Structure of the As Vacancies on GaAs(110) Surfaces

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We report a comprehensive study of the As vacancies (V_{As}) in the GaAs(110) surface via *ab initio* total energy minimization. Previous scanning tunneling microscopy (STM) images of the V_{As} in p-type GaAs(110) were interpreted with a structure with outward movement of the Ga next to the vacancy. While our simulation of the STM images, using *ab initio* wave functions, agrees with experiment, our total energy minimization suggests, however, inward movement of Ga. We explain this apparent conflict as a charge induced band bending effect. As a consequence, we predicted that the STM images will depend on the applied bias voltage. We show that the atomic geometry of the surface $V_{As}(q)$ depends critically on the charge state q in sharp contrast with *bulk* vacancy. [S0031-9007(96)00556-X]

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The electronic and atomic structures of point defects on surfaces could differ significantly from their bulk counterparts. For *bulk* As vacancy (V_{as}) in GaAs, *ab initio* total energy calculations [1] showed that the vacancy is stable in either the $q = 3+$ (p-type) or the $q = 1+$ (n-type) charge state and that the geometry of the vacancies does not depend on q (i.e., all the nearest neighbor Ga atoms of the vacancies are threefold coordinated). For the As vacancy in GaAs(110) *surfaces*, on the other hand, a recent scanning tunneling microscopy (STM) experiment [2], in connection with a tight-binding simulation, showed that the $q = 2+$ charge (p-type) is stable, and that the surface Ga atoms are twofold coordinated with a giant 0.7 Å outward relaxation. These findings for surface As vacancies were recently questioned (Table I) by a pseudopotential total energy calculation [3] which suggested instead a $1-$ charge for all doping types and an *inward* relaxation of Ga atoms by as much as 0.4 Å.

In this paper, we determine via a careful *ab initio* total energy minimization the equilibrium atomic positions of V_{As} on GaAs(110) for different charge states q, obtaining the Fermi level dependence of the vacancy formation energies. We find that (i) the geometries of the surface vacancies, in contrast to bulk and to previous calculations for surface As vacancies [2,3], depend critically on q, and thus on the Fermi level [4]. New and unusually long chemical bonds form between Ga atoms resulting in a Ga-Ga dimer in V_{As}^{+} and a Ga trimer in V_{As}^{-}. (ii) The charge state of V_{As} in p-type samples is neither $2+$ [2] nor $1-$ [3], but rather $1+$. This agrees with recent *quantitative* measurements [5,6]. (iii) Given that an STM image samples only the electronic states near the Fermi level, while the total energy represents the contribution of all states, it is possible that STM image reflects a different atomic geometry than that obtained from total energy minimization [7,8]. We find indeed (Table I) that our simulated STM images (from the *ab initio* wave functions) mimic well the experimental images (As moves inwards; Ga outwards by 0.6 Å), but that such images do not reveal the true atomic structure as obtained from total energy minimization (Ga moves inwards by 0.3 Å). We find that this reflects band bending near a *charged* defect: The band bending reduces (increases) the STM current for anions (cations) causing inward (outward) movement of the STM tip but not a real atomic displacement.

The calculation was carried out using *ab initio* pseudopotentials [9] in a plane wave basis set [10] and the local density approximation (LDA). We used the Ceperley-Alder exchange correlation as parametrized by Perdew and Zunger [11]. The work of Yi *et al.* [3] employed a small 2×2 surface cell plus they restricted atomic relaxations, thus precluding any rebonded geometries. In this work, we used instead supercells containing larger 2×3 surface cells and up to 10 layers of GaAs and 4 layers of vacuum. Nine layers of atoms were relaxed freely to equilibrium positions according to the calculated forces [10], while keeping only the passivated back surface layer fixed. Two k points in surface irreducible Brillouin zone were used. The basis set cutoff was 6.5 Ry. Increasing the cutoff to 10 Ry results in only small changes in atomic positions less than 0.1 Å. The band structure at 6.5 Ry is, however, not fully converged: The occupied (empty) surface band is about 0.5 eV too high (low) with respect to bulk valence (conduction) band.

