

## Geometry and Electronic Structure of the Arsenic Vacancy on GaAs(110)

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Tunneling microscopy and spectroscopy, in conjunction with tight-binding molecular dynamics, provide compelling evidence that the “missing As” defect on GaAs(110) is indeed an As vacancy. Neighboring Ga atoms relax upward by about 0.7 Å, but do not rebond. The defect is positively charged and most likely in a +2 state. Both the relaxation and the preponderance of As vacancies on *p*-GaAs are explained by the energetics of the defect levels. The essential features of the observations can be understood from qualitative arguments based on hybrid orbitals.

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Atomic-scale studies of semiconductor surface defects, using scanning tunneling microscopy and spectroscopy (STM and STS) [1–9], have enhanced the prospects for a fundamental understanding of their role in growth nucleation, carrier recombination, Fermi-level pinning, and initiation of surface chemical reactions. Since STM probes only valence levels, however, there are often ambiguities in interpretation, leaving even the *identity* of a defect in doubt. For example, the “missing dimer” defects at the Si(100) surface [2] have been interpreted as sub-surface interstitials [10] as well as divacancies [11], and other defects on this surface have yet to find definitive assignments. In addition, chemisorbed species can mimic vacancies [12] by suppressing the local state density near the Fermi level.

Here we argue that the identity of a simple native defect at the GaAs(110) surface—the “missing As” defect—can be established through a combination of (a) high resolution atom-selective imaging, (b) local spectroscopy, (c) qualitative chemical arguments, and (d) molecular dynamics simulations. We determine the nature, charge state, geometry, and electronic structure of this defect, and also explain its abundance on degenerate *p*-type GaAs [9].

Our *p*-GaAs samples were grown by the Bridgman technique, and Zn doped at  $2 \times 10^{19} \text{ cm}^{-3}$ . A fresh (110) surface was exposed by cleaving (001)-oriented wafers in UHV ( $\leq 5 \times 10^{-11}$  torr). The STM probe tips were mechanically cut from 0.1 mm Pt wire and conditioned *in situ* by field emitting to the sample. All scans were recorded using setpoint currents below 100 pA.

The structural features of the missing As defects observed on *p*-GaAs are displayed in the upper panels of Fig. 1, where we present topographic images simultaneously acquired [4,13] with sample biases of  $-1.8$  and  $+2.0$  V. As seen in the left panel, there is a localized reduction in the filled-state density directly above an As site, suggesting that a single atom has been removed from the As sublattice. Arsenic atoms in the same  $[1\bar{1}0]$  chain

adjacent to this defect appear to be symmetrically depressed. In the corresponding Ga image, two atoms near the defect appear to rise out of the surface. The registry of the As and Ga sublattices is established in the lower left panel of Fig. 1: Using the simultaneously acquired images, we employ a thresholding technique to locate the topographic maxima in each data set. The two images are then superposed [13] to pair the As and Ga rows into  $[1\bar{1}0]$  zigzag chains; we see that the symmetrically perturbed Ga atoms are nearest neighbors of the missing As defect.

The density of these defects is cleavage dependent, but roughly  $5 \times 10^{11} \text{ cm}^{-2}$ , or one per thousand surface

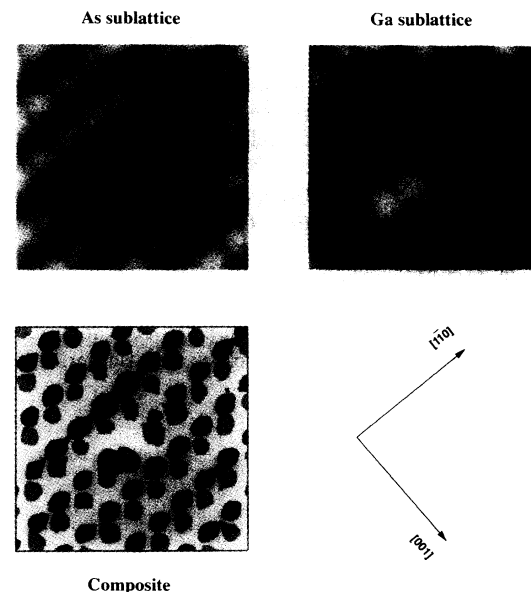


FIG. 1. Simultaneously acquired filled- and empty-state images of the missing As defect on degenerate *p*-GaAs(110). Defect composite shows the registry of the As (black) and Ga (gray) sublattices.

