# Vacancy-Induced 2 × 2 Reconstruction of the Ga(111) Surface of GaAs

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Vacancy formation on the GaAs(111) surface is calculated to be strongly exothermic in character. The creation of one vacancy in each 2 × 2 cell allows the remaining Ga surface atoms to have a large inward relaxation, resulting in a 2.3-eV reduction in energy. It also transforms the polar (111) surface into a nonpolar (110)-like surface. The calculations provide strong support for the vacancy model of Tong *et al.*, which is determined from analysis of low-energy-electron-diffraction data.

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The surface atomic structures of nearly all semiconductors deviate appreciably from the ideal ones expected from the bulk structure. The atomic motions and rebonding are usually accompanied by significant changes in the surface electronic structure. The correlation between atomic and electronic structure is generally so strong that a realistic description of the surface electronic structure cannot be obtained without a knowledge of the correct atomic geometry. Despite significant progress in the determination of a number of surface structures, the nature of most semiconductor surfaces remains unknown. In particular, very little is known with certainty about the surface atomic geometry of the polar faces of III-V semiconductors.

In this paper we consider the 2 × 2 reconstruction of the GaAs(111) surface. The total-energy calculations suggest that the vacancy model has a very low energy, thus providing strong support for the recent structural determination of Tong, Xu, and Mei[1] which is based on an analysis of low-energy-electron-diffraction (LEED) data. The most interesting aspect of the vacancy model, aside from the fact that it is found to be energetically favorable, is that it effectively transforms the polar surface into a nonpolar one. The various aspects of the surface structure and the calculations are discussed in detail below.

A top view of the vacancy model for the GaAs(111)-2 × 2 surface is shown in Fig. 1. The removal of one Ga atom from the center of the unit cell exposes three As-dangling bonds on the second-layer As atoms. As a result, the surface has equal densities of Ga and As threefold-coordinated atoms. These atoms form sixfold rings of nearest neighbors at the corners of the unit cell, as shown by the dark solid lines in Fig. 1. The nearest-neighbor bonding is chemically similar to that on the ideal (110) surface where each threefold-coordinated Ga atom is bonded to two threefold-coordinated As atoms and vice versa. The dangling-bond density is, however, 22.5% larger on the (111) surface than on the (110) surface, indicating that the surface energies should also differ by the same amount.

The creation of vacancies on the (111) surface allows the remaining Ga surface atoms to relax inward, thereby changing their bonding from $sp^3$ to $sp^2$. The energy-minimization calculations predict a large inward relaxation which reduces the surface interlayer spacing to $\frac{1}{5}$ of the bulk value of 0.82 Å. Without vacancies, this rehybridization would be opposed by a large lattice strain. The average of the bond angles around the threefold Ga and As atoms is calculated to be 119.2° and 93.8°, respectively. These values are close to the corresponding values for the (110) surface.[2]

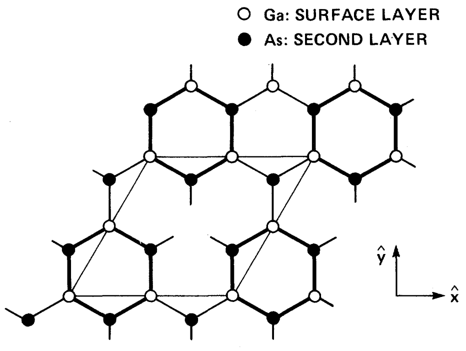

FIG. 1. A top view of the 25% vacancy model for the GaAs(111)-2 × 2 surface. The threefold coordinated Ga and As atoms lie on sixfold rings at the corners of the unit cell, as shown by the dark solid lines. The local bonding geometry for each threefold-coordinated atom is similar to that on the nonpolar (110) surface. The $\hat{z}$ axis is along the [111] surface normal.

An eight-layer slab geometry periodic in two dimensions was used in the structural studies. The top end of the slab forms a (111) Ga-rich surface whereas the bottom side is a $(\bar{1}\bar{1}\bar{1})$ As-rich surface. Calculations on several structural models for the (111) surface including vacancy and nonvacancy models were made. The calculations can be done much more easily when the As side of the slab is made to be nonpolar (and as it turns out nonmetallic), through the creation of 25% As vacancies. It should be noted, as discussed below, that vacancy formation on the $(\bar{1}\bar{1}\bar{1})$ As face is not energetically favorable, but it is useful for computational purposes. The surface relaxations on each side of the slab were checked and found to be independent and unaffected by the relaxation on the other side, as is to be expected.

The energy-minimization calculations were carried out using the tight-binding method.[2] The directions and relative magnitudes of atomic displacements were determined from a calculation of the Hellmann-Feynmann forces[3] acting on the atoms. Because of the success of the tight-binding[2] method in accurately determining the structure of the GaAs(110) surface[4–6] and the similarities in the surface bonding of the (111) and (110) surfaces, the results given below for the atomic electronic structure of the (111) surface vacancy model are expected to be as accurate as those obtained previously for the (110) surface. The magnitude of the vacancy relaxation energy, however, may be overestimated in the tight-binding calculation,[6] as discussed below.

