Metallic III-V (001) Surfaces: Violations of the Electron Counting Model

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We describe Sb-rich reconstructions of nearly lattice-matched AlSb and GaSb (001) surfaces using scanning tunneling microscopy/spectroscopy and first-principles electronic structure calculations. Whereas AlSb reconstructs to an insulating $c(4 \times 4)$ surface like that of other III-V compounds, GaSb forms $c(2 \times 10)$ and (2×10) surfaces that are weakly metallic and violate the electron counting model. We attribute the differences to a competition between the energy gain from Sb-Sb bond formation and the cost from the increased surface stress (which depends on the elastic properties of the substrate). [S0031-9007(97)03579-5]

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The phenomenal growth in wireless communications and optoelectronics technology is making zinc-blende III-V semiconductor substrates an increasingly important component of the semiconductor industry [1]. It is widely accepted that the surfaces of these polar semiconductors should reconstruct such that all the dangling bonds on the electropositive surface atoms (III) are unoccupied and all those on the electronegative atoms (V) are doubly occupied, with the resulting surface band gap similar to that of the bulk. This guiding principle, usually referred to as the electron counting model, represents the starting point from which III-V semiconductor surface structures are built [2–8].

Possibly the most prominent application of the electron counting model (ECM) has been to narrow the possible structural models for the many reconstructions observed on the technologically important III-V (001) surfaces [3,4,6–8]. For example, the number of plausible structural configurations for the much-studied As-terminated GaAs(001)-(2×4) surface can be limited to four [7]. The ECM has had similar success accounting for other reconstructions on III-As and III-P (001) surfaces. To our knowledge, however, there has been no consideration of the ECM with regard to III-Sb(001) surfaces, which have been reported to include "odd" reconstructions (e.g., 1×3) [9–11]. In this Letter, we describe the structure of Sb-rich reconstructions on AlSb and GaSb(001) as determined with scanning tunneling microscopy (STM) and first-principles electronic-structure calculations. AlSb and GaSb are a noteworthy pair of III-V compounds, having very similar lattice constants (AlSb is 0.7% larger) but differing only by one element; as such, they provide an opportunity to explore the possible role of material properties, as opposed to lattice constant, in determining surface reconstructions. We find that AlSb(001) forms as insulating $c(4 \times 4)$ reconstruction satisfying the ECM [similar to other III-V(001) surfaces], whereas GaSb(001) forms $(n \times 5)$-like surface reconstructions *that are weakly metallic and violate the ECM.*

Experiments were carried out in an interconnected, multichamber ultrahigh vacuum (UHV) facility that includes a III-V semiconductor molecular beam epitaxy (MBE) chamber equipped with reflection high-energy electron diffraction (RHEED) and a surface analysis chamber equipped with STM [12]. AlSb(001) surface reconstructions were studied on *p*-type (Be-doped, 10^{16} cm^{-3}) relaxed films (>1 μm thick) grown at 550 °C on GaSb(001) substrates. GaSb reconstructions were studied on undoped films (effectively *p*-type, 10^{16} cm^{-3}) grown at 500 °C. All STM images were acquired at a constant current and are displayed in gray scale. Tunneling current (I) vs sample bias (V) spectra were acquired at fixed tip-sample separation, with the separation adjusted to assure adequate signal at low bias voltages, and are displayed as normalized conductivity, $(dI/dV)/(\overline{I/V})$ [13].

First-principles total-energy calculations of equilibrium surface structure were performed in a slab geometry with appropriate periodicity. The slabs consisted of four layers of Ga and Sb atoms (plus any additional surface atoms) represented by norm-conserving pseudopotentials of the Troullier-Martins form [14], with hydrogenlike potentials [15] saturating the bottom Ga layer. Structural relaxation was performed using the Corning electronic-structure code of Allan, Teter, and Payne [16], which solves the Kohn-Sham equations in the local-density approximation with a plane-wave basis. Atoms in the bottom layer were held fixed at their bulk positions, while all other atoms were allowed to relax until their rms force was less than 0.1 eV/Å. A plane-wave cutoff of 12 Ry was used, with a *k*-point density equivalent to 36 *k*-points in the full (001)-1×1 surface Brillouin zone. After structural relaxation, numerically simulated STM images (constant current surfaces) were calculated by integrating the electronic local-state density over appropriate energy windows.

