Subsurface Dimerization in III-V Semiconductor (001) Surfaces

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We present the atomic structure of the $c(8 \times 2)$ reconstructions of InSb-, InAs-, and GaAs-(001) surfaces as determined by surface x-ray diffraction using direct methods. Contrary to common belief, group III dimers are not prominent on the surface, instead subsurface dimerization of group III atoms takes place in the *second* bilayer, accompanied by a major rearrangement of the surface atoms above the dimers to form linear arrays. By varying the occupancies of four surface sites the (001)-$c(8 \times 2)$ reconstructions of III-V semiconductors can be described in a unified model.

The (001) surfaces of III-V compound semiconductors show a wealth of surface reconstructions that play an important role in both homoepitaxial and heteroepitaxial growth. Knowledge of the atomic structure of these surfaces is particularly important because a wide variety of high-speed electronic and optoelectronic devices used in communications technology and fundamental studies (e.g., quantum transport) are fabricated on (001) wafers. It is generally believed that the basic building blocks in these reconstructions are dimers [1]. The presence of group V dimers on V-rich surfaces has been clearly established, e.g., Sb dimers on the InSb(001)-$c(4 \times 4)$ surface by scanning tunneling microscopy (STM) [2], and As dimers on InAs(001)-$\beta 2$-(2×4) by surface x-ray diffraction (SXRD) [3]. It has been assumed that group III dimers are the primary structural element on III-rich (001) surfaces [4–10] as suggested in the early STM study by Biegelsen *et al.* on *in situ* grown GaAs(001) surfaces [4]. However, on the Ga-rich surface it is difficult in STM to establish whether the features attributed to dimers are really made up of one or two atoms. If dimers at the surface are not the key structural element in III-rich surfaces, a substantial rethinking of the physics of III-V compound semiconductor surfaces would be required. Our surface x-ray diffraction results presented here demonstrate that this is indeed the case, since an essential part of the structure is *subsurface* dimerization of group III atoms in the second bilayer accompanied by the formation of linear chains of the atoms in the topmost layer.

A fundamental difficulty in structure determination is to identify whether the correct solution, i.e., the global minimum, or a local minimum, of the goodness-of-fit function has been found. For 3D structure determination with x-ray diffraction the ambiguity has been largely removed by using what are called direct methods [11]. Direct methods find probable values for the phases of the measured reflections, consistent with the atomicity of the crystal structure.

Combining the phases with the measured amplitudes allows approximate charge density maps to be calculated, and placing atoms at the peaks in these maps yields a good approximation to the structure. Direct methods eliminate the need to guess starting models for the structural refinement. While direct methods have been used successfully on two-dimensional SXRD or transmission electron surface diffraction data [12,13], extending them to three-dimensional SXRD data is not simple. We have recently shown that the mathematical approach of "feasible sets" [14] developed for image restoration problems can be applied to crystallographic problems [15], permitting additional constraints to be introduced that enable full, *ab initio* surface structure determination to be performed in three dimensions [16]. Since this is a truly model-independent approach, group III dimers will arise only in the data analysis if they are an intrinsic part of the structure.

All samples, GaAs, InAs, and InSb, were prepared in an ultrahigh vacuum (UHV) system by sputtering and annealing cycles as described in the literature [7,8]. STM images were measured prior to the SXRD measurements and were consistent with the images in the literature [7,8]. After preparation the samples were transferred to a small UHV chamber and brought to the BW2 wiggler beam line at Hamburg synchrotron radiation laboratory (HASYLAB) for the x-ray measurements. Extended in-plane and out-of-plane data sets were measured on all three systems at wavelengths between 1.24 and 1.42 Å. The intensity of each reflection was measured in a rocking scan by rotating the sample about its surface normal (ω scan). The scans were integrated, background subtracted, and corrected for the Lorentz factor, polarization factor, active sample area, and rod interception [17]. In the zinc-blende structure the III-terminated (001) surface has twofold rotational symmetry so there was only a single rotational domain. By averaging equivalent reflections using a $c2mm$ symmetry, systematic errors in $|F|^2$ of 7.2%, 7.8%, and

10.2% were determined for the in-plane data sets of GaAs, InSb, and InAs, respectively. The final data sets consisted of 112, 171, and 75 (GaAs, InSb, and InAs, respectively) inequivalent in-plane reflections, 17, 14, and 18 fractional-order rods (548, 282, and 566 reflections), and two, three, and five crystal truncation rods (CTRs) (71, 137, and 375 reflections). The InAs in-plane data set contained only (4×1) reflections since the eighth-order reflections were smeared out. The Patterson maps of the interatomic vectors from all three samples revealed no trace of III dimers oriented along the "2" axis [18].

