

H passivation of Si impurities in GaAs

L. Pavesi*

*Institut de Micro- et Optoélectronique (IMO),
Ecole Polytechnique Fédérale de Lausanne,
PHB-Ecublens, CH-1015 Lausanne, Switzerland*

P. Giannozzi

*Institut Romand de Recherche Numérique en Physique des Matériaux (IRRMA),
PHB-Ecublens, CH-1015 Lausanne, Switzerland*

(Received 18 September 1990)

The equilibrium sites, vibrational frequencies, and electronic properties of interstitial H in GaAs doped with Si have been studied by first-principles calculations in the local density approximation within a supercell approach. Two different Si sites in GaAs have been examined: Si replacing a Ga atom (Si_{Ga} donor) and Si replacing an As atom (Si_{As} acceptor). We find that the stable configuration for the H- Si_{Ga} complex is the antibonding-Si site. The lattice undergoes a large relaxation and the Si-As bond is almost broken. The stable site for the H- Si_{As} complex is along the Si_{As} -Ga bond. H binds to the Si and Ga atoms forming a three-center bond. In both cases the lattice relaxation is essential in order to obtain the passivation of the impurities. The computed localized vibrational frequencies and dissociation energies of the H-Si complexes agree reasonably well with experimental results.

I. INTRODUCTION

Si is one of the most widely employed shallow dopants in GaAs because of its high incorporation coefficient and its very low diffusivity. By varying the growth conditions it is possible to *n*-dope or *p*-dope GaAs with Si atoms.¹ Usually, Si is incorporated on the Ga site (Si_{Ga}) and forms a donor level, some 5.8 meV lower than the conduction-band minimum. On the other hand, Si can be incorporated on an As site (Si_{As}), where it behaves as an acceptor with a binding energy of 34 meV. More interestingly, a recent calculation² suggests that the donor impurity is metastable. In addition to the shallow state, a deep level is formed as the donor traps an electron and undergoes a large lattice relaxation. This deep level is identified with the *DX* center, which is typical of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloy and causes detrimental effects to the electronic properties of the alloy.³

It is now well established that the introduction of atomic H in semiconductors causes the passivation of a variety of centers, shallow as well as deep.⁴ In GaAs the reduction of the electrical activity of Si donors has been demonstrated.⁵ The physical mechanism for the passivation of shallow impurities is the bonding of the H atom to the dopant, with the formation of a neutral complex. Localized vibrational modes have indeed been observed for the H-Si complex both in *n*-type GaAs and in *p*-type GaAs.⁶⁻⁸ The localized vibrational frequencies measured by far-infrared transmission spectroscopy are summarized in Table I. The H sites are of C_{3v} symmetry along the $\langle 111 \rangle$ axis. In the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloy, the *DX*-center density is reduced by H diffusion but the microscopic details of the passivation are still unclear.

In our previous work⁹, we discussed neutral H in GaAs.

An amphoteric behavior has been found: H induces a deep donor level in the band gap when placed in the bond-center (BC) site and a deep acceptor level when placed in a high-charge-density region out of the bond. Hence, we have suggested that the passivation of impurities occurs through their neutralization, which follows the pairing between the H and the impurity (this is not merely a compensation mechanism because of the bonding between H and the impurity). The stable site for undoped GaAs is an antibonding site (AB) with an As atom as a first neighbor. Very recently, calculations of H passivation of Si-donors and Be-acceptors in GaAs were presented.¹⁰ Both impurities studied in Ref. 10 are substitutional on a Ga site.

In this paper, we present state-of-the-art first-principles calculations of the H passivation of Si impurities in GaAs. We have studied several high-symmetry

TABLE I. Vibrational frequencies of the H-Si localized modes in GaAs. ν_s is the stretching frequency and ν_b is the bending frequency of the complex. Experimental data are given at liquid-helium temperature. Theoretical data enclosed in parentheses are from 32-atom supercells; the other data are from 16-atom supercells.

	Expt.		Theor.	
	ν_s (cm^{-1})	ν_b (cm^{-1})	ν_s (cm^{-1})	ν_b (cm^{-1})
<i>n</i> -type GaAs	1717 ^a	897 ^a	1590 (1460)	790 (850)
<i>p</i> -type GaAs	2095 ^b		2240 (2100)	400 (260)

^a Reference 7.

^b Reference 8.

sites for H introduced in the GaAs lattice doped with Si_{Ga} or with Si_{As} . In this way, we have studied the passivation of impurities that are substitutional on both the Ga or As sublattice (see Fig. 1).