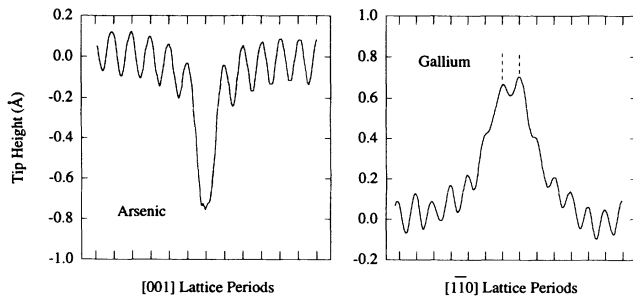


FIG. 2. Surface height contours through an As defect.

anions. A complementary “missing Ga” defect—which appears as a localized reduction in the empty-state density directly above a Ga site, accompanied by a symmetrical enhancement in the filled-state density at adjacent As sites—occurs with similar abundance on *n*-type material [9], but has *not* been observed in our experiments on degenerate *p*-GaAs.

The structure of an As defect is revealed by the surface height contours (through both filled- and empty-state images) shown in Fig. 2. The left panel illustrates the central depression in the As sublattice, which is  $\sim 0.7$  Å with typical sample bias conditions of  $-2$  V, and also quantitatively demonstrates the defect’s registry with the lattice period in the [001] direction. A [110] section through the Ga sublattice in the right panel shows that the nearest-neighbor Ga dangling bond states are symmetrically elevated by the same amount,  $\sim 0.7$  Å, for typical sample biases of  $+2$  V. It is especially noteworthy that these two orbitals maintain the periodic surface mesh, as evidenced by their regular spacing along the [110] zigzag chains (Fig. 2), as well as in the orthogonal [001] direction (not shown). Close examination of the data indicates that an increase or decrease in the mutual separation of these orbitals by 1 Å in the [110] direction (i.e., one-fourth the lattice period) is inconsistent with the measured peak positions (dashed vertical lines). We thus conservatively bracket the individual shifts to within  $\pm 0.5$  Å along the zigzag chains.

The surface height contours shown in Fig. 2 indicate that the As defects are also accompanied by weaker perturbations in the state density, which extend several unit cells in both crystallographic directions. This behavior has been previously attributed to the band bending associated with a localized surface charge [14]. From the direction of the band bending in these data, we infer that the As defects are positively charged. Fits to a semiclassical, screened Coulomb potential are in good qualitative agreement with the data, and yield screening lengths compatible with our sample doping levels [9].

To ascertain the influence of a defect on the local Fermi-level position, we performed spatially localized *I-V* measurements by momentarily interrupting the feedback loop at each imaging pixel to vary the sample voltage at

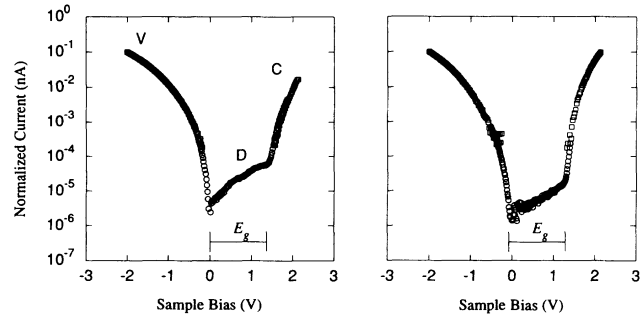


FIG. 3. Spectroscopy of the pristine *p*-GaAs(110) surface (left) compared with an isolated As defect (right). The spectra are acquired at two tip-sample separations ( $\square, \circ$ ) differing by 2.1 Å (left) and 2.8 Å (right).

fixed tip-sample separation [15,16]. A large dynamic range in the measured tunneling current was achieved by adjusting feedback conditions on the forward and return portions of each scan frame so that the mean tip-sample separations differed by 2–3 Å [17]. Topographic images simultaneously obtained with the spectroscopic data allowed us to subsequently select the individual *I-V*’s acquired directly over the defect site.