The *reduced* atomic coordinates ($R_x$, $R_y$, $R_z$) for the first four atomic planes on the GaAs(111)-2×2 reconstructed Ga-terminated surface are shown in Table I and compared with those for the ideal vacancy model and the LEED results of Tong, Xu, and Mei.[1] The atomic displacements from the ideal positions are also shown. The atomic positions ($r_x$, $r_y$, $r_z$) are related to ($R_x$, $R_y$, $R_z$) in Table I by

$$r_x = R_x a\hat{x}, \tag{1}$$

$$r_y = (R_y/\sqrt{3})\, a\hat{y}, \tag{2}$$

$$r_y = [R_z/(24)^{1/2}]\, a\hat{z}, \tag{3}$$

where $a \simeq 4$ Å is the surface hexagonal lattice constant. The results in Table I show that the reconstructed 2×2 surface maintains its threefold rotational symmetry about an axis going through the center of the unit cell shown in Fig. 1. The lateral (or in-plane) distortions are seen to be damped very rapidly away from the surface. The magnitude of the atomic displacements are smaller than 0.1 Å for all atoms below the first two Ga and As planes. The relaxation is dominated by the tendency of the surface Ga atoms to "sink" towards the adjacent As plane by 0.58 Å. This is accompanied by lateral displacements of the As atoms which act to keep the surface Ga-As bond-length shrinkage to 1.2% of the bulk value. The direction and overall magnitude of the atomic relaxations are in good agreement with independent LEED results that have been obtained recently by Tong, Xu, and Mei.[1]

Vacancy formation on the Ga(111) surface is calculated to be exothermic. The energy release $\Delta E$ in going from the ideal unrelaxed surface to the system consisting of the relaxed vacancy geometry plus a free Ga atom is

$$\Delta E = 2.3 \text{ eV per } 2\times 2 \text{ unit cell.} \tag{4}$$

Relaxation of the ideal surface with no vacancies leads to a distortion in the direction of vacancy formation, i.e., three surface Ga atoms (per 2×2 cell) move in towards bulk atoms while one Ga atom moves gradually out of the surface. The total-energy goes down steadily as the interlayer spacing between the Ga atoms increases. A local minimum in the total energy is obtained at a Ga-Ga interlayer separation of 1.06 Å for which some Ga-As surface bond lengths are stretched by 5.2%. The creation of the vacancy involves an energy barrier which is difficult to determine from the tight-binding calculations.

The surface electronic structure of the ideal and of the relaxed nonvacancy (111) surfaces is metallic. The Ga-derived dangling-bond orbitals form a band of states extending upward in energy from a position 0.15 eV below the conduction-band minimum. Vacancy formation is accompanied by a metallic-to-semiconducting surface electronic transition. For the relaxed vacancy, all surface states are removed from the bulk band gap, making the surface electronic structure similar to that of the GaAs(110) surface.[7,8] The highest occupied surface states are As derived with an energy of 0.8 to 1.1 eV below the valence-band maximum (VBM). The lowest unoccupied surface states are Ga-derived at 2.1 eV above the VBM with an upward dispersion of 1.03 eV. The surface Ga and As atoms are calculated to be neutral within $\pm 0.14e$ so that problems encountered in tight-binding calculations with large charge transfers ($\simeq 1e$) are not expected here. The prediction of a nonmetallic structure for the Ga-rich (111) surface is consistent with the preliminary results of recent photoemission measurements done in our laboratory.[9]

Total energy calculations were also done for the $\text{As}(\bar{1}\bar{1}\bar{1})$ surface which is known to exhibit a metastable 2×2 reconstruction.[10] Vacancy formation on

TABLE I. The *reduced* atomic coordinates $(R_x, R_y, R_z)$ for the relaxed and the ideal, unrelaxed vacancy models for the GaAs(111)-2×2 surface are given in columns 2 and 3, respectively. The actual atomic coordinates $(r_x, r_y, r_z)$ are related to those shown in the table by Eqs. (1)–(3). The atomic displacements from their ideal, unrelaxed positions are shown in column 4 for comparison with the LEED results of Tong, Xu, and Mei (Ref. 1) given in column 5. The surface has threefold rotational symmetry about axis going through the vacancy.