We have performed total-energy and forces calculations in the framework of the local-density-approximation (LDA) pseudopotential method. The technical details are similar to those of Ref. 9. A 16-atom supercell has been used to determine the lowest-energy H sites. These sites have also been studied with a 32-atom supercell, containing 16 As (Ga) atoms, 15 Ga (As) atoms, 1 Si atom on a Ga (As) site, and 1 H atom. All calculations have been performed at the bulk theoretical equilibrium parameter $a_0 = 5.61 \text{ \AA}$, with special points equivalent to the two special points in the zinc-blende Brillouin zone, and with plane waves up to a kinetic energy of 12 Ry.

A correct description of shallow impurities, such as Si in GaAs, requires very large supercells because the impurity wave function extends over several lattice parameters. With the supercells we have used (in the 32-atom cell, two neighboring H or Si atoms are at 9.72 \AA) the band structure of GaAs with substitutional Si (either Si_{Ga} or Si_{As}) strongly resembles that of pure GaAs. The impurity level is at the bottom of the conduction band for Si_{Ga} and at the top of the valence band for Si_{As} . On the other hand, convergence tests and previous experience^{9,11} indicate that our supercells are appropriate for the study of H-Si complexes.

Tables II and III summarize the results for p and n -doped GaAs. The labels of the different sites show the initial position of H in the GaAs lattice before the relaxation (see Fig. 1). All atoms in the cell are allowed to relax. In each case the displacements of H are along the bond direction.

II. SILICON DONOR

When Si substitutes for a Ga atom (Table II), the lowest-energy site turns out to be the AB site. The energy differences between this site and the others are

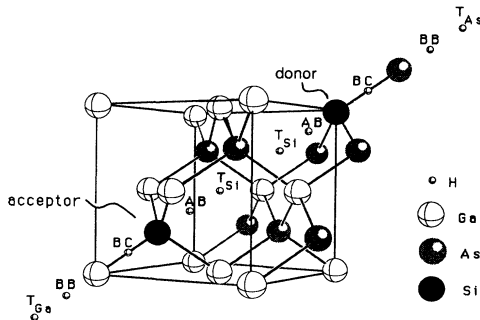


FIG. 1. Sketch of the high-symmetry interstitial sites for the H atom studied. The cube contains two Si atoms to describe the notation for both Si_{Ga} and Si_{As} . BC is the bond-center site, AB is the antibonding site (with a Si atom as a nearest neighbor), BB is the antibonding site (with a Ga or As atom as a nearest neighbor), and T is the tetrahedral site with the subscript indicating the nearest-neighbor atoms in the (111) direction.

TABLE II. Total-energy differences for interstitial H in n -doped GaAs. The Si atom substitutes for a Ga atom. The zero of the energy is the total energy for H in an antibonding position. The last three rows give the distances between H and the nearest-neighbor atoms in the (111) direction, and the Si-As bond length. The resulting Si-As bond length in the relaxed crystal without the H interstitial atom turns out to be 2.39 \AA (2.41 \AA). (The asterisk denotes a 32-atom-supercell calculation.) In GaAs the theoretical bond length is 2.43 \AA . The different columns correspond to the results for H in the different high-symmetry interstitial sites shown in Fig. 1. The data refer to 16-atom supercells unless specified otherwise.

	BC	AB	T_{As}	T_{Si}
(eV)	0.81	0.00	0.62	0.36
$d_{\text{H-Si}}$ (\AA)	1.53	1.61 (1.63*)		1.93
$d_{\text{H-As}}$ (\AA)	2.11		2.43	
$d_{\text{Si-As}}$ (\AA)	3.64	2.68 (2.67*)	2.42	2.59

higher than those found for neutral H in GaAs.⁹ The Si atom relaxes from its lattice site away from the As atoms (0.51 \AA) towards the H atom and becomes almost coplanar with its three nearest-neighbor Ga atoms. The As atom moves towards the Si atom of 0.26 \AA . The H-Si distance is somewhat larger than the typical bond length found in a silane molecule (about 1.5 \AA),¹¹ indicating a slight weakening of the bond. The energy gain during the relaxation is 2.3 eV . A similar relaxation of the nearby Si is found for the donor passivation in Si (Ref. 12), though the H-Si distance ($\approx 1.66 \text{ \AA}$) is larger than in GaAs. It is interesting to remark that in Si the H does not bind to the donor impurities but to the host lattice.¹² In GaAs, the configuration with H in the T_{Si} site has a higher energy with respect to the AB site, and the Si atom relaxes only by 0.27 \AA towards the H atom. The T_{As} site has a negligible relaxation. The BC site has a higher energy than both the AB and the T_{As} sites. When H sits along the bond, it is nearer to the Si atom than to the As atom, with a H-Si distance similar to the bond length in the silane molecule. The BB site is unstable, and when H is placed in this position it relaxes towards the T_{As} .