The use of periodic structures restricts our calculation to neutral unit cells. We achieve neutrality of supercells containing charge q by placing a compensating charge $-q$ as a uniform (jellium) background. The formation energy of an n-fold charged vacancy with respect to a neutral vacancy can thus be expressed as

$$\Delta E(n/0) = E_{\mathrm{tot}}^{\mathrm{LDA}}(q) - E_{\mathrm{tot}}^{\mathrm{LDA}}(0) + n(\epsilon_{\mathrm{VBM}} + \epsilon_f), \tag{1}$$

where E_{tot} is the total electron and ion energy, ϵ_f is the Fermi level (measured from the valence band maximum,

TABLE I. Direction of atomic displacements (↑ = outward, ↓ = inward, ↔ = little displacement) near an As vacancy in GaAs(110). TB and PS stand for tight-binding and pseudopotential total energy calculations

	From total energy minimization			From STM images	
Site	TB (Ref. [2])	PS (Ref. [3])	PS (Present)	Expt. (Ref. [2])	Calc. (Present)
As	?	?	↔	↓	↓
Ga	↑ (0.7 Å)	↓ (≤0.4 Å)	↓ (0.3 Å)	↑ (0.7 Å)	↑ (~0.6 Å[a])

[a]Inferred from the calculated dsplacement (0.4 Å) with respect to the third nn Ga atom and the measured [2] displacement of the third nn Ga and Ga distance away (0.2 Å).

ϵ_{VBM}). The last term in Eq. (1) accounts for the energy of the n electrons or holes in the reservoir. Assuming that L_i is the supercell's ith dimension where $i = x$, y, and z (z is normal to the surface) and that $\Delta z = z_2 - z_1 \ll L_z$ can be any interior, bulklike region of the GaAs slab, ϵ_{VBM}, in principle, can be determined [1] by aligning the average potential

$$\overline{V} = \frac{1}{L_x L_y \Delta z} \int_x \int_y \int_{z_1}^{z_2} V(\mathbf{r})\, d\mathbf{r} \qquad (2)$$

with that in 3D bulk solid. We found that Eq. (2) converges with L_z slower for *charged* defects than for neutral defects. In fact, with the supercell used by Yi *et al.* [3], it is difficult to determine the relative positions of the defect levels with respect to ϵ_{VBM}. To overcome the difficulty, we expressed $\epsilon_{\mathrm{VBM}}(q \neq 0)$ as $\epsilon_{\mathrm{VBM}}(q = 0) + \Delta\overline{V}$, where the volume-($V_{R^-}$) averaged quantity

$$\Delta\overline{V} = \overline{V}(q) - \overline{V}(q = 0)$$

$$= \frac{1}{V_R} \int_{V_R} [V^q(\mathbf{r}) - V^{q=0}(\mathbf{r})]\, d\mathbf{r} \qquad (3)$$

is now a *difference*. We then used the fact that the value of $\Delta\overline{V}$ does not depend on the region R over which the average is performed so long as R is sufficiently far from any defects. Here, we calculated $\Delta\overline{V}$ using a thin slab in the y ([$\bar{1}$10]) direction, not in the z direction as in Eq. (2), and found small and converged $\Delta\overline{V}(q)$'s (of the order of 0.1 eV). The calculated $\Delta E(n/0)$ is estimated to be accurate to within ± 0.15 eV.

We found in our energy minimization of $V_{\mathrm{As}}^{(n)}$ only inward relaxations of the two surface Ga atoms [denoted in Fig. 1, as Ga(1)] regardless of n (see side views in Fig. 1). This general trend contradicts the tight-binding result of Ref. [2] but agrees with the pseudopotential result of Ref. [3]. Unlike bulk vacancies [1], V_{As}^- and V_{As}^+ in GaAs(110) were found to prefer *rebonded* geometries, contradicting both Ref. [2] and Ref. [3]: (i) The structure of the rebonded V_{As}^- center is shown in Fig. 1(b). Here, three Ga atoms [Ga(1)s and Ga(2) in Fig. 1] form a trimer. The Ga(1)-Ga(2) bond length is 2.54 Å, compared with bulk Ga-As distance of 2.42 Å. The Ga(2) atom thus becomes fivefold coordinated. The two Ga(1) atoms moved inwards by 0.34 Å while the Ga(2) atom moved outward by 0.24 Å. The neighboring As atoms (designated as As(1) in Fig. 1] show small inward displacement (~0.04 Å). The only gap state in V_{As}^- is about 0.5 eV above the valence-band maximum (VBM) and is doubly occupied. (ii) The structures of the V_{As}^+ centers are shown in Figs. 1(c) and 1(d), respectively. The nonrebonded structure [Fig. 1(c)] is 0.16 eV higher in energy than the rebonded structure [Fig. 1(d)]. In the nonrebonded structure, the Ga(1) atoms relax inwards by 0.29 and 0.31 Å, respectively, reflecting the tendency of the twofold Ga atoms to form sp hybrids. In the rebonded structure, one of the Ga(1) atoms forms a dimer with Ga(2) (bond length = 2.73 Å). The inward relaxations of the Ga(1) atoms are 0.16 Å for the twofold Ga and 0.29 Å for the dimerized Ga. In either case, the As(1) atoms relax outwards by only 0.01 to 0.02 Å. We observed a single empty gap state, 0.73 and 0.41 eV above the VBM, respectively, for the rebonded and nonrebonded structures.