Because III-V semiconductor-based electronic devices are typically prepared under V-rich conditions, the V-terminated reconstructions are of the greatest interest. We have used RHEED to systematically characterize the temperature and Sb_4 flux dependence of the Sb-terminated surface reconstructions on AlSb and GaSb(001) [11]. On AlSb we observe a (1×3) structure above ~400 °C, similar to previous reports [17,18]; however, at lower

temperatures a clear $c(4 \times 4)$ is observed (similar to InSb, GaAs, AlAs, and InAs) that, to our knowledge, has not been previously reported for this surface. On GaSb(001) we observe the previously reported structures [10,17–19], (1×3), $c(2 \times 6)$, (1×5), and (2×5), as the substrate temperature is lowered from ~500 °C to ~300 °C and the surface Sb coverage increases [10].

STM images of AlSb(001)-(1×3) appear similar to those previously published for GaSb [19] and InSb [9], with complicated kinked and buckled features of unknown origin, and are discussed elsewhere [11]. The AlSb(001)-$c(4 \times 4)$ surface has a much simpler structure, as shown in Fig. 1. The filled-state topography consists of bricklike structures, each composed of three dimerlike segments [Fig. 1(a)], just as observed on GaAs [20] and InSb [9]. As previously discussed for these other (001) surfaces [7], this double-Sb-layer reconstruction (which satisfies the ECM) has rows of Sb dimers on top of a (1×1) plane of Sb, with every fourth dimer missing along the $[\bar{1}10]$ direction [Fig. 1(b)]. As expected [2], tunneling spectroscopy reveals that this surface is insulating (Fig. 2)—there is little conductivity within the bulk band gap—as is typically observed for III-V surfaces [13,21,22].

Unlike AlSb(001) and all other III-V's studied to date, GaSb(001) does *not* reconstruct to $c(4 \times 4)$ at any substrate temperature or Sb_4 flux. Rather, (1×5) and (2×5) RHEED patterns are observed at low temperatures/high Sb_4 pressures. Atomic-resolution STM images of a "(1×5)" surface are displayed in Fig. 3. The filled-state topography is dominated by double rows of identical dimerlike structures, with the row pairs separated by lower dimerlike features having an orthogonal orientation. Although the double rows have a (1×5) periodicity, the rotated features give the reconstructed surface a $2\times$ periodicity along $[\bar{1}10]$. On the most well-ordered surfaces these features are staggered from row to row, making the (1×5) phase a $c(2 \times 10)$ surface reconstruction [23]. The structure is shown in more detail in Fig. 3(b), where an image is rendered to highlight the atomic-scale topography (the node in the center of each dimer is <5 pm deep). Note that the slight asymmetry of the right dimer row of each row pair is a feedback artifact resulting from the large gain required to resolve the internal structure of the dimers.

It has previously been shown by quantitative, high-resolution core-level photoemission spectroscopy that the $c(2 \times 6)$ and $(n \times 5)$ surfaces of GaSb(001) are terminated by >1 layer of surface Sb, with *only bulklike Ga*, ruling out any structures incorporating surface or substitutional Ga [10]. Given these results and our STM images, the only plausible structure of the (1×5) reconstruction [actually $c(2 \times 10)$] is two adjacent rows of Sb dimers on top of a full plane of Sb, separated by rotated Sb dimers in the second layer [Fig. 3(c)]. This model is strongly supported by simulated STM images for the calculated equilibrium geometry of such a structure [Fig. 3(d)]: our calculations accurately reproduce both the positions and relative heights of the topographic features observed experimentally.