The clean surface spectrum shown in the left panel of Fig. 3 is consistent with earlier studies [17]; in particular, we note the clearly identifiable valence-band (*V*), conduction-band (*C*), and dopant-induced (*D*) contributions to the tunneling current on degenerate material [13,17]. The Fermi level lies just below the valence-band edge, and the observed band gap is in excellent agreement with the established value of 1.42 eV for bulk GaAs (horizontal bar). The influence of tip-induced band bending is small because of two factors: (1) the very high sample doping and (2) a large tip work function that leads to hole accumulation (rather than depletion) throughout the voltage regime corresponding to the semiconductor band gap. The spectrum presented in the right panel of Fig. 3 is representative of the *I-V* characteristics measured at defect sites. A small, rigid shift ( $\sim 100$  meV) in the positions of the conduction- and valence-band edges relative to zero bias is apparent. The magnitude and direction of this shift are consistent with a surface Fermi level that now lies in the band gap, but within  $\sim 100$  meV of the valence-band edge. The influence of the tip’s electric field is again negligible, as demonstrated by our observation that the band gap remains in excellent agreement with the bulk value (horizontal bar). A partial quenching of the tunneling into dopant-induced states is also evident. As pointed out previously [17], these states are easily pinched off from the surface by a charge-induced depletion region. On *p*-GaAs, this requires a positively charged defect, consistent with our other observations.

We can rule out the possibility that the missing As defects are dopant atoms, since Zn substitutes for Ga, not As, in the host lattice and creates a shallow acceptor level

in bulk GaAs which is negatively charged at room temperature. The notion that trace bulk impurities are involved is also untenable, since the observed defect density is too high [18], and surface segregation from the bulk is unlikely at room temperature. One might ask if the defects are adsorbates from the residual gas (primarily hydrogen) which tie up the individual As dangling bonds, but the defect density neither increases nor decreases noticeably with time. It is also unreasonable to attribute these defects to the Ga on As antisite ( $Ga_{As}$ ), since the surface antisite should be neutral on  $p$ -type material [19], not positively charged. Finally, the observation of tip-induced defect migration [9] supports a vacancy interpretation and makes the antisite unlikely. The most natural explanation of the accumulated experimental findings, therefore, is that these point defects are indeed As vacancies.

Three features of our observations are not easily reconciled with this simple picture, however: (1) Why are the in-plane relaxations of the nearest-neighbor Ga dangling bonds so small? Near a missing As atom, one might expect substantial lateral relaxations, driven by the tendency of the unsatisfied neighbors to rebond. (2) Why are only As vacancies observed in our experiments? The same number of bonds are broken in forming Ga vacancies. (3) Why is the local Fermi level so close to the valence-band edge? The defect states for III-V (110) surface vacancies might be expected to give a local Fermi level well within the bulk band gap [19].

Seeking answers to these and related questions, we performed tight-binding molecular dynamics simulations [20] for a theoretical As vacancy on GaAs(110). The basic model we employed has been successfully applied by Chadi [21,22] and ourselves [23,24] in studies of the relaxation and electronic states at both the defect-free GaAs(110) and vacancy-reconstructed GaAs(111) surfaces. The electronic states are obtained from an  $sp^3s^*$  Hamiltonian [23], and the repulsive potential is fit to the lattice constant, cohesive energy, and bulk modulus of