Figure 2(a) shows the calculated formation energies $\Delta E(n/0)$ [Eq. (1)] of the As surface vacancies as a function of the Fermi level. We see that V_{As}^+ is stable for ϵ_f between ϵ_{VBM} and $\epsilon_{\mathrm{VBM}} + 0.3$ eV; V_{As}^- is stable for ϵ_f from $\epsilon_{\mathrm{VBM}} + 0.4$ eV to the conduction band minimum (CBM), while V_{As}^0 is stable only over a narrow energy range. These results differ from Yi *et al.* [3] (V_{As}^- only) and Lengel *et al.* [2] (V_{As}^{2+} for ϵ_f close to ϵ_{VBM}). We tested the V_{As}^{2+} structure proposed in Ref. [2] where the two surface Ga(1) atoms are fixed at a 0.7 Å outwardly relaxed position. The resulting structure was 1.4 eV *higher* in energy than the one in Fig. 2(a).

When compared with bulk [Fig. 2(b) [1,12,13]], we found that surface indeed plays an important role in defining the physical properties of the defects. For example, the (+/0) transition energy is at 0.32 eV for surface and 1.70 eV for bulk vacancy. In general, all surface defect transition energies are lowered by approximately 1 eV with respect to their bulk counterparts.

We next simulated the STM images using calculated atomic positions and wave functions. The simulation was carried out following Tersoff and Hamann [14], as detailed by Wang *et al.* [15] for semiconductor surfaces. In this approach, the tunneling current $I(\mathbf{r})$ at position $\mathbf{r}$ is proportional to surface (s) wave function squared $\rho_S(\mathbf{r}, \epsilon)$, summed over states between surface Fermi energy $\epsilon_f(s)$ and tip (t) Fermi energy $\epsilon_f(t) = \epsilon_f(s) + V_{\mathrm{bias}}$, where V_{bias} is the applied bias:

$$I(\mathbf{r}) \propto \int_{\epsilon_f(s)}^{\epsilon_f(s)+V_{\mathrm{bias}}} \rho_S(\mathbf{r}, \epsilon)\, d\epsilon\,. \qquad (4)$$