The high quality InSb data were analyzed first using direct methods, and the structure was found straightforwardly in both the two-dimensional and the three-dimensional analyses; here we present only the three-dimensional results shown in Fig. 1. Contrary to prior models for the structure, which contain indium dimers in the top layer [4–9], we find an indium dimer in the second bilayer and rows of In atoms on the surface along the $[110]_{bulk}$ direction. The 2D analysis of the GaAs data revealed the same basic structure as InSb; however, the occupancies of some sites were different. The three-dimensional solutions were just about stable, indicating that the basic structure was correct, but again with different occupancies. Because of the missing eighth-order reflections the InAs data could not be analyzed with 3D direct methods, but the 2D results were similar to those of GaAs and InSb.

Starting from the model found by direct methods a full structural refinement with a least-squares algorithm was carried out. The data analysis revealed that essentially the same model describes both the InSb and GaAs $c(8 \times 2)$ reconstructions, but with different (isotropic) Debye-Waller factors and occupancies for some atomic sites. The good agreement with the data is demonstrated by the χ^2 values of 2.2 and 2.4 for GaAs and InSb, respectively. The model also reproduced the integer-order data correctly, even though the starting model was derived by direct methods using only fractional-order reflections. This consistency provides additional evidence for the correctness of the model. Figure 2 shows the structure of the InSb-$c(8 \times 2)$ surface—in the top view two bilayers are depicted, and the side view shows three bilayers. Four InSb bilayers were included in the analysis, but the deviations of the fourth bilayer atoms from bulk positions were minimal. The InAs data did not refine so easily because one of the surface sites exhibited in-plane disorder. This explains the diffuse eighth-order reflections found for this sample. The data analysis confirmed that the model correctly describes the InAs surface reconstruction. The InAs data were particularly useful because, unlike the other compounds, the difference in the electron density of the In and As atoms permitted clear identification of the atomic numbers of all the atoms in the unit cell. More details on all three models with the atomic coordinates and the x-ray data will be published elsewhere [18]. The differences be-
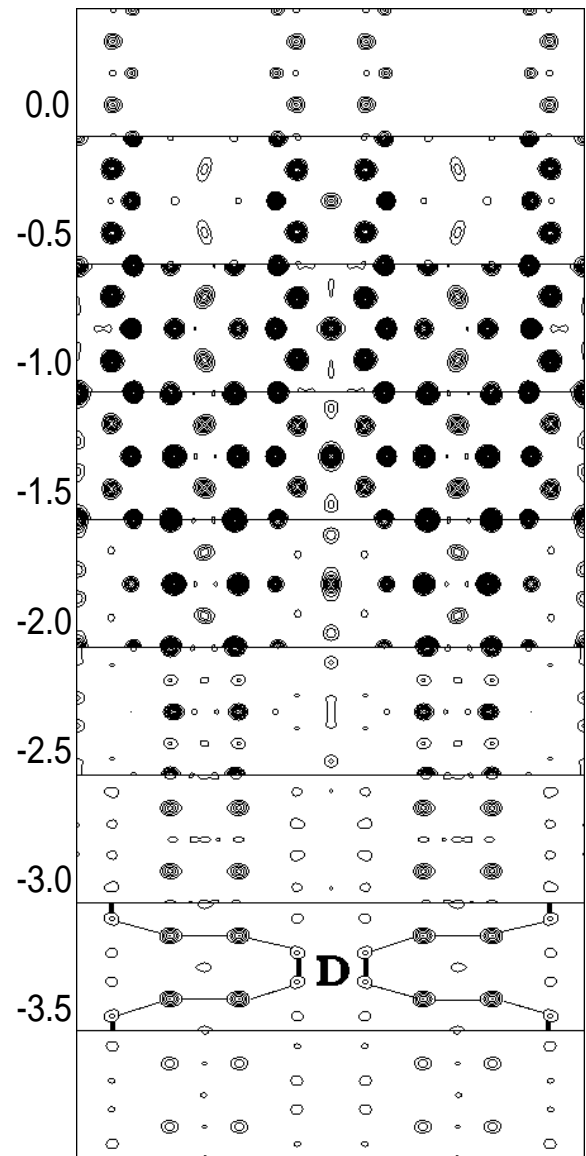

