

## *Ab Initio* Calculations on the Passivation of Shallow Impurities in GaAs

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The results of the first *ab initio* calculations performed on the complexes formed between hydrogen and both donor and acceptor atoms in gallium arsenide are reported. The equilibrium geometries and electronic properties are presented. For the first time a parameter-free determination of the vibrational properties of the entire defect complex has been performed, allowing a more complete comparison with infrared-absorption experiments. Local structural distortions far larger than previously expected are proposed to account for the absence of certain absorption lines.

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There has recently been a great deal of interest in the properties associated with hydrogen (H) when incorporated in semiconductors.<sup>1-5</sup> Most of the experimental effort<sup>2,3</sup> and almost all of the previous theoretical treatments<sup>4,5</sup> have focused on the hydrogen passivation of shallow impurities in silicon and little has been said about the situation in III-V materials such as gallium arsenide. In the case of silicon, the impurity atom is left in its preferred valence state (with three bonds for P or B) and each host silicon remains fourfold coordinated. In a III-V compound, the situation is considerably different due to the presence of two different host species, each of which may prefer to be threefold coordinated in the presence of a defect. Furthermore, all previous calculations have focused on the structural properties of the complex and any consideration of vibrational properties has been limited to the hydrogen atom, assuming it to move in a rigid lattice. The purpose of this study is to explore the different complexes formed in GaAs between hydrogen and the defects produced by substituting a Ga atom with Si (a donor) and Be (an acceptor). The vibrational properties of the entire defect complex are determined, and an explanation is given of why several absorption lines are not observed.

First-principles calculations presented used the local-density-functional theory with the *ab initio* pseudopotentials of Bachelet, Hamann, and Schlüter.<sup>6</sup> Hydrogen-terminated clusters of around 100 atoms are used with a basis of up to 500 *s*- and *p*-type Gaussian functions. An intermediate fit to the charge density is performed, also using a basis of Gaussian orbitals. The methodology has been presented in detail previously<sup>7</sup> and as such no details will be given here. Three stoichiometric clusters of Ga<sub>13</sub>As<sub>13</sub>H<sub>30</sub>, Ga<sub>22</sub>As<sub>22</sub>H<sub>42</sub> (Fig. 1), and Ga<sub>26</sub>As<sub>26</sub>H<sub>50</sub> in which a central Ga atom was replaced by an impurity have been used in this investigation.

Using this approach, structural properties can be obtained by calculating the forces on each atom and allowing the atoms to move in the directions of these forces until the energy changes are negligible.<sup>7</sup> For each defect

considered a total of nine atoms were relaxed. In fact, the total energies were only slightly changed by the relaxation of the outermost shell of these, but this procedure was nevertheless carried out in each case. To illustrate this, the procedure was carried out on the 56- and 86-atom clusters to check that the bulk properties of GaAs were reproduced correctly. We found average bond lengths and angles deviating from the experimental values by 1%–2%.

The vibrational properties of GaAs were then calculated by assuming that an eight-parameter Musgrave-Pople potential,<sup>8</sup> containing interactions up to second-nearest neighbors, was sufficient to describe the interatomic potential. The parameters were extracted from a least-squares fit to second derivatives of energy obtained from the *ab initio* program. The procedure has previously been described in detail.<sup>7</sup> This gave an optical-phonon frequency of 8.8 THz, to be compared with LO and TO phonon frequencies of 8.8 and 8.1 THz, respectively.<sup>9</sup>

In the vicinity of a defect, the interatomic potential is of course modified, making this valence-force potential inadequate. Clearly, any elements of the dynamical matrix associated with the motion of atoms that are first- or second-nearest neighbors of a defect atom will be

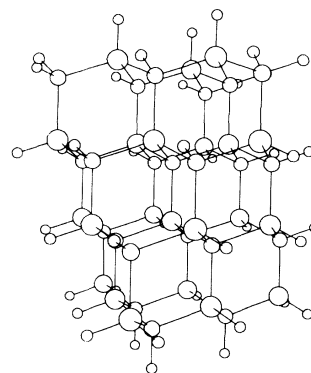


FIG. 1. The 86-atom cluster used in the calculations.

