Variable Stoichiometry Surface Reconstructions: New Models for GaAs($\overline{1}\overline{1}\overline{1}$) (2×2) and ($\sqrt{19}\times\sqrt{19}$)

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The ($\overline{1}\overline{1}\overline{1}$) surface of GaAs exhibits three stable reconstructions. Two are (2×2), As stabilized and Ga stabilized, respectively, and the third is ($\sqrt{19}\times\sqrt{19}$). Transitions between these structures are obtained by variation of the experimental conditions. We propose new models for all of the above reconstructions, based on *ab initio* total-energy calculations and experimental information regarding surface composition.

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Among the surfaces of technologically important materials that have been studied extensively, the ($\overline{1}\overline{1}\overline{1}$) As-terminated surface of GaAs stands out as a system that is very poorly understood. Even the relative abundance of Ga and As atoms in the surface region is not established with sufficient accuracy.[1] The multitude of diffraction patterns observed on this surface [e.g., (2×2), (3×3), ($\sqrt{19}\times\sqrt{19}$)] and their sensitivity to preparation conditions make the problem very intriguing. The layer of exposed As atoms that constitutes the unreconstructed ($\overline{1}\overline{1}\overline{1}$) bulk plane is apparently highly unstable, leading to a rich variety of surface reactions and atomic rearrangements. No model has yet to emerge as a satisfactory candidate for any of these reconstructions.

In this paper we will concentrate on the two most stable observed patterns, namely the (2×2) and ($\sqrt{19}\times\sqrt{19}$). Four different surface stoichiometries of the ($\overline{1}\overline{1}\overline{1}$) surface of GaAs are investigated. For each stoichiometry the energetically most stable (2×2) structure is identified and analyzed in light of experimental data. The structures were obtained by performing *ab initio* total-energy calculations on many possible reconstruction models. From these calculations we find a new bonding unit which is energetically very stable. It consists of three Ga (or As) atoms bonded together in an equilateral triangle which in turn is connected to three atoms on the surface. Another favorable reconstruction is a staggered vacancy geometry, which is a variation of the vacancy buckling model proposed for GaAs ($\overline{1}\overline{1}\overline{1}$)(2×2).[2,3] The Ga and As triangles, together with the staggered vacancy, are shown to be responsible for the most stable reconstructions. The extreme stability of the triangle bonding units leads us to suggest that such units may be responsible for the reconstruction on many other III-V surfaces and may play an important role in the growth process.

Before introducing the models we briefly review two types of relevant experiments: (a) diffraction experiments (e.g., low-energy electron diffraction), which establish the surface periodicity, given as an ($m\times n$) multiple of the original unreconstructed unit cell (m and n are not necessarily integers); and (b) spectroscopic experiments (e.g., Auger-electron spectroscopy), which measure the relative amount of As and Ga atoms in the surface layer. Two different (2×2) reconstructions have been observed by experiment.[4–7] The first has an Auger As/Ga intensity ratio equal to 4.2[4] and is termed "As stabilized" since it is obtained only in an As-rich environment.[5,6] The second has an Auger ratio of 2.4 and is obtained after simultaneous Ar-ion bombardment at high energies (1 keV) and annealing at high temperatures (870 K).[7] The Auger ratio indicates that this second reconstruction has much lower As content in the surface layer. Taking into account the very low sticking coefficient of As on GaAs surfaces, we can infer that the surface layer is almost depleted of As after the ion bombardment and annealing treatment. The ($\sqrt{19}\times\sqrt{19}$) reconstruction has an Auger ratio of 3.1[4] and can be obtained from the As-rich (2×2) structure by heating to 845 K.[6] Heating induces desorption from the surface of approximately half a monolayer of As.

The experimental situation can then be summarized as follows: Under As-rich conditions a (2×2) structure with high As surface content is obtained, which reverts to a ($\sqrt{19}\times\sqrt{19}$) structure through As desorption. Ion bombardment and annealing produce a second (2×2) structure of lower As content. Table I summarizes the experimental results along with our theoretical predictions.