Given the structure of the (1×5) surface, STM images of the Sb-richer (2×5) reconstruction are straightforward to interpret. An image of a surface with both (1×5) and (2×5)-like reconstructed regions is displayed in Fig. 4(a). Although such coexistence is atypical, it enables a direct comparison of the two structures under identical tunneling conditions. As seen in the image, (2×5)-like regions appear topographically higher (~1 Å at this bias), with maxima orthogonal to the (1×5) double dimers,

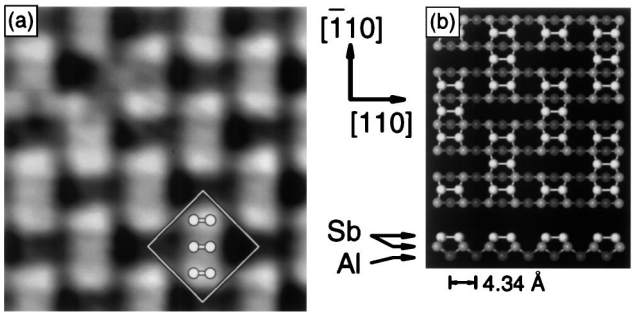

FIG. 1. (a) Filled-state STM image of AlSb(001)-$c(4 \times 4)$, 48 Å × 48 Å, acquired at 3.3 V. A unit cell is indicated along with some of the surface Sb dimers. (b) Structural model of the surface, consisting of an Sb double layer (see, for example, Ref. [7]).

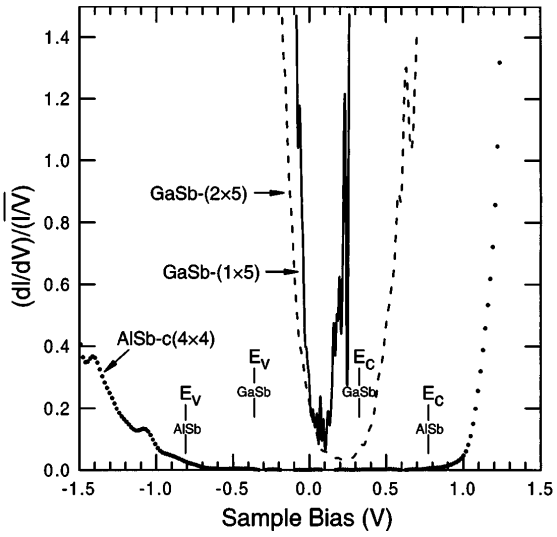

FIG. 2. Tunneling spectra acquired on AlSb(001)-$c(4 \times 4)$ (dotted line), GaSb(001)-(1×5) (solid line), and GaSb(001)-(2×5) (dashed line). The spectra are displayed as normalized conductivity, $(dI/dV)/(\overline{I/V})$ (approximately proportional to the density of states), calculated from the measured I vs V, with $(\overline{I/V})$ exponentially broadened with a width of 0.7 V (see Ref. [13]). The bulk band edges for both substrates are indicated. Note that the Fermi level is approximately in the middle of the bulk band gap on both surfaces. Whereas the AlSb surface is insulating, the GaSb surfaces are weakly metallic, with nonzero conductivity for all voltages.