modified by its presence. These modified elements were calculated directly using the *ab initio* program and the remainder found by using the valence-force potential determined for pure crystalline gallium arsenide, thus giving a complete description of the defect potential. In this way, the dynamical matrix describing several hundred atoms containing a single defect can easily be generated and diagonalized to give the vibrational frequencies. A feel for the strengths of the bonds present in the defect complex can then be obtained by fitting the modified double derivatives of energy by a "local" valence-force potential with parameters which are allowed to take different values from the bulk values and which vary from atom to atom. Details of the fitting procedure and the exact choice of the local valence-force basis functions will be given in a future publication.

Recently, detailed infrared-absorption experiments have been performed which studied the complex formed between silicon donors and hydrogen.<sup>10</sup> Two hydrogen-related lines at 876 and 1717  $\text{cm}^{-1}$  were observed. Evidence that the H bonds directly to the silicon donor was provided by the observation of small changes of the frequency of the 1717- $\text{cm}^{-1}$  line due to the presence of the three different isotopes of silicon: <sup>28</sup>Si, <sup>29</sup>Si, and <sup>30</sup>Si.

To investigate this passivation of the silicon donor, a silicon atom was inserted into each of the clusters (replacing a gallium atom) and then a hydrogen atom added. In this study, three high-symmetry positions were considered for the hydrogen atom (see Fig. 2): (a) the antibonding (AB) site of the silicon donor; (b) near the center of one of the bonds between the silicon and its four neighbors, which will be referred to as the "bond-centered" (BC) site (even though the hydrogen atom

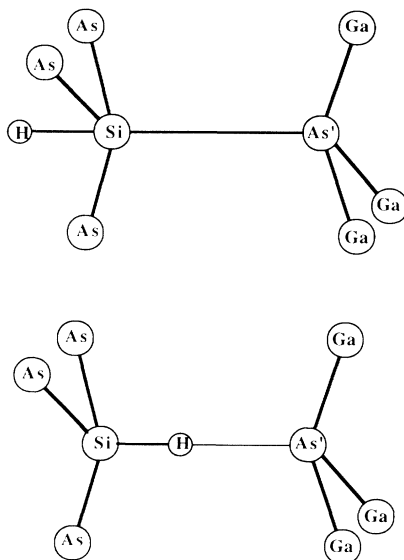


FIG. 2. Two possible sites for the H atom, the Si antibonding (upper diagram) and bond centered (lower diagram).

will not lie exactly in the geometrical center of the bond); and (c) the AB site of one of the four arsenic atoms which are nearest neighbors of the silicon atom.

Sites (a) and (b) were suggested by Pajot *et al.*<sup>10</sup> with the first of these being preferred. They suggested that the silicon atom became fivefold coordinated with the electron from the hydrogen atom and the excess electron from the silicon donor forming the fifth bond and thereby removing the free electron from the system. The third model, although not consistent with all of the experimental information, is included for completeness as this is the stable site for a hydrogen-donor complex in silicon.<sup>3,5</sup>

Consider first the hydrogen atom at the antibonding site of the Si atom. The presence of the hydrogen atom caused one of the Si-As bonds to lengthen to 3.1 Å with the Si atom relaxing into the plane of the other three As atoms—a far larger distortion than was originally proposed by Pajot *et al.* The resulting Si-H bond had a length of 1.59 Å. This effect was obtained with all three clusters and a variety of basis sizes. The defect level was pushed towards the valence band in all cases indicating that the donor had been passivated.