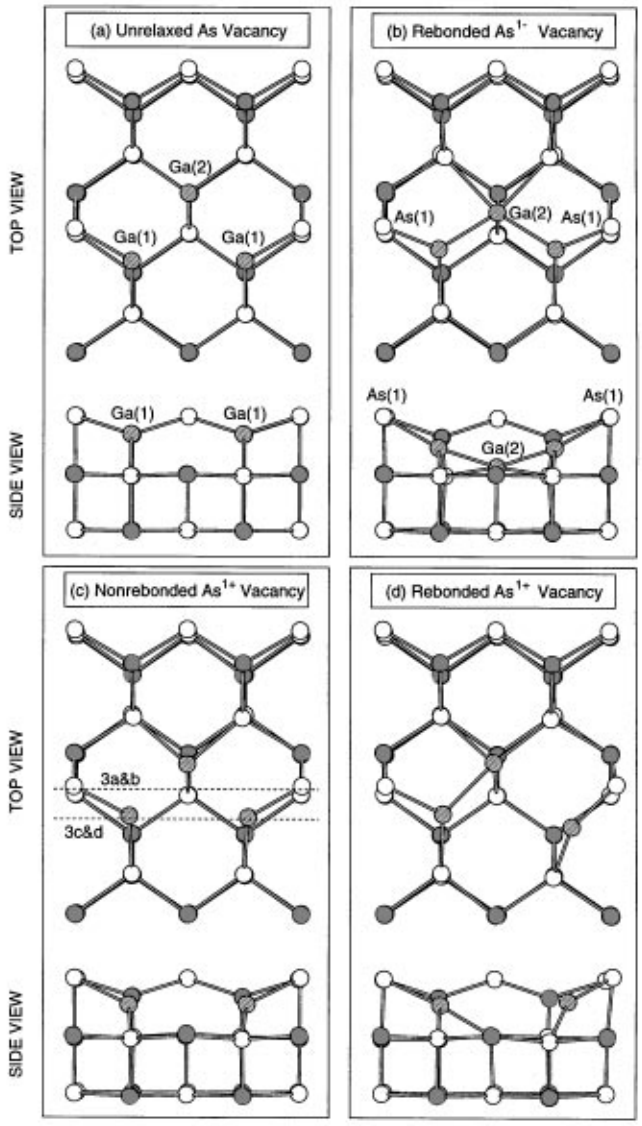

FIG. 1. Top and side views of the relaxed GaAs(110) surface with (a) unrelaxed As vacancy, (b) rebonded V_{As}^{1-}, (c) unrebonded V_{As}^{1+}, and (d) rebonded V_{As}^{1+}. Open and shaded circles denote As and Ga atoms, respectively.

Because of the size limitation of our computational supercell, it is not possible to position the tip at the experimental tip-surface separation (up to 8 Å [15]); in our simulation, the maximal tip-surface separation is about 4.9 Å.

We used, in the simulation, an elongated $c(2 \times 12)$ unit cell and, for simplicity, the nonrebonded V_{As}^{+} structure [Fig. 1(c)] for p-type samples [$\epsilon_f(s) = \epsilon_{\mathrm{VBM}}$]. Figure 3 shows the cross sections of the calculated 3D STM images along $[1\bar{1}0]$ passing through As and Ga atoms. The vacancy site is at the center of the x axis, and vertical arrows denote displacements of atoms with respect to distant atoms (i.e., the third nearest neighbors in Fig. 3). With a -1.8 V bias [Fig. 3(a)], a small inward As displacement is observed. At -1.3 V [Fig. 3(b)], a 0.2 Å

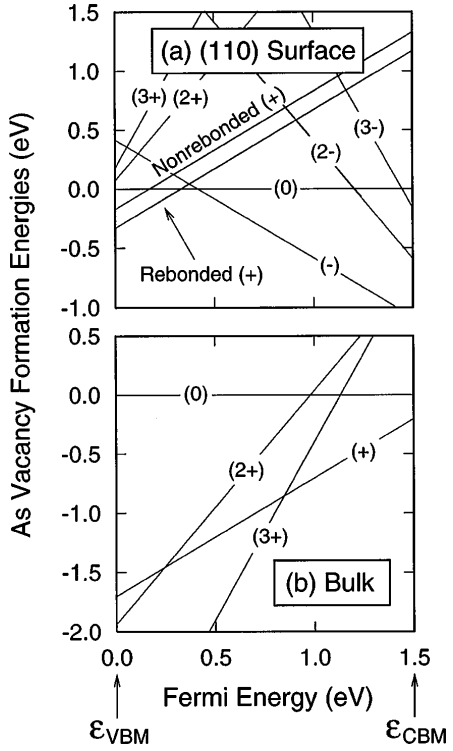

FIG. 2. Fermi level dependence of the formation energies $\Delta E(n/0)$ [Eq. (1)] of differently charged As vacancies (a) on the (110) surface and (b) in the bulk [1,12,13].

inward As displacement can be clearly seen. With a positive bias of +1.5 V [Fig. 3(c)], one sees a ~0.4 Å *outward* motion of Ga. With a larger, +2.0 V bias [Fig. 3(d)], much of the outward motion of the STM image has disappeared. The experimental data at +2.0 V [reproduced in Fig. 3(c)] shows a 0.5 Å outward displacement for the Ga atoms, while our calculation gives a similar displacement at +1.5 V. The difference of 0.5 V reflects the underconvergence of our calculated surface vs bulk band positions with respect to basis set size.

We conclude that the calculated STM image agrees with the measured STM image and both conflict with the calculated atomic displacement (Table I). We interpret this disagreement as a charging effect: a positively charged defect pulls down locally the band energies, as schematically shown in Fig. 4. Similar effects have been used to interpret STM images of oxygen [16] and Si donors [17] on GaAs(110) surfaces. We will examine two cases.

