# Atomic Structure of the $(2\times 2)$ Reconstructed GaAs $(\bar{1}\,\bar{1}\,\bar{1})$ Surface: A Multivacancy Model

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A new vacancy-complex model for the $(2\times 2)$ reconstructed As-stabilized $(\bar{1}\,\bar{1}\,\bar{1})$ surface of GaAs in which the surface bilayer contains two As and three Ga atoms per unit cell is proposed. Half the surface As atoms occupy stacking-fault sites, leading to nearly optimal rehybridizations of surface-bonding orbitals. The surface As coverage is consistent with both mass spectrometry and Auger data. The calculated surface electronic structure is nonmetallic and provides a satisfactory description of polarization-dependent angle-resolved photoemission data.

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The determination of the surface atomic structure of crystalline solids is a challenging problem of surface science. Numerous studies have shown that substantial departures from the ideal bulk structure occur on many surfaces leading to reconstruction, i.e., to a periodicity different from that in a corresponding bulk plane. An interesting phenomenon is the occurrence of two or more reconstructions on a clean surface of a given orientation as a function of temperature or surface preparation. The surfaces of tetrahedrally bonded group-IV and III-V semiconductors exhibit a variety of such reconstructions. For a compound semiconductor such as GaAs there is, in comparison to an elemental semiconductor, an additional important determinant of surface structure: surface stoichiometry. This factor is especially significant on polar surfaces where chemical composition strongly influences surface periodicity.

The $(\bar{1}\,\bar{1}\,\bar{1})$ polar surface of GaAs exhibits a number of reconstructions which are correlated with the surface As coverage.[1–3] Very little is known about the atomic structure of these surfaces. In this paper I examine the atomic structure of the $(2\times 2)$ reconstructed $(\bar{1}\,\bar{1}\,\bar{1})$ surface of GaAs and propose a new vacancy-complex model to explain experimental data from mass spectrometry,[2] Auger intensity analysis,[3] and angle-resolved photoemission measurements.[4,5] The new multivacancy model is more stable than a single-vacancy model of the type occurring on the (111) surface.[6–8]

The As-stabilized GaAs $(\bar{1}\,\bar{1}\,\bar{1})$-$(2\times 2)$ surface is observed during crystal growth by molecular-beam epitaxy[1–5] (MBE) and is stable at 450 K. An important result relevant to the problem of surface structure comes from mass spectrometry[2] which shows 0.5 monolayer of As (in the form of $As_2$ molecules) desorbing from the surface when the temperature is raised to 845 K. A transformation from $(2\times 2)$ to $(\sqrt{19}\times\sqrt{19})$ periodicity accompanies the As desorption. The surface As coverage of the latter structure was determined to be less than 0.1 monolayer.[2] Vapor-pressure data from flash-desorption experiments are also found to be consistent with a surface As coverage of 0.5 monolayer on the $(2\times 2)$ surface.[2] In contrast, Auger studies[4] suggest a significantly higher surface As concentration of $\simeq 0.75$–$0.87$ monolayer. Even though the two measurements give apparently incompatible results the structure discussed below is shown to provide a satisfactory explanation for both sets of data.

The proposed multivacancy model for the $(2\times 2)$ reconstructed GaAs $(\bar{1}\,\bar{1}\,\bar{1})$ surface is shown in Fig. 1 and a perspective view is shown in Fig. 2. The surface bilayer contains two As and three Ga atoms per $(2\times 2)$ cell. The Ga atoms are in "normal" sites directly above As substrate atoms. It can be seen from Figs. 1 and 2 that half the surface As atoms must occupy stacking-fault sites. All atoms in the surface bilayer in addition to substrate As atoms located in hollow sites are threefold coordinated. There are no "wrong" atom bonds, i.e., all bonds are between Ga and As atoms. The stacking-fault geometry for As atoms is energetically very favorable since it forces each surface Ga atom to become very nearly coplanar with the three

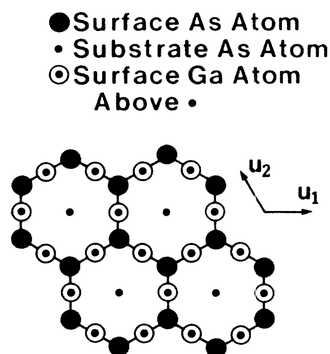


FIG. 1. Top view of the vacancy-complex structure for the $(2\times 2)$ reconstructed GaAs $(\bar{1}\,\bar{1}\,\bar{1})$ surface. The four "hollow site" substrate As atoms define a $(2\times 2)$ unit cell. The primitive translation vectors of the $(1\times 1)$ lattice are denoted by $\mathbf{u}_1$ and $\mathbf{u}_2$.


