. The final model for InSb is obtained in a four-parameter least-squares fit: There is an arbitrary scale factor, an overall Debye-Waller thermal parameter of $B = 1.1 \pm 1.1$ Å^2 for all atoms, a radial outward displacement of the three equivalent Sb atoms of 0.45 ± 0.04 Å, and a radial inward displacement of 0.23 ± 0.05 Å for the three In atoms. The residual has dropped to $\chi^2 = 1.8$ with the correct assignment of atoms. The corresponding displacements for GaAs are 0.28 Å for As and 0.10 Å for Ga from LEED experiments.[5] The total-energy—minimization calculation of Chadi gives very similar values of 0.30 and 0.15 Å, respectively, for As and Ga.[4] The thermal parameter corresponds to a one-component vibration amplitude of 0.12 Å, which compares favorably with the value of 0.13 Å for bulk InSb.[8]

Visual inspection of Fig. 3 and detailed analysis of the structural parameters in Table II show a clear trend from GaAs to InSb. The LEED analysis[5] shows the surface layer of GaAs(111) to be extremely flat, within 0.2 Å: The bond lengths and angles are well approximated by their values in projection onto the surface plane, to within 0.01 Å and 0.2°, respectively. If the InSb(111) surface is correspondingly flat, then the projected bond lengths and angles derived in Table II are equally significant. The surface bond lengths are found to be very close to the bulk values in both cases;

TABLE II. Derived structure parameters for InSb(111) and comparison with GaAs(111). Atom A refers to the three group-III elements (Ga or In), atom B_1 refers to the three group-V elements (As or Sb) in the "hexagon," and B_2 refers to the lone group-V element on the threefold axis (see Fig. 3).

Parameter	InSb(111) This work	GaAs(111) Ref. 5	GaAs(111) Ref. 4
B_1 bond angle	$96 \pm 2°$	$104°$	$102°$
A bond angles	$144 \pm 2°$	$136°$	$138°$
	$108 \pm 2°$	$112°$	$111°$
AB_1 bond length	2.82 ± 0.5 Å	2.42 Å	2.41 Å
AB_2 bond length	2.87 ± 0.5 Å	2.41 Å	2.46 Å
Bulk bond length	2.81 Å	2.45 Å	

the fact that the bonds are very slightly *longer* than the bulk not only confirms that the surface is flat but also rules out any possibility of π bonding between the surface atoms. The trend in bond angle from As to Sb reflects the increasing tendency down the group-V elements to form p-type bonds (90° angle) instead of sp^3 (109° angle). The observed bond angles at the trivalent surface Sb and As are close to the ideal values found in simple compounds: $SbBr_3$ has an angle of 95°; $AsBr_3$ has 100°.[9] The bond angles for the trivalent surface In atoms are less close to the ideal 120° for sp^2 bonding. This may imply that the electronic rehybridization is less complete for In than Sb, but may be simply a consequence of the sp^2 bond angles being less stiff than those of the p type.

In summary, we have presented the most accurate x-ray surface crystallographic data measured to date and demonstrated that a surface structure can be derived *without* reference to models. Useful stereochemical data have been obtained, even though all the measurements considered were strictly two-dimensional and so resulted in a projection of the surface atomic arrangement.

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