Theoretical Scanning Tunneling Microscopy Images of the As Vacancy on the GaAs(110) Surface

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The atomic and electronic structure of an As vacancy on the GaAs(110) surface is examined using ab initio pseudopotentials. The relaxed atomic structure reveals an inward movement of the neighboring surface Ga atoms which is in disagreement with recent interpretations of the scanning tunneling microscopy (STM) images for this system. However, a careful analysis of the wave-function character of the vacancy states, and the theoretical STM image, for this geometry yields excellent agreement with the experimental STM images.

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Native point defects in semiconductor surfaces, such as vacancies and antisites, are interesting as they play an important role in the growth process of thin films and Fermi-level pinning at metal-semiconductor interfaces. These point defects have been successfully identified by scanning tunneling microscopy (STM) which has provided insights into their structural and chemical nature [1–4]. However, since STM measures the local density of states [5], the STM images may not reflect the atomic geometries [6]. Recently, STM studies have been reported on the (110) surfaces of III-V semiconductors [7,8]. These images indicate the presence of an isolated missing atom, identified as a surface anion vacancy, within the anion sublattice of p-type materials. Another feature of these images is the presence of two bright spots in the cation sublattice around an anion vacancy. This enhancement has been interpreted as an outward relaxation of two surface cation atoms adjacent to the anion vacancy. Furthermore, these vacancies are inferred to be in positive charge states for p-type materials judging from the local band bending observed [9,10]. The symmetric counterpart, i.e., the negative cation vacancy accompanying the enhanced filled-state image, has been observed for n-type materials [11].

In this Letter, we present a comprehensive ab initio investigation of a singly charged positive As vacancy \(V^+_\text{As}\) on the GaAs(110) surface. The minimum-energy geometry determined from our study shows an inward relaxation of the neighboring surface Ga atoms, contrary to both the experimental interpretation and the theoretical confirmation of an outward relaxation [7]. Our results are also contrary to experimental interpretations of the geometry for anion vacancies on other III-V compounds [8]. However, our geometry yields a theoretical STM image which is in excellent agreement with the experimental images. Our work suggests that previous workers have misinterpreted the STM images as the reflection of the surface atomic geometry rather than the electronic structure.

Our calculations were performed using the plane-wave pseudopotential method [12,13] based on the density functional theory within local-density approximation [14]. Troullier-Martins pseudopotentials [15] were used within the Kleinman-Bylander form [16], and the Ceperley-Alder exchange-correlation potential is incorporated as the parametrized version of Perdew and Zunger [17]. A supercell geometry was used to model the system. The supercell was composed of a \(4 \times 2\) surface unit cell, five atomic layers, five vacuum layers, and hydrogen passivation of the dangling bonds on one of the exposed surfaces. The kinetic energy cutoff was chosen to be 9 Ry and a single special \(\mathbf{k}\) point \((\frac{1}{4}, \frac{1}{4}, 0)\) was used for the Brillouin-zone integrations. The theoretical lattice constant of GaAs for the pseudopotentials employed in this work is 5.58 Å, which deviates by 1.2% from the experimental lattice constant of 5.65 Å. To optimize the surface geometry, three outermost layers were allowed to relax. The criterion for minimizing the interatomic forces was to demand any residual force be less than 0.005 Ry/a.u. in each direction. A uniform negative compensating background was used to maintain the charge neutrality of the supercell.

The fully relaxed atomic geometry of the \(V^+_\text{As}\) is shown in Fig. 1 to provide an overview of the relaxation. The structural deformation is well localized around the vacancy site, and the surface angle (which is 43° next to the vacancy site) rapidly converges toward the clean surface value (30°) on the boundary of the \(4 \times 2\) surface cell within \(\sim 7\%\) error. The magnitudes of the relaxations are listed in Table I for the nearest and the next nearest neighbors of the vacancy site. The largest relaxation (0.40 Å) occurs at the surface Ga neighbors, which is 17% of the bulk bond distance. This is somewhat larger than the relaxation in bulk As vacancy [18]. The general feature of the relaxation is that the three neighboring Ga atoms move towards the vacancy site. The subsurface Ga neighbor [Ga(1)] relaxes predominantly across the zigzag chain within the subsurface. The surface Ga neighbors [Ga(2)]...
and Ga(3)] relax inwards, with comparable displacements in both across and along the chain directions.

Another interesting feature is the formation of weak bonds (with a bond distance of 2.78 Å, which is 15% larger than that of the bulk) between the surface and the subsurface Ga neighbors (indicated by thick grey bonds in Fig. 1). As a result, the coordination number of the subsurface Ga(1) is changed to five from the ideal vacancy value of three. The neighboring five atoms [Ga(2), Ga(3), As(4), As(5), and As(6)] form a very flat nearly pyramidal cage, with As(4) at apex, encompassing the Ga(1) atom. The Ga(1) atom lies slightly above the base of the pyramid. This local geometry is manifested as a $d$-like wave-function character around the Ga(1) atom.

There are three orbitals associated with each surface vacancy, since three dangling bonds are formed by creating an ideal (or unrelaxed) surface vacancy. (These three dangling bonds hybridize to form three vacancy states.) The total density of states in Fig. 2 shows the three nondegenerate vacancy levels: one deep inside the valence band complex (A) and the other two within the band gap (B and C). For $V_{\text{As}}^+$, both B and C are unoccupied. The nondegenerate nature of the vacancy states is in accordance with the absence of any symmetry-breaking (Jahn-Teller type) relaxation in our calculations.