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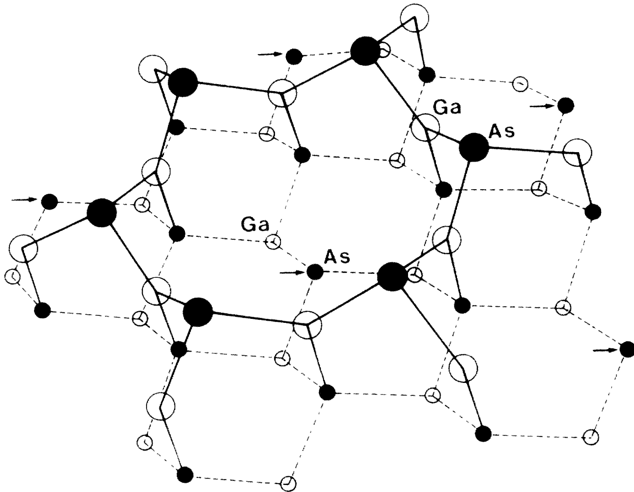


FIG. 2. A perspective drawing of the vacancy-complex model. The arrows point to three-fold coordinated substrate As atoms in hollow sites. The surface Ga atoms are coplanar with their nearest-neighbor As atoms. The dashed lines indicate Ga—As bonds in the substrate layer.

As atoms to which it is bonded. Two of these As atoms are in the surface plane above the Ga atoms and the third is in the layer below, as shown schematically in Fig. 2. This arrangement of atoms does not introduce any additional strain as compared to the normal stacking sequence. The surface Ga atoms would be exactly coplanar with their three surrounding As atoms if the very small lateral relaxations of third-layer As atoms (shown in Table I) are ignored. The nearly planar configuration for Ga leads to optimal $sp^2$ orbital rehybridization.

The surface As concentration of 0.5 monolayer for this model is the same as that obtained experimentally from mass spectrometry.[2] The model is also consistent with Auger data[3] suggesting an As coverage of $\simeq 0.75$ monolayer because of the presence of the threefold-coordinated substrate As atom at the hollow site of the unit cell. This atom should give as strong an Auger signal as a surface atom. The desorption of only 0.5 monolayer of As from the surface at elevated temperatures[2] indicates a higher mobility and recombination probability for surface relative to substrate As atoms.

The structure of the vacancy-complex model was optimized via tight-binding-based energy-minimization calculations[9] and the resulting surface atomic coordinates are given in Table I. Minimal strains on substrate layers are caused by the surface reconstruction; even the surface Ga atoms are close to their bulk terminated positions. The largest strains are in the surface As to Ga bonds which are stretched by 4% from their normal bulk value. The angular distributions are nearly ideal with values of 103.1° for As and 115.7°, 114.9°, and 129.4° for Ga surface atoms, respectively. The hollow-site As lies on a threefold axis of symmetry and has angular distribution of 101.8°.

TABLE I. The *reduced* atomic coordinates $(a,b,c)$ in a hexagonal coordinate system for the $(2\times 2)$ ideal and for the multivacancy $(2\times 2)$ reconstructed $(\bar{1}\bar{1}\bar{1})$ surfaces of GaAs. Atomic coordinates are determined from the relation $\mathbf{r} = a\mathbf{u}_1 + b\mathbf{u}_2 + c\mathbf{u}_3$, where $\mathbf{u}_1$ and $\mathbf{u}_2$ are lattice vectors of the $(1\times 1)$ lattice shown in Fig. 1 and $\mathbf{u}_3$ is the outward normal to the surface with magnitude equal to the bulk bilayer spacing of $\simeq 0.816$ Å.