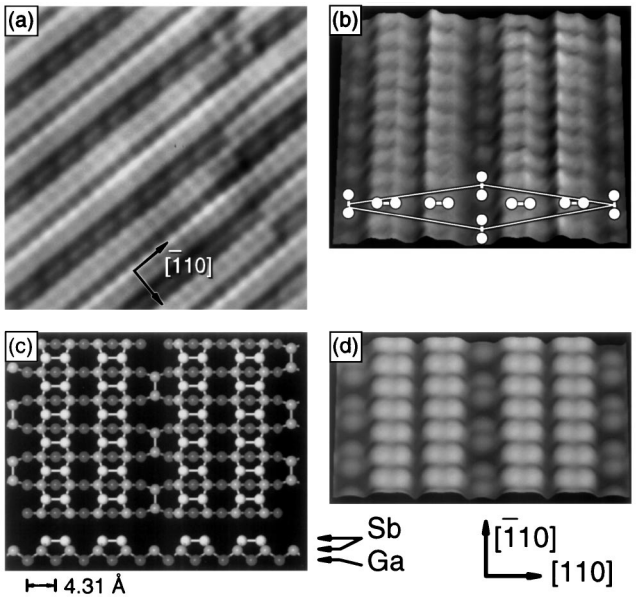

FIG. 3. Filled-state STM images of GaSb(001)-(1×5) acquired at 1.8 V: (a) 80 Å $\times$ 80 Å, (b) 48 Å $\times$ 48 Å. The lower dimers give the surface a $2\times$ periodicity along [$\bar{1}$10]; a $c(2 \times 10)$ unit cell is indicated. Note that the slight asymmetry of the right dimer row of each row pair is a feedback artifact resulting from the large gain required to resolve the internal structure of the dimers. (c) Proposed $c(2 \times 10)$ structural model for this surface. (d) Simulated STM image of this structure calculated for filled states within 1.8 eV of the Fermi level.

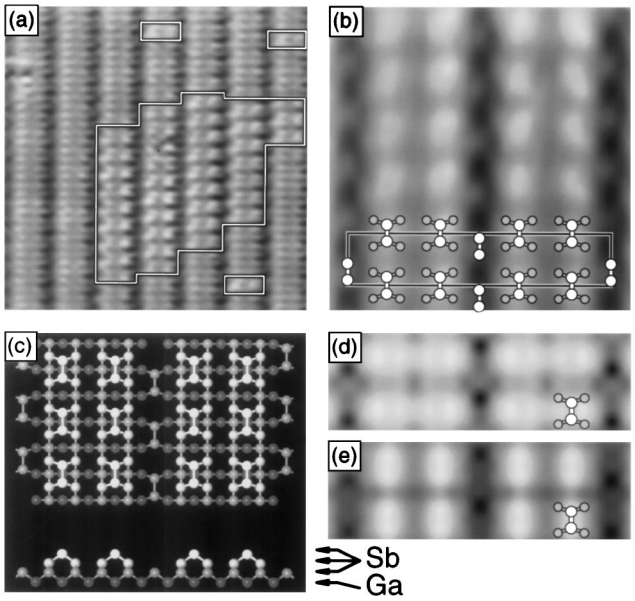

FIG. 4. (a) Filled-state image of a GaSb(001) surface with both (1×5)-like and (2×5)-like regions (2.4 V, 150 Å $\times$ 150 Å). The (2×5)-like regions are outlined. (b) Higher magnification image of a well-ordered (2×5) (by RHEED) surface (0.4 V, 52 Å $\times$ 52 Å). A (2×10) unit cell is indicated. (c) Proposed (2×10) structural model for this surface, consisting of the simple addition of Sb dimers on top of the dimer rows of the structure shown in Fig. 3. Simulated filled state images of this structure calculated for (d) 0.4 eV and (e) 2.4 eV.

suggestive of additional Sb dimers on top. Atomic-scale features of the "(2×5)" reconstruction are illustrated in Fig. 4(b), where a higher magnification image from a well-ordered (2×5) surface is shown. In this image, acquired at lower bias, the features within the double rows have a flatter, more rectangular appearance. As observed for the (1×5) surface, distinct maxima with a $2\times$ periodicity along [$\bar{1}$10] are observed between the double rows. The features within both the double rows and the rows in between sometimes shift by a lattice constant from row to row, giving the surface an overall (2×10) symmetry. Our proposed structure for this surface [Fig. 4(c)] consists of an additional layer of Sb dimers on top of the Sb atoms that initially form the (1×5) dimer rows. The topographic features observed experimentally, including variations with tunneling bias, are accurately reproduced by simulated images of this (2×10) structure [Figs. 4(d) and 4(e)].

It is straightforward to show that *the two* $(n \times 5)$*-like reconstructions observed on GaSb(001) violate the ECM.* For both structures, with all the surface Sb-Sb bonds and Sb dangling bonds doubly occupied (there are no surface Ga bonds), *there are three valence electrons remaining per* (2×5) *unit cell.* Because these electrons must occupy midgap or conduction band states, in the absence of strong electron correlation these surfaces should be metallic. As demonstrated by the tunneling spectra displayed in Fig. 2, nonzero conductivity is indeed observed for all voltages on both surfaces. In both cases there is substantial conductivity right up to the Fermi level (E_f at 0 V). On the (1×5) surface, there is a pseudogap of $\sim$0.2 eV above E_f where the conductivity (and by implication the density of states) appears small, but distinctly nonzero, followed by a rapid rise in empty state conductivity. On the (2×5) surface the pseudogap is slightly larger, $\sim$0.35 eV, but the conductivity still does not reach zero. Note that on III-V(001) surfaces that obey the ECM very little conductivity is ever observed within the band edges, *even in the presence of a high density of charged surface defects* [21]. In contrast, midgap conductivity *is observed* on these GaSb surfaces *as a direct consequence of the violation of the ECM.*