The vibrational frequencies associated with this complex were also found, as described above. It was found that the lengthened Si-As bond had a much reduced stretching force constant (of only 1.5  $\text{eV}/\text{Å}^2$ ) while the strength of the three remaining Si-As bonds was slightly increased (to 9.3  $\text{eV}/\text{Å}^2$ ). This is to be expected as these bonds are  $sp^2$  in character and it is known that such bonds are stronger than the  $sp^3$  bonds found in pure GaAs. The resulting local vibrational modes had frequencies of 1813 ( $A_1$ ), 982, and 983  $\text{cm}^{-1}$  ( $E$ ) for H-related modes and 446 and 449  $\text{cm}^{-1}$  ( $E$ ) for the Si-related modes. These were obtained using the derivatives obtained directly from the *ab initio* program—the lack of degeneracy gives some indication of the numerical errors involved in taking a second derivative. The experimentally observed absorption occurs at 1717, 896, and 410  $\text{cm}^{-1}$ .<sup>10</sup> The corresponding eigenvectors showed that the Si modes correspond to motion in the plane of the three As atoms. The remaining mode, associated with motion along the extended bond, fell into the one-phonon spectrum, thus accounting for it not being observed.

We then investigated the BC structure (b) above. The Si-As bond expanded by 46% to make way for the H atom. Both the 86- and 102-atom clusters showed the H atom to lie closer to the silicon atom than the arsenic atom, giving 1.49 and 1.48 Å, respectively, for the Si-H bond length and 2.04 and 2.11 Å for the H-As distance. The Si atom therefore became fourfold coordinated and the As atom threefold coordinated—in each case their preferred valencies. The strong Si-H bond led to a high vibrational frequency (2200  $\text{cm}^{-1}$ ) and the electronic donor level fell into the valence band. In both cases the

total energy was 0.4 eV higher than the result for the antibonding configuration (a) above. The 56-atom cluster produced a different result,<sup>11</sup> implying that the H atom would lie roughly midway between the Si and As atoms leading to a lower vibrational frequency ( $1339\text{ cm}^{-1}$ ). This is now seen to be an artifact of the small cluster size. However, the total energy was still higher by 1.2 eV than the antibonding structure so the conclusion would not be affected. An *ab initio* interatomic potential for this defect was determined, leading to Si-related vibrational frequencies of  $354 (A_1)$ ,  $424$ , and  $428\text{ cm}^{-1} (E)$ .

Finally, the hydrogen atom was placed at the antibonding site of one of the arsenic atoms neighboring the silicon, position (c) above. It was found that the energy of this defect was 0.81 eV higher than the defect with the hydrogen at the antibonding site. The H-As bond was found to be  $1.93\text{ \AA}$  in length, showing the hydrogen to be only weakly bonded. This is inconsistent with the large reactivation energy of 2.1 eV found by Chevallier *et al.*<sup>12</sup> and the large splitting between the vibrational frequencies of  $1717$  and  $896\text{ cm}^{-1}$ —weakly bound hydrogen would give three almost degenerate values. In addition, the donor activity was not removed—the doubly occupied defect level remained close to the conduction band.

These calculations have therefore been able to identify the Si antibonding site as the global minimum for hydrogen in the hydrogen-donor complex.

This result differs from the situation in silicon,<sup>4,5</sup> where a donor atom (such as phosphorus) is passivated by hydrogen which bonds, not to the donor atom itself, but to one of the silicon atoms adjacent to the impurity. This difference can readily be understood on chemical grounds as in both silicon and GaAs, the complex favored leaves all of the host atoms and the donor atoms in their preferred valence states (four for group-IV elements, three for group-V elements).

We now turn to passivation of acceptors. The first observation of this was by Johnson *et al.*,<sup>13</sup> who showed that the depth of hydrogen or deuterium penetration and the depth to which the acceptors were compensated were equal to the experimental accuracy. Once again, infrared-absorption experiments have been performed<sup>14</sup> determining the localized vibrational models of the H and Be atoms. In this study, only two high-symmetry

sites for the hydrogen atom were considered: (a) near the center of one of the four Be-As bonds, and (b) at the antibonding site of one of the As atoms adjacent to the Be atom.