| Atom | $(a,b,c)$ Ideal $(2\times 2)$ surface | $(a,b,c)$ Reconstructed surface |
|---|---|---|
| As | (0.667,0.333,0) | Vacancy |
| As | (1.667,1.333,0) | Vacancy |
| As | (0.667,1.333,0) | (0.667, 1.333, 0.323) |
| As | (1.667,0.333,0) | (1.333, 0.667, 0.323) |
| Ga | (0.000,0.000,−1) | Vacancy |
| Ga | (1.000,0.000,−1) | (1.000,0.000,−1.014) |
| Ga | (0.000,1.000,−1) | (0.000,1.000,−1.014) |
| Ga | (1.000,1.000,−1) | (1.000,1.000,−1.014) |
| As | (0.000,0.000,−4) | (0.000,0.000,−3.648) |
| As | (0.000,1.000,−4) | (0.005,1.003,−4.029) |
| As | (1.000,1.000,−4) | (0.997,1.003,−4.029) |
| As | (1.000,2.000,−4) | (0.997,1.995,−4.029) |
| Ga | (0.333,0.667,−5) | (0.319,0.638,−4.989) |
| Ga | (0.333,1.667,−5) | (0.319,1.681,−4.989) |
| Ga | (1.333,0.667,−5) | (1.333,0.667,−4.981) |
| Ga | (1.333,1.667,−5) | (1.362,1.681,−4.989) |

The $(\bar{1}\bar{1}\bar{1})$-$(2\times 2)$ surface prepared by MBE is observed to be stable when there are no beams of Ga atoms or $As_2$ molecules incident upon or desorbing from the surface.[2] The stability of a structural model for this surface requires that, in equilibrium, the free energy of the combined surface-substrate-bulk system should be a minimum with respect to (i) atomic positions, and (ii) exchange of atoms between the surface and the bulk. The first condition can be met by finding the atomic coordinates which minimize the total energy for a given atomic configuration. The second condition requires a comparison of competing structural models. In general, these will have different stoichiometries since an exchange of atoms between the surface and bulk leads to an alteration of the surface chemical composition. In order for the lowest-energy structure obtained in this way to be "correct" its surface stoichiometry must be consistent with that observed experimentally. Otherwise, a search for a new structure must be made. The stability of the vacancy-complex configuration relative to two other plausible structures, a Ga adatom model and a simple $\frac{1}{4}$-monolayer As vacancy model, both derived from it via the exchange of surface and bulk atoms, is discussed below.

The model shown in Fig. 1 can be obtained from the ideal surface through the addition of two As and three

Ga atoms per $(2\times 2)$ unit cell. The energy of this surface is calculated to be lower than the system consisting of the ideal surface, a free $As_2$ molecule, and three free Ga atoms in the vapor phase by 14.6 eV per $(2\times 2)$ unit cell. Starting from the ideal surface the three Ga and two As atoms can be used to create a different structure: Two Ga and two As atoms per $(2\times 2)$ cell are used to create the next Ga-As bilayer (covering $\frac{1}{2}$ the sample surface)[10] and the remaining Ga atom is put into an adatom geometry in which it is bonded to three surface As atoms. In this process two Ga and two As surface atoms of the vacancy-complex model have been, effectively, incorporated into the bulk. With use of the total-energy calculations of Kaxiras *et al.*[11] for the Ga adatom model, the vacancy-complex model is found to be stable by 0.3 eV with respect to this rearrangement. The above exchange of atoms can be taken one step further: The Ga adatom and a surface As atom can, in principle, be removed and incorporated into the bulk creating a $(2\times 2)$ single-vacancy model in which $\frac{1}{4}$ monolayer of As atoms are missing from the ideal surface. This structure, after allowance for atomic relaxation, is also found to be $\simeq 0.3$ eV less stable than the vacancy-complex model. These results are consistent with those obtained from analyses of low-energy-electron-diffraction data[12] which show that neither the simple vacancy nor the adatom structure provide a satisfactory description of the observed $I$-$V$ spectra.

Vacancy-complex formation on the GaAs $(\bar{1}\bar{1}\bar{1})$ surface transforms this polar surface into a nonpolar one. It is interesting to note that on the (111) surface such a transformation comes about from the ordering of $\frac{1}{4}$ monolayer of Ga vacancies.[6,7] The nonpolarity of the resulting (111) surface is easy to see from the close similarity of its local-bonding configuration to that on the (110) surface. For the $(\bar{1}\bar{1}\bar{1})$ surface the nonpolarity of the surface can be derived explicitly by following a procedure introduced by Harrison[13] or, more qualitatively, by noting that the vacancy-complex structure and the simple $\frac{1}{4}$-monolayer As vacancy structure (which is also nonpolar) are related, as noted above, by a rearrangement of atoms in which no Ga—Ga or As—As bonds are introduced.