TABLE III. Total-energy differences for interstitial H in p -doped GaAs. The Si atom substitutes for an As atom. The zero of the energy is the total energy for H in a bond center position. The last three rows give the distances in the (111) direction between H and the nearest-neighbor atoms, and the Si-As bond length. The resulting Si-Ga bond length in the relaxed crystal without the H interstitial atom turns out to be 2.36 \AA (2.41 \AA). (The asterisk denotes a 32-atom-supercell calculation.) The different columns correspond to the results for H in the different high-symmetry interstitial sites shown in Fig. 1. The data refer to 16-atom supercells unless specified otherwise.

	BC	AB	BB	T_{Ga}	T_{Si}
(eV)	0.00	0.36	1.17	1.61	0.40
$d_{\text{H-Si}}$ (\AA)	1.53 (1.55*)	1.56			1.57
$d_{\text{H-Ga}}$ (\AA)	1.66 (1.70*)		1.57	2.43	
$d_{\text{Si-Ga}}$ (\AA)	3.19 (3.25*)	2.51	2.38	2.43	2.60

Figure 2 shows the contour plot of the calculated charge density in the (110) plane for the H-Si complex. We can see that the total charge density has a large value at the H site and is distributed along the H-Si line. The bond between the Si atom and the As atom is strongly weakened: The Si passes from a sp^3 bonding configuration to a sp^2 configuration, and the surplus electron is taken by the bonding between the Si and H. The defect level induced by the Si_{Ga} atom in bulk GaAs is at the bottom of the conduction band. When H is introduced in the AB site, and relaxation is not allowed, the defect level does not move. After the relaxation, the defect level is pushed toward the valence band. The Fermi level for the neutral H-Si complex at the AB site is located at the bottom of the conduction band. Hence the gap state induced by the donor Si impurity is full, and the donor is neutralized. The gap state has an antibonding character between the Si and As atoms and bears no charge on the H atoms. The bonding level, whose charge density is localized on the H atom (see Fig. 2), is deep in the valence band.

In view of the analysis of DX centers, we have performed a calculation for the H- Si_{Al} complex in AlAs and found similar results for the stable site and lattice relaxation to those presented here for GaAs. The model of the DX center proposed in Ref. 2 indicates a stretching of the bond (which becomes 3.6 Å long) between the As and the Si atoms when Si binds an extra electron (i.e., it passes from a simple substitutional donor to a negatively charged DX^- center). Our finding of a large lattice relaxation of the Si atom when H is introduced (see Table II) fits well the H passivation of the DX center, assuming that this model is correct. The total charge density shown in Ref. 2 for the DX center is compatible with our Fig. 2, where H shares its electron with the neighboring Si atom. Globally the H-Si complex is neutral. We remark that in order to have passivation one needs to place the H atom near the Si atom in the AB position. H in

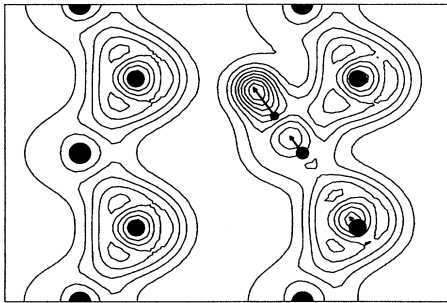


FIG. 2. Contour plot in the (110) plane of the valence charge density for interstitial hydrogen in relaxed n-doped GaAs. The H (indicated in the figure by a small solid-circle) was initially placed at the antibonding site with a Si atom as a nearest neighbor. The new positions of H and of the Si atom after the relaxation are indicated by the arrow tip. The unrelaxed atomic positions of the Si, Ga, and As atoms are indicated by solid circles (the bigger ones are for Ga and the smaller ones are for As). Due to the small relaxation of the As and Ga atoms, the relaxed positions have not been indicated.

the T_{Si} site does not interact enough with the Si atom to form a complex and drive the Si atom into the sp^2 configuration.