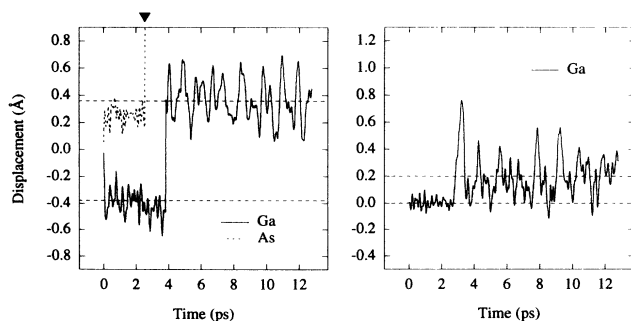


FIG. 4. Molecular dynamics simulation of the [110] (left) and  $[1\bar{1}0]$  (right) displacements following formation of an As surface vacancy (arrow). The mean position of a Ga atom before and after vacancy formation is indicated by horizontal dashed lines. This simulation is for a defect charge state of +2.

GaAs. The model slab used in the simulations was 6 layers thick, with a  $2 \times 3$  surface unit cell. The  $360 \times 360$  electronic Hamiltonian is diagonalized, and the Hellmann-Feynman forces calculated, every femtosecond of the simulations.

Results from a typical simulation are shown in Fig. 4. When an As atom is removed to form a vacancy, each of its surface Ga neighbors quickly relaxes upward by 0.7–0.8 Å, with a relatively small lateral shift. (The results for only one Ga atom are shown in Fig. 4, but the symmetrically situated neighbor shows similar behavior.) This relaxation provides a remarkably straightforward explanation of the STM images in Fig. 1, and the surface Ga atoms *do not rebond*.

We can understand why As vacancies occur in higher concentration than Ga vacancies on  $p$ -GaAs if we examine the levels for *unrelaxed neutral* vacancies, shown in Fig. 5. Suppose the bond-breaking and relaxation energies are comparable for the two kinds of vacancies. Then the difference on  $p$ -GaAs is the energy gained when electrons fall from occupied states of the neutral defect to unoccupied states at the valence-band edge. Both vacancies act as compensating surface donors, but a naive interpretation of Fig. 5 suggests the As vacancy is lower in energy than the Ga vacancy by about 1.5 eV. The arguments given below reduce this number, but indicate it may still be  $\sim 1$  eV.

This result may be rationalized by regarding the conduction- and valence-band states, respectively, as Ga and As derived. When an As atom is removed, its bonds to three Ga neighbors are broken, and three levels are pulled down from the conduction band. Since eight valence-band states but only five electrons are removed with the As, three electrons must be accommodated in these defect levels. Similarly, three levels are pushed up above the valence band by the creation of a Ga vacancy, and electron counting indicates that they must hold three

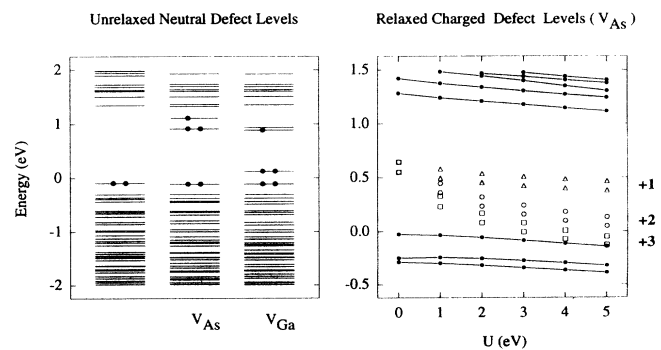


FIG. 5. Left: Electronic states of a pristine slab, neutral As vacancy, and neutral Ga vacancy, omitting defect relaxation. Solid circles represent electrons in the highest occupied levels. Right: Arsenic vacancy levels, when relaxation and Coulomb repulsion are included, for each of three possible charge states ( $\Delta$ , +1;  $\circ$ , +2;  $\square$ , +3). Solid circles represent bulk levels.

electrons. It is reasonable to expect that defect states split from the Ga-derived conduction band will be higher in energy than those split from the As-derived valence band, so that the As vacancy is preferred on *p*-type material.