FIG. 1. Two-dimensional sections of the three-dimensional map showing contours of the charge density in x-y planes at different heights z. Numbers in the left margin indicate the z coordinate in Å, $z = 0$ corresponds to the height of the uppermost In atoms on an unreconstructed In-terminated surface. In the second bilayer the dimers are marked "D" and lines between the atoms are drawn to guide the eye.

tween the final GaAs, InAs, and InSb models are listed in Table I.

The new structural model differs significantly from all previously proposed models of III-V semiconductor surfaces. To our knowledge it is the first time that a single model describing the surface structure of three different III-V compound semiconductors has been found experimentally. The most significant new feature is the subsurface dimerization of the In atoms in the *second* bilayer (colored pale green and labeled "9" in Fig. 2) with an In-In distance of 2.89 Å (2.64 Å for GaAs—the corresponding covalent radii are 1.44 and 1.27 Å). Subsurface dimers

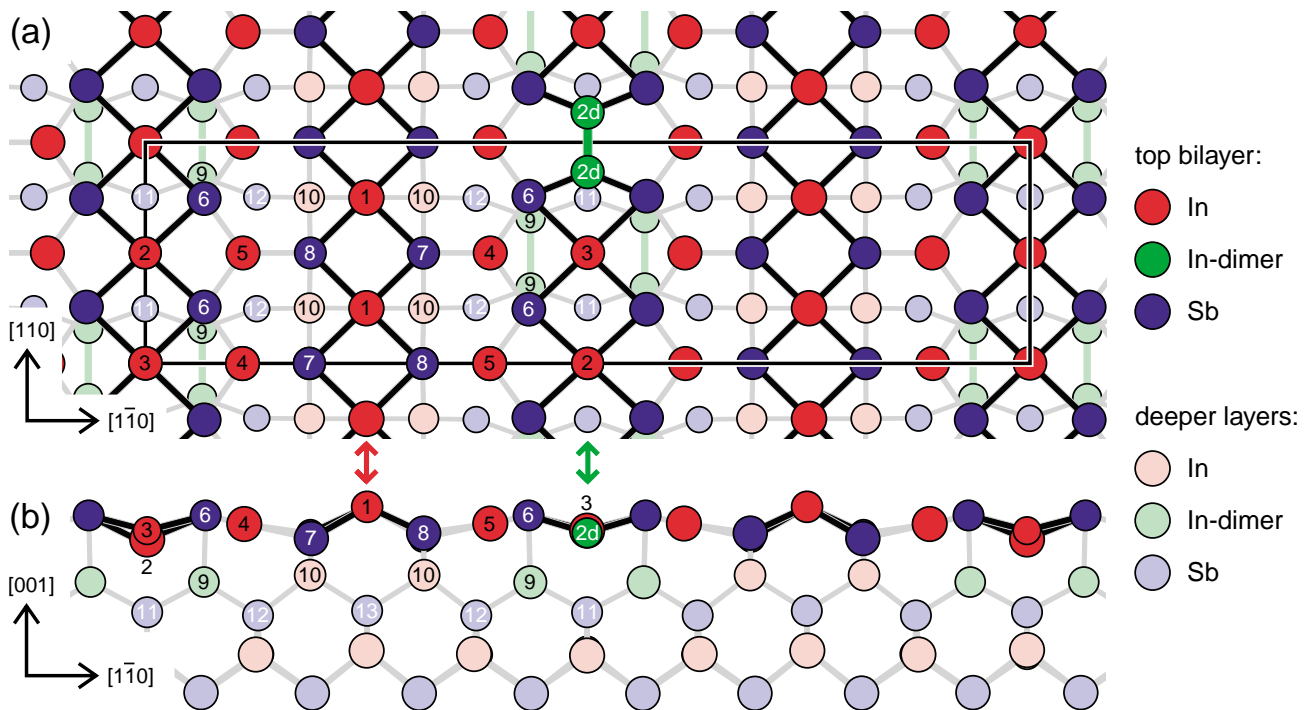FIG. 2 (color).   The structural model for InSb(001)-$c(8 \times 2)$ viewed from above (a) and from the side (b). In dimers are colored green. The important atoms in the structure are labeled, and the dimer site In2d is shown only at one location. Bonds are indicated only schematically. In GaAs the sites 1, 2, and 3 are practically unoccupied, whereas 2d has a high occupancy (see Table I).