We have considered a wide variety of possible (2×2) reconstructions.[8] Each reconstruction was relaxed to obtain the lowest-energy geometry. These model geometries are presented in Fig. 1, according to

TABLE I. Summary of experimental results and theoretical predictions for GaAs($\overline{111}$). The Auger ratios refer to the As/Ga intensity ratio. N_{As} (N_{Ga}) is the number of As (Ga) atoms in the surface layer. S = stoichiometry (defined in the text).

Periodicity (expt.)	Reconstruction (theory)	Composition (theory) N_{As}	N_{Ga}	S	As/Ga Auger ratio (expt.)[a]
(2×2)	Staggered As vacancy	3	4	-0.25	4.2 ± 0.24
$(\sqrt{19}\times\sqrt{19})$		6	19	-0.68	3.14 ± 0.06
(2×2)	Ga Triangle	0	3	-0.75	2.4

[a]From Refs. 4 and 7.

the surface stoichiometry, S, and the total energy per (2×2) unit cell. The stoichiometry is defined as the number of As atoms minus the number of Ga atoms per (1×1) unit cell. Thus, for example, a stoichiometry of $S=-0.25$ indicates that in the first bilayer of the (2×2) unit cell there are three As and four Ga atoms, or two As and three Ga atoms, etc. We consider surfaces with $S=n/4$ (n odd), because only for these surfaces do the (2×2) reconstructions have semiconducting character.

The total energy of each configuration is calculated completely *ab initio,* with the pseudopotential formalism.[9] All the energies are given with respect to the unreconstructed ideal surface, in electronvolts per (2×2) unit cell. Within each stoichiometric class, energy comparisons are straightforward provided the number of atoms is constant. For reconstructions differing from each other by a GaAs pair (same stoichiometry), the calculated cohesive energy of GaAs (6.8 eV per pair) is included in the energy comparison. This amounts to assuming equilibrium with bulk GaAs. Comparison of the energies for different stoichiometries is more subtle, since one is then dealing with different numbers of atoms. The proper comparison is to include the total electronic energy of each added or subtracted atom minus the binding energy of the appropriate atomic reservoir. This amounts to assuming equilibrium of the chemical potentials of different phases. The atomic reservoirs considered here are dictated by common experimental conditions[5,6]: As_2 gas and Ga bulk, with binding energies 2.0 and 2.8 eV per atom, respectively.[10]

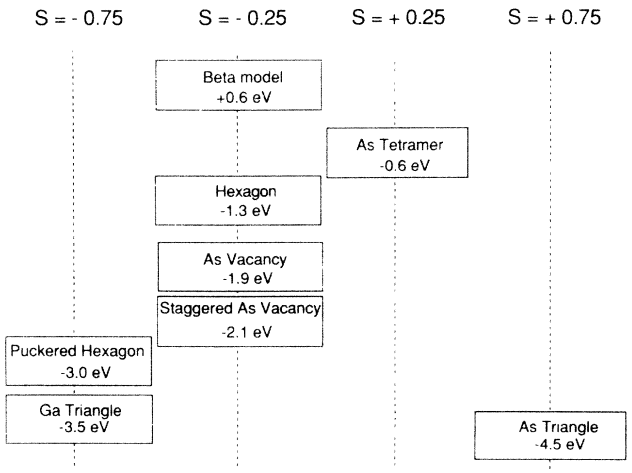

FIG. 1. Models for the (2×2) reconstructions of GaAs($\overline{111}$). The columns indicate different stoichimetric classes (defined in the text). The vertical position indicates energy relative to the ideal surface (the positions are not to scale). The exact energy differences are given in electronvolts per (2×2) unit cell.