In treating the charge states and true energy levels of an As vacancy, we must include the effects of relaxation and Coulomb repulsion. As the surrounding atoms relax in our simulations, the uppermost defect level rises to become a resonance in the conduction band, but the two lower levels descend by  $\approx 0.4$  eV. The amount of relaxation and its effect on the levels are found to be almost independent of charge state (e.g., 0, +1, and +2), so long as the defect levels are occupied by at least one electron. For a charge state of +3, however, only a weak relaxation is observed. *Occupied defect levels thus provide the driving force for the upward motion of the Ga neighbors.*

There is a simple interpretation of the relaxation for a neutral vacancy, based on hybrid orbitals and the polar nature of GaAs. Initially, two in-chain  $sp^3$  bonding orbitals, one backbonded  $sp$  orbital, and one dangling-bond  $p$  orbital are associated with each surface Ga. [These are the natural choices consistent with the  $27^\circ$  rotational relaxation of the GaAs(110) surface.] After an As vacancy is created, the neighboring surface Ga atoms move up, as in-chain hybrids directed toward the vacancy convert to  $sp$  and backbond hybrids convert to  $sp^3$ . The surface Ga defect state thereby acquires more *s* character, lowering its energy. This argument is similar to the one used in explaining the (110) surface relaxation, except that it focuses on occupied *defect* states rather than occupied *surface* states. We note that the vacancy relaxation opposes the original surface relaxation, pushing Ga atoms back toward and beyond the positions they would occupy in an ideal bulk termination.

After determining the vacancy relaxation, we estimated the effect of Coulomb repulsion by adding a Hubbard-like term,  $U\Delta n$ , to each diagonal energy in the tight-binding Hamiltonian. (Here  $\Delta n$  is the change in electron occupancy relative to the neutral atom.) The electronic energies computed with this new Hamiltonian are shown in Fig. 5, where reasonable physical values of  $U$  are 4–5 eV. A charge state of +1 is inconsistent with the STS results, since it requires local midgap pinning, and a charge state of +3 is inconsistent with the relaxation seen in the STM images. The most probable charge state on degenerately doped *p*-GaAs is then +2, since the levels for this state produce relaxation *and* a local Fermi level near the valence-band edge, in agreement with our experimental findings.

In summary, we have demonstrated that the “missing As” defect on GaAs(110) has all the features expected of an As vacancy. Both the STM observations and the molecular dynamics simulations show that the surface Ga atoms neighboring this vacancy relax upward, but do not

shift laterally to rebond. Experiment and theory also indicate the defect is positively charged on degenerate *p*-GaAs, and is most likely in a +2 state. The positions of the theoretical vacancy levels, including relaxation and Coulomb repulsion, are then in accord with the STS results. Finally, the observed preponderance of As over Ga vacancies on *p*-GaAs is explained by arguments involving the energetics of the defect states. This level of agreement inspires hope for a similarly detailed understanding of other point defects at semiconductor surfaces.

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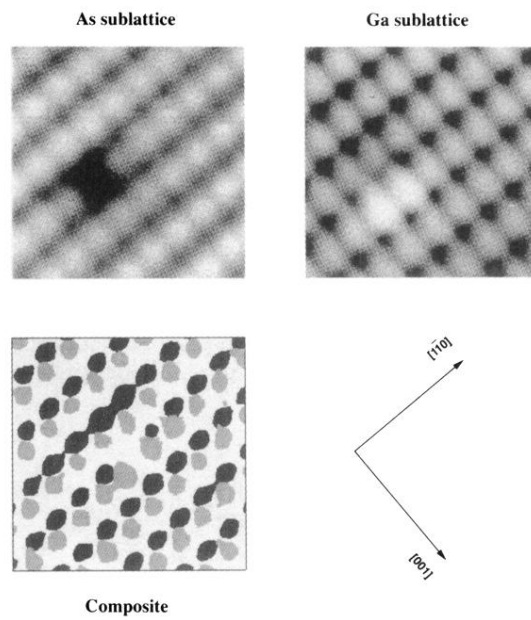


FIG. 1. Simultaneously acquired filled- and empty-state images of the missing As defect on degenerate  $p$ -GaAs(110). Defect composite shows the registry of the As (black) and Ga (gray) sublattices.