(A) Negative bias $V_{\mathrm{bias}} = -V1$ (imaging anions).— In this case, electrons with energies from $\epsilon_{\mathrm{VBM}} - V1$ to ϵ_{VBM} will tunnel out of the GaAs surface. With a positively charged vacancy, surface bands bend downwards near the vacancy [compare Figs. 4(a) and 4(b)]. This results in the reduction of the number of states available for tunneling [compare the shaded areas in Figs. 4(b) and 4(a)]. To maintain a fixed current in a constant current STM experiment, the tip near the vacancy moves closer to the surface so that the lost current can be compensated by a reduction in tip-sample separation.

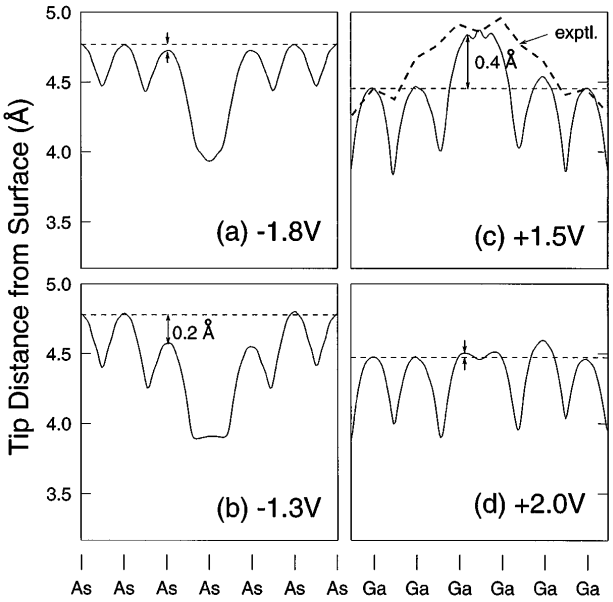

FIG. 3. Cross sections [see Fig. 1(c)] of the calculated 3D STM images at various biases for the nonrebonded V_{As}^{1+} center. The experimental data in (c) are taken from Ref. [2] and are aligned with the calculated results at the third nearest neighbor Ga atoms.

Thus, it is not the As that moves inwards; it is the tip that moves in. Only when $\epsilon_f(t)$ is positioned inside the surface band (as assumed here) or slightly below, band bending effect can be seen. This bias voltage dependence of the STM images for V_{As}^{+} needs to be studied experimentally in order to test our theory.

(B) Positive bias $V_{\mathrm{bias}} = +V2$ (imaging cations).— Here, electrons will tunnel into the surface from the tip. Band bending will increase the density of tunneling states near the center of the vacancy [again, compare the shaded areas in Figs. 4(b) and 4(a)]. To maintain a constant current, here the tip has to move *out* near the vacancy.

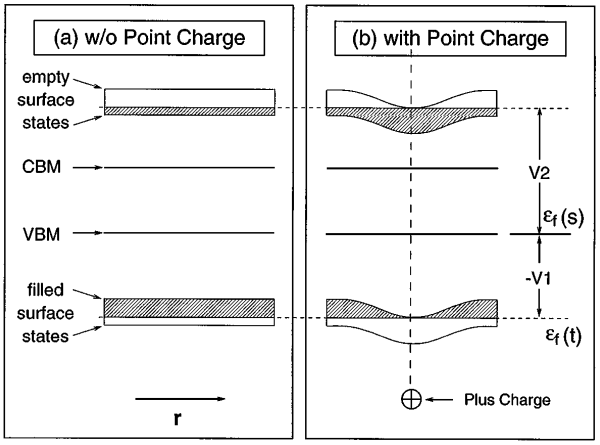

FIG. 4. A schematic drawing of the real space distribution of the surface states contributing to STM current (shaded areas) (a) without and (b) with a charged defect.

Thus, it is not Ga that moves outwards; it is the tip that moves out. *It both cases, the movement of the tip images local electrical effects, not the atomic displacements.*

In summary, we determined the atomic geometries and charge states of the As vacancies on GaAs(110) using *ab initio* total energy calculations. The geometries of the surface vacancies were found to be strongly charge state dependent, thus qualitatively different from bulk. We showed that surface Ga atoms relax only inwards, never outwards. The discrepancy between previous experimental STM images and calculations on surface Ga positions is quantitatively explained via a charge induced band bending effect.

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