For the rest of this paper we shall concentrate only on low-energy models. Starting at the lower left of Fig. 1, we observe that the lowest-energy configuration is the Ga triangle, consisting of three Ga atoms bonded to the surface in a triangular configuration [shown in Fig. 2(a)]. Its low energy and low stoichiometry make this geometry an excellent candidate for the As-depleted (2×2) reconstruction with measured Auger ratio 2.4. The other geometry in the same stoichiometric class, the "puckered hexagon," [Fig. 2(b)] consists of four Ga atoms and one As atom in the first bilayer of the (2×2) unit cell. All of the surface atoms are threefold coordinated. The bonds of three of the surface Ga atoms lie in planes perpendicular to the surface. The fourth Ga atom is bonded to the other three in an almost planar configuration forming three Ga—Ga bonds. The pattern is characterized by puckered hexagons composed of nine Ga and three As atoms. The energy of this geometry is sufficiently low to make it an interesting reconstruction, but still higher than that of the Ga triangle geometry.

Consider now replacing the Ga atom which forms three Ga—Ga bonds by an As atom. This gives a similar geometry with hexagons composed of six As and six Ga atoms.[11] This model has stoichiometry $S=-0.25$ (Fig. 1). There are, however, other models in the same stoichiometric class with lower energy. The lowest-energy geometries in this class are

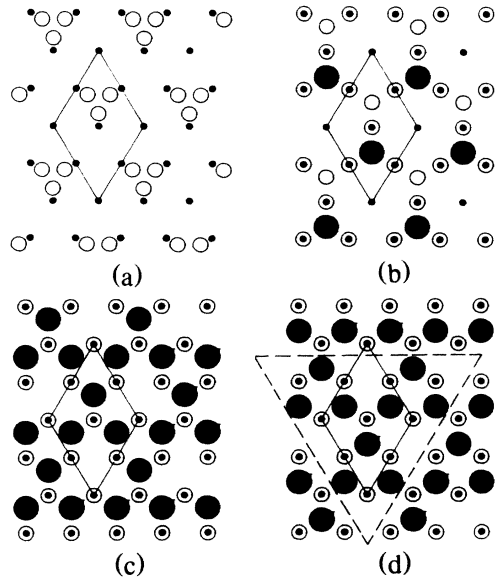

FIG. 2. Four different (2×2) reconstruction models for GaAs($\overline{111}$): (a) Ga triangle model; (b) puckered hexagon model; (c) As vacancy model; (d) staggered As vacancy model. The (2×2) unit cell is indicated in each model. Atoms on the three uppermost planes are shown. Solid circles, As atoms; open circles, Ga atoms; open circles containing solid circles, a Ga atom directly above an As atom. The size of the circles indicates proximity to the surface. The atomic relaxation is schematic for (a) and omitted for the rest.

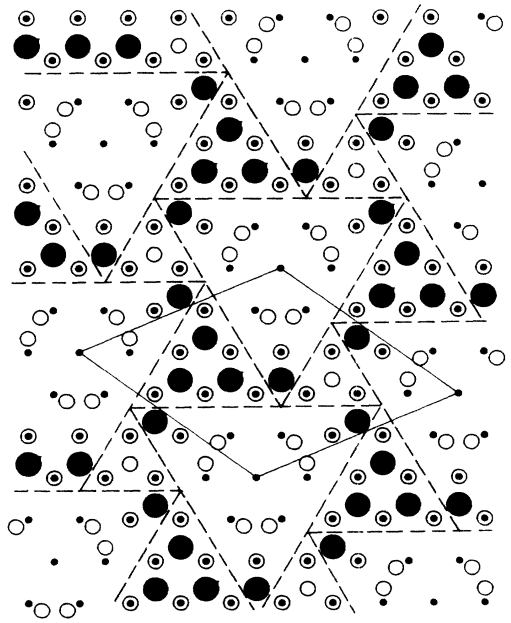

FIG. 3. The ($\sqrt{19}\times\sqrt{19}$) model, incorporating features of the staggered As vacancy and Ga triangle models. Symbols have the same meaning as in Fig. 2. The relaxation is schematic.

associated with missing As atoms. The As vacancy geometry simply involves the removal of one As atom per (2×2) unit cell from the ideal surface [Fig. 2(c)]. The staggered vacancy geometry, on the other hand, consists of the same number of atoms in a different configuration: The uppermost As surface layer is rotated by 60° as shown in Fig. 2(d). The resulting geometry resembles closely the structure of two consecutive wurtzite planes along the (111) direction, with an As vacancy in the upper plane. This structure allows for much more efficient relaxation of the threefold-coordinated surface Ga and As atoms, leading to a lower energy than the simple vacancy geometry. Although the energy difference of the two vacancy geometries is small, we suggest that the staggered vacancy structure could be feasible experimentally, as a result of the favorable geometric coordination of the threefold-bonded atoms. If so, this model is a possible candidate for the As-stabilized (2×2) reconstruction.