Table I

| Atom Type | Relaxed Vacancy $(R_x, R_y, R_z)$ | Unrelaxed Vacancy $(R_x, R_y, R_z)$ | Atomic Displacements in Å: This work | Atomic Displacements in Å (Tong *et al.*: Ref. 1) |
|---|---|---|---|---|
| Ga | (+0.032, 0.032, −0.714) | (0.0, 0.0, 0.0) | (+0.128, +0.074, −0.582) | ( 0.09, 0.05, −0.71) |
| Ga | (+0.968, 0.032, −0.714) | (1.0, 0.0, 0.0) | (−0.128, +0.074, −0.582) | (−0.09, 0.05, −0.71) |
| Ga | (+0.500, 1.436, −0.714) | (0.5, 1.5, 0.0) | ( 0.000, −0.148, −0.582) | ( 0.00, −0.10, −0.71) |
| As | (−0.064, 1.064, −0.928) | (0.0, 1.0, −1) | (−0.256, +0.148, +0.059) | (−0.24, 0.14, 0.04) |
| As | (+1.500, 2.372, −0.928) | (1.5, 2.5, −1) | ( 0.000, −0.295, +0.059) | ( 0.00, −0.28, 0.04) |
| As | (+1.064, 1.064, −0.928) | (1.0, 1.0, −1) | (+0.256, +0.148, +0.059) | ( 0.24, 0.14, 0.04) |
| As | (+0.500, 2.500, −1.095) | (0.5, 2.5, −1) | ( 0.000, +0.000, −0.078) | ( 0.00, 0.00, −0.08) |
| Ga | (−0.005, 1.005, −3.927) | (0.0, 1.0, −4) | (−0.020, +0.001, +0.060) | ( 0.00, 0.00, 0.01) |
| Ga | (+1.500, 2.490, −3.927) | (1.5, 2.5, −4) | ( 0.000, −0.023, +0.060) | ( 0.00, 0.00, 0.01) |
| Ga | (+1.005, 1.005, −3.927) | (1.0, 1.0, −4) | (+0.020, +0.001, +0.060) | ( 0.00, 0.00, 0.01) |
| Ga | (+0.500, 2.500, −4.064) | (0.5, 2.5, −4) | ( 0.000, +0.000, −0.052) | ( 0.00, 0.00, −0.08) |
| As | (−0.002, 1.998, −5.005) | (0.0, 2.0, −5) | (−0.008, −0.005, −0.004) | – – – – |
| As | (+1.002, 1.998, −5.005) | (1.0, 2.0, −5) | (+0.008, −0.005, −0.004) | – – – – |
| As | (+0.500, 3.504, −5.005) | (0.5, 3.5, −5) | ( 0.000, +0.009, −0.004) | – – – – |
| As | (+1.500, 3.500, −4.936) | (1.5, 3.5, −5) | ( 0.000, +0.000, +0.052) | – – – – |

this surface is found to be endothermic. The relaxation of the ideal surface leads to an equilibrium configuration in which all four surface As atoms move out, three by 9% of the bulk interlayer spacing and one by 13%. The energy lowering is very small (≃ 0.04 eV per unit cell), indicating that this is probably not the best structure for the surface. Vacancy formation on the ideal surface is calculated to require an energy of 2.8 eV per 2×2 cell. A large part (75%) of this energy is gained back as a result of lattice relaxation occurring *after* vacancy formation, but overall, the 2×2 vacancy structure remains energetically unfavorable. This result is supported by the most recent experimental determination[10] of the $(\bar{1}\bar{1}\bar{1})$ surface stoichiometry which shows that the surface consists of a full monolayer of As in contrast to previous work[11] which had indicated an As depletion. The LEED analysis of Tong *et al.*[12] also suggests that a vacancy model does not work well for this surface.

The asymmetry between the Ga(111) and As$(\bar{1}\bar{1}\bar{1})$ vacancy structures, both of which have identical densities of threefold-coordinated Ga and As atoms, can be largely attributed to the low energy of an As dangling bond as compared to that of a Ga dangling bond. Vacancy formation on the

Ga(111) surface leads to an appreciable lowering of the electronic energy resulting from the elimination of high-energy Ga dangling-bond states near the conduction band and their replacement by low-energy As dangling-bond states lying below the valence band. A similar lowering in total energy does not occur on the As($\bar{1}\bar{1}\bar{1}$) surface upon vacancy formation because the As dangling-bond states do not have a high energy on the ideal surface. This leads to the expectation that, in general, vacancy formation on the (111) [($\bar{1}\bar{1}\bar{1}$)] face of polar III-V and II-VI semiconductors should become more [less] favorable as the ionicity *and* the band gap of the material increase [decrease]. Similar calculations for C(111) and Si(111) surfaces show that vacancy formation is endothermic on nonpolar surfaces.[13]

Finally, the question of the accuracy of the tight-binding result for the energy reduction $\Delta E$ given by Eq. (4) needs to be addressed. As for the case of the (110) surface,[6] the tight-binding method probably overestimates the magnitude of $\Delta E$. The major source of the error is in the position of the Ga-derived metallic states near the conduction-band minimum for the ideal (111) surface with no vacancies. From a comparison of previous calculations for the (110) surface,[7,8] the energy of these states may be high by $\simeq 0.25$ eV. From the definition of $\Delta E$, it can be seen that this can lead to an overestimation of the vacancy formation energy by $\simeq 1$ eV per $2\times 2$ cell. This is not large enough to alter the results discussed above concerning the energetics of vacancy formation.

In summary, the vacancy-induced $2\times 2$ reconstruction of the Ga(111)-terminated surface of GaAs was examined via total-energy calculations. Vacancy formation is found to be strongly exothermic when lattice relaxation resulting from vacancy creation is taken into account. The polar (111) surface is effectively changed into a nonpolar-(110)-like surface upon vacancy formation. The calculated surface atomic structure of the vacancy model provides strong support for an independent structural determination[1] from LEED.

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