The symmetries of the vacancy states are in agreement with the semiempirical Green function (GF) results of Daw and Smith [19] for the ideal vacancy. For instance, the state A has largely $s$-like character, while states B and C are odd and even with respect to the mirror symmetry of the (110) surface, respectively. However, the location of vacancy levels and the detailed wave-function characters are quite different from the GF results. This is a consequence of the strong structural relaxation. State A appears just above the valence band maximum for the ideal vacancy as predicted by the GF method, but this state merges deep inside the valence band complex when relaxed.

The charge density isosurfaces are shown in Fig. 3 to provide the overview of the wave-function character of the vacancy states. State A has mainly the $s$-like character of the subsurface Ga(1). There is a considerable amount of bonding character between the $s$ orbital of Ga(1) and the $sp$ hybrid [directed towards Ga(1)] of Ga(2) and Ga(3). There also exists the $sp_z$ hybrid of the third-layer As(4) atom reflecting a little mixing between this vacancy state and the valence band states. State B has bonding character between the surface Ga neighbors and the subsurface Ga(1) atom. The $sp^3$ hybrid of surface Ga neighbors and the $d_{xy}$ orbital of Ga(1) form the bonding orbital reminiscent of the flat pyramidal geometry mentioned above. Another noteworthy character of this state is the bonding between the $p$ orbitals of the surface Ga neighbors and their nearest neighbor As atoms. The third vacancy state C has a $pp\pi$ bonding character between two surface Ga neighbors. This state is thought to cause the characteristics of the STM image of $V_{\text{As}}^+$—the enhanced empty-state image at the surface Ga neighbors. We also predict that the surface Ga neighbors would relax further towards each other along the chain direction as the vacancy accommodates two or three electrons to allow the occupation of the third vacancy state C.

The theoretical STM images are generated within the Tersoff-Hamann approximation [5]. Within this approximation, the tunneling current is proportional to the

### TABLE I. Relaxations of nearest and next nearest neighbor atoms in Å from their positions in the clean relaxed surface.

The positive sign denotes the relaxation towards the vacancy site. The atomic indices are the same as in Fig. 1.

<table>
<thead>
<tr>
<th>Atom</th>
<th>[100]</th>
<th>[001]</th>
<th>[110]</th>
<th>Displacement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ga(1)</td>
<td>0.000</td>
<td>0.262</td>
<td>0.126</td>
<td>0.291</td>
</tr>
<tr>
<td>Ga(2)</td>
<td>0.164</td>
<td>0.264</td>
<td>0.254</td>
<td>0.401</td>
</tr>
<tr>
<td>As(4)</td>
<td>0.000</td>
<td>0.027</td>
<td>−0.018</td>
<td>0.032</td>
</tr>
<tr>
<td>As(5)</td>
<td>0.078</td>
<td>0.061</td>
<td>0.129</td>
<td>0.162</td>
</tr>
<tr>
<td>As(7)</td>
<td>0.146</td>
<td>0.075</td>
<td>0.006</td>
<td>0.164</td>
</tr>
<tr>
<td>As(9)</td>
<td>0.101</td>
<td>0.007</td>
<td>0.121</td>
<td>0.158</td>
</tr>
</tbody>
</table>

![FIG. 1. The relaxed geometry of the singly positive As vacancy ($V_{\text{As}}^+$) on the GaAs (110) surface: (a) top view and (b) side view of top four layers. The solid and open circles denote the As and Ga ions, respectively. The nearest and the next nearest neighbors to the vacancy site are indexed from 1 to 10. The weak bonds formed by relaxation are indicated by the thick grey lines.](image)

![FIG. 2. Total density of states of the GaAs (110) surface with the singly positive As vacancy ($V_{\text{As}}^+$). The three vacancy levels are labeled by A, B, and C.](image)
local density of states at the tip position integrated over the energy range restricted by the applied bias voltage. Figure 4 shows the theoretical constant-current STM images (the tip-height contour of an isosurface of the local density of states) around the singly positive As vacancy on the GaAs(110) surface. The maximal tip-surface distances are 3.7 and 3.1 Å for negative and positive sample biases, respectively. A filled-state (As sublattice) image at the bias voltage, $-1.5$ V, is shown in Fig. 4(a). It is clear that the As vacancy manifests itself as a *single localized depression* in the filled-state image. The enhancement, *two bright spots*, in the empty-state (Ga sublattice) image around the As vacancy is shown in Fig. 4(b) for the bias voltage of $+1.0$ V. This feature can be attributed to the wave-function character of the third vacancy state, *$pp\pi$* bond between surface Ga neighbors [20]. The smaller bright spots next to the major enhancement are reflecting the wave-function character of the second vacancy state. Since the enhancement in the Ga image next to the As vacancy site originates from the wave-function character of the vacancy states, we predict that the feature will disappear as one increases the positive sample bias voltage so that more surface states (predominantly surface Ga dangling bond states) are encompassed.

In conclusion, the theoretical STM images coincide very well with experiments, while the calculated atomic relaxation is very different from the interpretation in the experimental work [7,8]. The STM image should be reinterpreted as the manifestation of the *electronic structure* rather than the *surface atomic geometry* as has been done in previous work [7,8]. Also, our calculations suggest caution when implementing tight binding models to determine surface structures. For example, it is unlikely that simple parametrized tight binding models can accurately describe the Ga atom rebonding near the As vacancy as we find in our pseudopotential work. It is difficult in tight binding models to describe accurately coordination changes. This
may account for the absence of Ga rebonding as found by tight binding models for this system [7].

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[20] The local band bending induced by a localized charge distribution is already included in the \textit{ab initio} studies as the change in the Hartree and exchange-correlation potential within the local-density approximation.