Another interesting geometry consists of replacing the fourfold-coordinated surface Ga atom in the staggered vacancy by an As atom. The resulting structure contains clusters of four As atoms in the surface bilayer. This is the "As tetramer" model in Fig. 1. We note that its energy is fairly high. A much lower-energy geometry consists of a triangle of As adatoms bonded to the ideal surface, in a configuration analogous to the Ga triangle described earlier. In principle, from energy considerations alone, such a structure should be attainable. Kinetic effects, however, may play an all-important role in determining whether this particular reconstruction is actually realized experimentally. The very low As sticking coefficient indicates that its observation is unlikely. Thus, two possible candidates for the observed (2×2) reconstructions are the Ga triangle and the staggered As vacancy geometries for the Ga- and As-stabilized surfaces, respectively.

Total-energy calculations on the ($\sqrt{19}\times\sqrt{19}$) geometry are not feasible at present. Nevertheless, we suggest a reasonable reconstruction guided by the available experimental data and the knowledge gained from our calculations on the (2×2) geometries. Specifically, the Auger measurements indicate that the relative abundance of As and Ga atoms on the ($\sqrt{19}\times\sqrt{19}$) surface lies between that of the As-stabilized and the Ga-stabilized (2×2) reconstructions. For low stoichiometries S, our calculations suggest that the Ga triangle should be an important building block. Finally, we recall that transitions are possible to and from the ($\sqrt{19}\times\sqrt{19}$) geometry and the As-stabilized (2×2) geometry.[5-7] The amount of As desorbing during the transition from the As-stabilized (2×2) geometry to the ($\sqrt{19}\times\sqrt{19}$) reconstruction is ~ 0.44 of an As monolayer.[6]

On the basis of the above considerations we propose a ($\sqrt{19}\times\sqrt{19}$) geometry which embodies features of

both the Ga triangle and the staggered As vacancy configurations. The $(\sqrt{19}\times\sqrt{19})$ geometry is constructed in the following way: Starting with the staggered vacancy we can remove the three As atoms shown in the (2×2) unit cell of Fig. 2(d). A large triangular unit can then be identified and is shown by dashed lines in Fig. 2(d). This unit contains ten Ga atoms and six As atoms. Rearrangement of the As atoms and displacement of the central Ga atom allows the formation of three smaller, energetically favorable Ga triangle units. This in turn suggests that the large triangle itself may be a low-energy building block for a larger surface reconstruction. Indeed, a close-packing arrangement of such triangles leads immediately to a $(\sqrt{19}\times\sqrt{19})$ structure as indicated in Fig. 3.

The final proposed reconstruction, shown in Fig. 3, consists of six As atoms and nineteen Ga atoms in the first bilayer of the $(\sqrt{19}\times\sqrt{19})$ unit cell. All the surface As atoms are threefold coordinated, including the one exposed As atom in the second bilayer (situated in the center of the large triangle, Fig. 3). The surface Ga atoms are threefold or fourfold coordinated. The composition of the surface layer is in agreement with available experimental information. In particular, no Ga atoms desorb during the transition from the As-stabilized (2×2) reconstruction to the $(\sqrt{19}\times\sqrt{19})$ geometry.[6] Furthermore, the amount of As desorbing during this transition is 0.43 of a monolayer, in excellent agreement with experiment.[6] Finally, we note that any $(\sqrt{19}\times\sqrt{19})$ geometry must be metallic because of symmetry constraints. The structure that we propose is very weakly metallic with an excess of only $\frac{3}{4}$ of an electron per $(\sqrt{19}\times\sqrt{19})$ unit cell.

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