III. SILICON ACCEPTOR

When Si substitutes for an As atom (Table III), the stable site turns out to be the BC. A large bond enlargement occurs. The H atom is positioned in about the middle of the bond, slightly closer to the Si atom than to the Ga atom. The Si and Ga atoms move away from the H atom a distance of 0.38 and 0.45 Å, respectively (for neutral H placed along the bond of a GaAs lattice, the H moves toward the Ga atom and away from the As atom, and the Ga-H distance becomes 1.68 Å). The energy gain during the relaxation amounts to 3.5 eV. The AB site has an energy higher by only 0.36 eV with respect to the BC site and the distance between the H and the Si is similar for the two configurations. In Si, detailed calculations have been reported for the passivation of the B acceptor impurity.¹³ The stable site turns out to be the relaxed BC site, as in GaAs. The energy differences between the AB, BB, and BC sites turn out to be very similar to what we have found for the passivation of the acceptor in GaAs. In the BC site of Si, H is positioned closer to the acceptor (a distance of 1.36 Å) than to the Si atom (1.65 Å), where H is positioned nearer to the Si impurities.

Figure 3 shows the contour plot of the calculated charge density in the (110) plane. The charge density has a large value at the H site and is distributed along the Si-H-Ga line. A three-center bond is formed. The Fermi level is located in the band gap between the top of the valence band and the unoccupied gap states. Hence the acceptor has been neutralized. The H atom supplies the missing electrons and binds together the Si and Ga atoms. The charge density of the gap states is localized on the H atom and behaves as an antibonding state between the Si and Ga atoms.

IV. VIBRATIONAL AND DISSOCIATION ENERGIES

The vibrational energies of the H-Si complex have been evaluated by moving the H atom and calculating the Hellmann-Feynman restoring forces, which act on the H

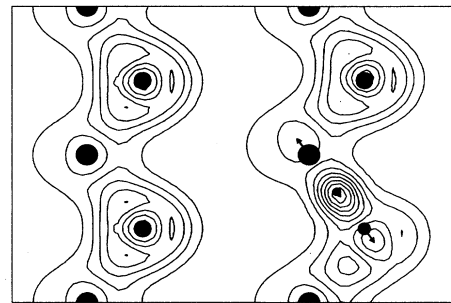


FIG. 3. Contour plot in the (110) plane of the valence charge density for interstitial hydrogen in relaxed p-doped GaAs. The H was initially placed at the bond center between the Ga and the Si atoms. The same notations as in Fig. 2 have been used.

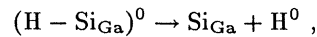
atom (see Ref. 11 for more details). The values for the stretching and bending mode energies are reported in Table I for the stable H sites. The computed vibrational frequencies are in overall agreement with those found in experiments considering that the theoretical estimates for the silane stretching and bending mode frequencies point toward an underestimate of the H-Si interaction.¹¹ For comparison, neutral H has a stretching frequency of 1945 cm⁻¹ in the BC site of pure Si,¹⁴ 2400 cm⁻¹ in the BC site of pure GaAs,⁹ 1600 cm⁻¹ in the As antibonding site of pure GaAs,⁹ and 1460 cm⁻¹ in the Si antibonding site of *n*-doped Si.^{11,12} The vibrational frequencies we find for H-Si_{Ga} confirm that the donor passivation of Si in GaAs is similar to the complexing between H and Si in *n*-doped Si. For the H-Si_{As} we find a value of the stretching vibration frequency that is between the values found for the pure H-Si bond and the Ga-H-As bond. This fact confirms our picture of the formation of a three-center bond when the acceptor is passivated. Indeed, a dependence of the localized vibrational energy on the acceptor atoms has been experimentally found (2036 cm⁻¹ for Be acceptors and 2147 cm⁻¹ for Zn acceptors).⁷

Our results show that the line at 972 cm⁻¹ found in *p*-type GaAs (Ref. 8) is not due to the H-Si vibrational mode, but it could be due to more complex configurations. In addition, in *p*-doped GaAs the bending mode for H in the BC at 260 cm⁻¹ is not experimentally observed because it is degenerated with the longitudinal-optical-phonon Raman frequency.

We have found a qualitative agreement with the results of Ref. 10 obtained by a cluster calculation. However the details of the lattice relaxation, and consequently the vibrational frequency of the hydrogen-dopant complex, are different. In particular, a H-Si bond length shorter than in our calculation has been found (possibly due to a stronger H-Si interaction). Moreover, for the H-acceptor

configuration, we have not found any tendency for the H to move off of the axis.