were proposed recently in an independent study on GaAs using density functional theory (DFT), supported by simulated STM images and LEED experiments [19]. The InSb structure contains two different chains of surface atoms along the $[110]_{bulk}$ direction; in Fig. 2 the chains are indicated by the red and green arrows and emphasized by the thick black lines. In the first chain (red arrow) the Sb atoms (sites 7 and 8) are located at bulk positions, the In site 1 represents an additional (nonbulklike) site with a reduced occupancy of 57%. In the second chain (green arrow) the Sb atoms (site 6) are shifted by $\frac{1}{4}(110)_{bulk}$ relative to the Sb bulk position. In a bulk-terminated crystal each In atom in the second bilayer (sites In9 and In10) has two bonds to Sb atoms at the surface (like the atoms on site In10, which have bonds to Sb7 and Sb8). For the In9 atoms one of these bonds is broken since the Sb6 atoms are shifted [by $\frac{1}{4}(110)_{bulk}$] from their bulk positions; consequently the In9 atom moves downwards by ~0.2 Å and towards the neighboring In9 atom forming a dimer bond as shown in

Figs. 2a and 2b. The stability of this reconstruction is confirmed by DFT calculations [19]. Note that it is the ordering of the subsurface dimers that produces the $c(8 \times 2)$ unit cell. The top layer has basically a (4×1) symmetry, apart from a small buckling of ≈0.3 Å of the sites In2 and In3. This explains why observing the $c(8 \times 2)$ ordering is difficult in STM [2,8], yet easy with LEED [2,6,10].

In the InAs structure the occupancies of all sites are very similar to InSb. An additional site was identified, which is of minor importance for InSb and InAs, but prominent for GaAs. It is labeled In2d and is indicated by the green atoms in the chain marked with a green arrow in Fig. 2. In GaAs this site has 63% Ga occupancy and sites 2 and 3 are unoccupied. The Ga occupancy of site 1 in the other chain (marked with the red arrow) is significantly lower (19%). Thus, a clear trend exists from lighter to heavier III-V compounds, favoring surface dimerization in GaAs. The arrangements of atoms in the top surface layer for the different compounds must be similar in energy, making the reconstruction prone to some disorder, in agreement with recent [18] and published STM images of GaAs (see Fig. 4 of Ref. [8]). We believe that the degree of disorder depends strongly on the sample preparation. Furthermore, in agreement with Ref. [19], atoms In4 and In5 have an sp^2 bonding configuration with charge transfer to the neighboring atoms Sb7 and Sb8. Hence, there are no unsaturated dangling bonds at the surface; however, when site In1 is unoccupied, lone pairs form at sites Sb7 and Sb8. Our model is consistent with early ion scattering measurements that

TABLE I.   Comparison of the occupancies of the sites labeled In1, In2, In2d, and In3 for the three different III-V compound semiconductors.

	In1	In2	In2d	In3
GaAs	19%	0%	63%	0%
InAs	~100%	70%	13%	100%
InSb	57%	72%	28%	100%

show strong evidence of intermixing in the surface layer [20]. Some of the features are similar to the model proposed by Jones *et al.* [21]. However, when we tested their model with our data the fit was unacceptable ($\chi^2 > 20$).

In summary, we have found a unique model for the III-rich (001)-surface reconstruction of III-V semiconductors. The model is in agreement with recent DFT calculations [19]. It consists of subsurface III dimers and chains of atoms located at nonbulk sites along the $[110]_{bulk}$ direction at the surface. The tendency to dimer formation within the chains decreases with increasing atomic weight of the compounds. The model explains the discrepancy between (4×1) symmetry found earlier in STM experiments and $c(8 \times 2)$ diffraction patterns. The model is probably valid for other III-V semiconductors since, with varying surface site occupancies, it describes the $c(8 \times 2)$ reconstructions of three different compounds in a unified manner.

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