The calculated surface electronic structure for the vacancy-complex model is nonmetallic and the first empty surface state lies $\simeq 2.35$ eV above the bulk valence-band maximum. The occupied surface states lying within 1 eV of the valence-band maximum are shown in Fig. 3. These states are all predominantly As-$p_z$ in character. This result is consistent with that derived from photoemission meausrements[4,5] which show maximum electron emission for $p$-polarized light. The band labeled 1 in Fig. 3 has a mixed As- and Ga-$p_z$ character. Band 3 is the most strongly surface localized state and is primarily (80%) As-$p_z$ derived with some (20%) Ga-$(p_x+p_y)$ mixing. The wave function for band 2 is localized on the As atoms located in the hollow sites. The position of this band is sensitive to substrate relaxation with the band moving down by $\simeq 0.25$ eV when the substrate is allowed to relax. The contribution of this band to the surface As-derived electronic density of states is calculated to be only about 30% of that of band 3.

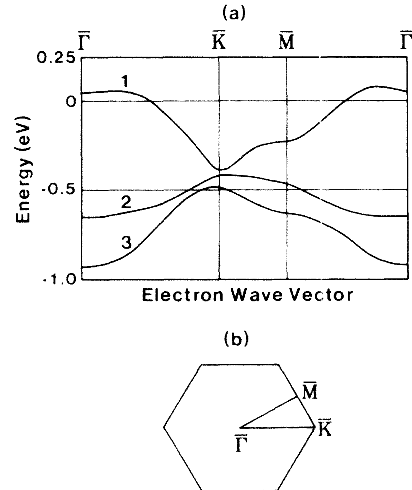


FIG. 3. (a) The dispersion of As-derived surface states near the bulk valence-band maximum along symmetry directions of the surface Brillouin zone. (b) The two-dimensional Brillouin zone.

The angle-resolved measurements of Bringans and Bachrach[5] show several surface states. Two strong states with energies at $\Gamma$ of 0.7 and 1.75 eV below the valence-band maximum can be identified with bands 1 and 3 of the present calculation. The measured (calculated) splittings of the bands are $\simeq 1.05$ eV (0.98 eV) at $\Gamma$ and $\approx 0$ eV (0.13 eV; less if band 2 is included) at the $K$ point of the Brillouin zone shown in Fig. 3(b). The calculated and measured bandwidths of $\simeq 0.4$–$0.45$ eV for each band are also in good agreement. The only major discrepancy is a uniform upward shift of 0.75 eV of the calculated bands with respect to the measured ones which is probably caused by the neglect of electrostatic effects at the surface.[14] Overall, the multivacancy model does much better in explaining the experimental photoemission results than the simpler single-vacancy model (with $\frac{1}{4}$ monolayer of As vacancies) for which either the bandwidths are smaller by a factor of 2 or the bands have the wrong disperison.

The vacancy-complex model provides a microscopic explanation for why crystals grown on the $(\bar{1}\bar{1}\bar{1})$ surface by MBE generally give poor luminescence, indicative of a large defect concentration.[15] For crystal growth to proceed an As atom on a stacking-fault site has to break at least one bond to move to a normal site. Defects would be generated if as a result of the

activation barrier for this process some As atoms remain in stacking-fault positions.

In summary, the proposed multivacancy model for the As-stabilized $(\bar{1}\bar{1}\bar{1})$ surface of GaAs provides a satisfactory explanation of experimental data from mass spectrometry,[2] Auger,[3] and photoemission measurements.[4,5] The present work suggests, in agreement with previous expectations,[12,16] that the $(2\times 2)$ ordered (111) and $(\bar{1}\bar{1}\bar{1})$ surfaces of III-V semiconductors have characteristically different reconstructions. The simple vacancy model of the (111) surface (after replacing anions with cations and vice versa) is not suitable for the $(\bar{1}\bar{1}\bar{1})$ surface even though, after relaxation, it would lead to essentially the same local atomic environments for the surface Ga and As atoms as on the (111) surface. Ion-scattering measurements[17,18] which have proven sensitive to stacking order on the Si(111)-$(7\times 7)$ surface[19] should prove very useful in similar tests on the $(\bar{1}\bar{1}\bar{1})$ surface. It remains to be seen whether the vacancy-complex model which should be appropriate for $(\bar{1}\bar{1}\bar{1})$ surfaces prepared by MBE is also applicable to the $(2\times 2)$ structure observed recently when a simultaneous ion bombardment and annealing procedure was used in preparing the surface.[20]

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