Dissociation energies of about 1.6 eV for H-Zn_{Ga} (where Zn_{Ga} is an acceptor) and of about 2 eV for a H-donor complex were found by thermal recovering of the passivated dopants.¹⁵ To compute the dissociation energy of the H-Si_{Ga} complex one has to consider the following reaction:

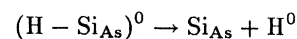


where the H-Si_{Ga} complex is dissociated in a donor Si_{Ga} and a H atom in the GaAs lattice. The dissociation energy (E_d) is the energy difference between the initial and final configuration of the reaction

$$E_d = -E(H - Si_{Ga}) + E(Si_{Ga}) + E(H^0) - E(GaAs),$$

where $E(H - Si_{Ga})$ is the total energy of the Si_{Ga} doped lattice with H in the AB site, $E(Si_{Ga})$ is the total energy of Si_{Ga} doped GaAs, and $E(H^0)$ is the total energy of the GaAs lattice with a H atom in the minimum energy site. We find $E_d \simeq 2.2$ eV.

For the H-Si_{As}, the dissociation reaction is



and the corresponding dissociation energy is $E_d \simeq 1.75$ eV.

In conclusion, the stable configuration for the H-donor complex in GaAs is an antibonding donor site, and the stable configuration for the H-acceptor complex in GaAs is a site along the bond near the bond center. The relaxation is very important to obtain the passivation of the impurity.

This work has been supported by the Fonds National Suisse pour la Recherche Scientifique, under Grant No. 20-5446.87, and by Thomson-CSF.

*Present address: Physics Department, University of Trento, I-38050 Povo (Trento), Italy.

¹The *Technology and Physics of Molecular Beam Epitaxy*, edited by E. H. C. Parker (Plenum, New York, 1985).

²D. J. Chadi and K. J. Chang, *Phys. Rev. B* **39**, 10 063 (1989).

³For a recent review, see *Physics of DX Centers in GaAs Alloys*, guest editor J. C. Bourgoin [Diffusion and Defect Data Pt. B **10**, 1 (1990)].

⁴S. J. Pearton, J. W. Corbett, and T. S. Shi, *Appl. Phys. A* **43**, 153 (1987).

⁵J. Chevallier, B. Clerjaud, and B. Pajot, in *Neutralization of Defects and Dopants in III-V Semiconductors*, in *Hydrogen in Semiconductors* edited by J. I. Pankove and N. M. Johnson [Semiconductors and Semimetals, series editors R. K. Willardson and A. C. Beer (Academic, New York, 1990)].

⁶B. Pajot, in *Proceedings of the 3rd International Conference on Shallow Impurities in Semiconductors, Linköping, Sweden, 1988*, Inst. Phys. Conf. Ser. No. 95, edited by B. Monemar (IOP, Bristol, 1989), p. 435.

⁷B. Pajot, R. C. Newman, R. Murray, A. Jalil, J. Chevallier,

and R. Azoulay, *Phys. Rev. B* **37**, 4188 (1988).

⁸J. Chevallier, B. Pajot, A. Jalil, R. Mostefaoui, R. Rahbi, and M. C. Boissy, in Vol. 104 of *Materials Research Society Symposia Proceedings*, edited by M. Stavola, S. J. Pearton, and G. Davies (MRS, Pittsburgh, 1988), p. 337.

⁹L. Pavesi, P. Giannozzi, and F. K. Reinhart, *Phys. Rev. B* **42**, 1864 (1990).

¹⁰P. R. Briddon and R. Jones, *Phys. Rev. Lett.* **64**, 2535 (1990).

¹¹A. Amore Bonapasta, P. Giannozzi, and M. Capizzi, *Phys. Rev. B* **42**, 3175 (1990).

¹²P. J. H. Denteneer, C. G. Van de Walle, and S. T. Pantelides, *Phys. Rev. B* **41**, 3885 (1990); S. B. Zhang and D. J. Chadi, *ibid.* **41**, 3882 (1990).

¹³P. J. H. Denteneer, C. G. Van de Walle, and S. T. Pantelides, *Phys. Rev. B* **39**, 10 809 (1989).

¹⁴C. G. Van de Walle, P. J. H. Denteneer, Y. Bar-Yam, and T. S. Pantelides, *Phys. Rev. B* **39**, 10 791 (1989).

¹⁵S. J. Pearton, W. C. Dautremont-Smith, J. Chevallier, C. W. Tu, and K. D. Cummings, *J. Appl. Phys.* **59**, 2821 (1986).