The same three clusters (56, 86, and 102 atoms) were used in the investigation and a beryllium atom and hydrogen atom were inserted accordingly. The hydrogen and its nearest two shells of atoms were relaxed and the equilibrium geometry and total energies determined. Once in the equilibrium geometry, the vibrational properties of the hydrogen atom were determined, assuming the surrounding lattice to be rigid. Two experimental properties need to be reproduced and explained—the H stretching frequency of  $2037\text{ cm}^{-1}$  and the absence of “wag” frequencies which would be expected from either structural model.

First, the hydrogen atom was inserted into the center of a Be-As bond and nine atoms relaxed. This was performed for each of the three clusters and the resulting structural and vibrational properties are presented in Table I. The close agreement illustrates the degree to which the results are converged in cluster size. It was found that the H atom had tendency to move slightly ( $\sim 0.15\text{ \AA}$ ) off axis, although the energy changes involved were very small ( $\sim 0.01\text{ eV}$ ). The transverse vibrational frequencies of the H atom were therefore determined by a numerical integration of its Schrödinger equation using the *ab initio* program to determine the potential. The resulting values were anomalously low, with the 102-atom cluster producing a result roughly equal to the Raman frequency, although the static lattice approximation is probably not valid in this case. However, it seems very likely that this mode falls into the one-phonon excitation spectrum, explaining why it has not been observed. The acceptor level fell into the valence bond.

The hydrogen atom was then inserted at the antibonding site of one of the arsenic atoms surrounding the Be atom. The resulting As-H bond length was  $1.55\text{ \AA}$ , with the unique Be-As bond lengthening to  $3.29\text{ \AA}$ . The corresponding vibrational frequencies of the hydrogen atom were found to be  $852$ ,  $853 (E\text{ modes})$ , and  $2069\text{ cm}^{-1}$  (the  $A_1$  mode). The energy, however, was 0.3 eV higher than that of the bond-centered structure above and this, together with the very high wag frequency, effectively rules this out as the equilibrium structure of the BeH

TABLE I. Structural and vibrational properties of the BeH complex.

| Cluster  | Be-H (Å) | As-H (Å) | Be-As (Å) | As-Ga (Å) | As-Be-As (deg) | Ga-As-Ga (deg) | H wag frequency (cm <sup>-1</sup> ) (expt., not seen) | H stretch frequency (cm <sup>-1</sup> ) (expt., 2037 cm <sup>-1</sup> ) |
|----------|----------|----------|-----------|-----------|----------------|----------------|---|---|
| 56-atom  | 1.78     | 1.54     | 2.19      | 2.43      | 119            | 116            | 346,383   | 2083  |
| 86-atom  | 1.84     | 1.54     | 2.16      | 2.45      | 119            | 117            | 495   | 2163  |
| 102-atom | 1.85     | 1.52     | 2.16      | 2.42      | 120            | 117            | 301   | 2018  |

complex.

To conclude, the calculations have established that, for the Si-doped material, the stable site for hydrogen is the antibonding site, adjacent to the silicon atom. This has the lowest energy and also gives vibrational properties in close agreement with experiment. This model is similar to that postulated by Pajot *et al.* but with one major difference—here the silicon is fourfold coordinated, whereas those workers suggested that it should be fivefold coordinated. This has turned out to be a significant difference as it is just the broken bond that causes the “missing” silicon mode to fall into the one-phonon spectrum. However, for Be-doped material, the BC site is favored. The stretching frequency of the Be-H bond has been reproduced, together with a prediction that the unobserved mode falls into the one-phonon band. These calculations have therefore been able to distinguish between different models previously put forward for the microscopic structure of donor and acceptor complexes with hydrogen in semiconductors. Quantitative agreement has been obtained with experimental values of the vibrational frequencies of both the hydrogen atom itself and the modes of the paired donor or acceptor atom. This shows that these *ab initio* calculations can produce reliable results which can give information about the microscopic structure of defects. They are especially valuable as a complementary tool to be used alongside experimental results as then enable measurements which only give indirect information about the structure of a defect to be correlated with this structure.

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