To our knowledge, the only other clean III-V surface thought to violate the ECM is the Ga-terminated $(\sqrt{19} \times \sqrt{19})$ reconstruction of GaAs($\bar{1}\,\bar{1}\,\bar{1}$) [20]. Although tunneling spectra for this surface have not been reported, tunneling becomes unstable for $|V| < 0.3$ V, suggesting the reconstruction has a reduced surface band gap but is not metallic. The proposed model for this GaAs surface requires partial occupation of Ga dangling bonds, presumably the origin of the midgap conductivity, although the structure has yet to be examined theoretically. In contrast, on GaSb(001)-"$(n \times 5)$" surfaces stable tunneling can be maintained at very small bias voltages ($<$10 mV), consistent with the metallic characteristics of the tunneling spectra. Our calculations reveal the density of states at E_f

arises from partial occupation of conduction states associated primarily with the surface Sb dimers.

It is interesting to consider why GaSb(001) forms the $(n \times 5)$-like reconstructions under the most V-rich conditions when other III-V's, including nearly lattice-matched AlSb, reconstruct to $c(4 \times 4)$. These multilayer structures, best described as trigonally bonded chemisorbed V overlayers [24], should be favored under the most V-rich conditions because V-V bonds are stronger than III-V bonds [25]. Moreover, each Sb-dimer atom has an elemental Sb-like configuration, bonded to three other Sb atoms and having a filled lone-pair orbital. Multilayer epitaxial adsorption of elemental Sb (or As, etc.) is inhibited, of course, by the stress associated with the mismatch between the crystal structures. On a double-layer surface (the first stage of multilayer adsorption) the stress will be primarily associated with the Sb dimer bonds, as it is for the much-studied dimer-based (2×1) reconstruction on Si(001) [26]. We propose that on the III-V surfaces that reconstruct to $c(4 \times 4)$ the dimer-related stress is relieved by the periodic dimer vacancies [27], such that the $3/4$ of a layer of V atoms in dimers represents a balance between adding V-V bonds and the resulting surface stress. Two factors favor the formation of the alternate (1×5) structure on GaSb. First, the GaSb(001)-(1×1) surface has the smallest misfit with Sb tetrahedra of all the V-on-III-V combinations (0.04% in the $[\bar{1}10]$ direction [28]). More importantly, the Ga-Sb bond is one of the softest of the III-V compounds (only In-Sb is softer) [29], reducing the misfit-related strain energy: It takes 7% less energy to stretch Ga-Sb bonds the same distance as Al-Sb bonds. The net effect is to permit GaSb(001), in contrast with AlSb, to reconstruct to the (1×5)—with slightly more Sb than on the $c(4 \times 4)$ and *continuous* dimer rows [30].

Finally, we note that the Sb-terminated (1×3) reconstruction, observed on all three III-Sb (001) surfaces, may also violate the ECM. Unlike the (001) surfaces of III-(As,P) compounds, that have single-layer As(P) reconstructions under slightly As- (P-) rich conditions, even this least Sb-rich reconstruction is composed of an Sb double layer [9–11,19]. Although the detailed structure of this complicated reconstruction is not yet clear, preliminary results indicate that these (1×3) surfaces may also be metallic. It appears that the larger bond strength and longer bond length of Sb (as compared with As and P), combined with the (related) larger lattice constants of the III-Sb compounds, make it possible for these systems to violate the ECM in some cases by lowering the structural surface energy enough to overcome the electronic energy penalty associated with occupying conductionlike states. The electron counting model may not be nearly as universal as it is currently regarded.

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