Amphoteric behavior of H^0 in GaAs

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We present the results of pseudopotential density-functional supercell calculations of the properties of neutral hydrogen in bulk GaAs. The equilibrium sites are determined, and the electronic properties for the equilibrium positions are studied. We find that the equilibrium site for unrelaxed GaAs:H is in the low-valence-charge-density region, whereas if the relaxation of the whole lattice is allowed, a shallow equilibrium minimum occurs at an antibonding site near an As ion. The diffusion path is in the high-valence-charge-density region around the As ions with a barrier as low as 0.1 eV. From our results, we suggest that H behaves as a deep acceptor in n-type GaAs and as a deep donor in p-type GaAs, and occupies different positions. Hence passivation of dopants occurs by neutralization.

The behavior of hydrogen (H) in crystalline semiconductors has attracted considerable interest in the past. H diffusion into semiconductors could be used as a post-growth technique for improving the optical and electrical properties of these materials through the removal of many defects.[1,2]

An extensive literature on H diffusion in elemental semiconductors, like Si and Ge,[1] already exists. As a general result, atomic hydrogen causes a passivation of dopant ions, a reduction of the free carrier density, an increase of the electron mobility, and a decrease in the deep-level concentration. Sometimes defects may be induced by H. For Si, these effects are more pronounced in p-type materials.

As far as compound semiconductors are concerned, such as the III-V semiconductor GaAs, a great deal of experimental results has been accumulated in recent years.[2] The general experimental features are similar to the behavior of H in Si. Moreover, passivation of n-type GaAs as well as of p-type GaAs was reported.[3] Thus some authors[4] suggest that H diffuses as a neutral state (H^0). The activation energies for the diffusion are quite low (0.2–0.5 eV).[3,5] In doped GaAs, the passivation depth is inversely proportional to the impurity concentration suggesting the possibility of a pairing between H and the impurity. This was indeed confirmed by high-resolution infrared absorption experiments.[6] Dissociation energies of about 1.6 eV for H-Zn_{Ga} and of about 2 eV for H-donor complex were found by thermal recovering of the passivated dopants.[5] Hence, H passivation of acceptors is less stable than the donor passivation in GaAs.

For H in Si, detailed first-principles calculations have been done.[7-9] It was found that the equilibrium sites for H are in interstitial positions: as a positively charged H in the bond-center site (BC) if the material is p doped and as a negatively charged H in the tetragonal site (T) for n-type doped Si. A model of diffusion of a positively charged H (H^+) through a high-charge-density path (which includes the bond-center region) was proposed by static calculations[7] and confirmed by a Car-Parrinello dynamic simulation.[9] Dynamic calculations show also that H is extremely mobile in Si and that Si ions cannot adiabatically follow the proton. The lattice may not have the time to undergo the large relaxation needed for the high-valence-charge sites to become energetically favorable and another diffusive path through the low-density-charge region is possible. The relative occurrence frequencies of the two diffusive paths possible in Si have not been computed. The transit time in the equilibrium sites for H could be very short, at least at the high temperature used in the simulations. In p-type materials, the mechanism of passivation is explained[10] as a compensation phenomenon (H loses its electron which in turn annihilates a free hole of an acceptor) followed by a pairing of the negatively charged dopant with H^+.

Only few theoretical works have been published for H in GaAs. In Ref. 11 the electronic configuration of neutral H (H^0) in the bond-center position of a $Ga_4As_4H_{18}$ cluster is studied; an overall agreement with the results of muon spectroscopy measurements is obtained, but the experimental relaxation of the As and Ga ions is not well reproduced (possibly due to the small size of the

cluster used). On the other hand, the study of Ref. 12 presents results for the equilibrium positions of H in a $Ga_{13}As_{13}H_{30}$ cluster. The tetrahedral site turns out to be more stable than the BC site in contrast with the other findings for Si. Other interstitial high-symmetry sites (see Figs. 1 and 2) have not been studied at all. For this reason we have undertaken an investigation of the behavior of H in GaAs using state-of-the-art pseudopotential-density-functional techniques.

We have used norm-conserving pseudopotentials[13] in a plane-wave basis set and large supercells. The exchange-correlation functional of Ceperley and Alder in the parametrized form given by Perdew and Zunger[14] has been used. Matrix diagonalization has been performed exactly with iterative methods. The sum over the Brillouin zone (BZ) requires some care. For neutral H, the unit cell contains an odd number of electrons, so that the special point technique does not apply without modifications. A simple and efficient way to deal with the Fermi surface is given by the Gaussian broadening scheme.[15]

The introduction of H into the GaAs lattice induces a lattice relaxation which must be taken into account. Initially, H is in one of the selected high-symmetry sites;

we calculate a new equilibrium position from Hellmann-Feynman forces[16] and an estimate of the dynamical matrix,[17] and repeat the process until the forces becomes very small. All atoms in the cell are relaxed. Such a relaxation process conserves the initial crystal symmetry, so that we use similar notations for the sites before and after the relaxation: A superscript R indicates that H has moved from the initial position. The relaxation is very weak for interstitial positions where the bulk charge density is low (like, e.g., the T sites); it is very important for the BC site, and significant for all other sites where the bulk charge density is high.

Several tests have been performed in order to determine the minimum supercell size, energy cutoff for the plane waves, and k-point mesh, needed to yield reliable results. The supercell size is especially critical. The dispersion of the H-induced levels is a good indication of the interaction between H in different cells. For a 16-atoms supercell, the dispersion can be as big as 0.7 eV; for a 32-atoms supercell, it is about 0.2 eV. For comparison, the theoretical bulk gap is 1.2 eV. We have found that energy differences between different sites can have variations up to 0.4 eV when passing from a 16-atoms supercell to a 32-atoms supercell. In particular, energy differences between high-density sites with big lattice relaxations (especially the BC site) and low-density sites with small lattice relaxations are quite sensitive to the smallness of the cell.

The calculations have been performed with a k-point mesh equivalent to the (4,4,4) Monkhorst-Pack mesh in the zinc-blende unit cell, a broadening of 0.01 Ry, and a kinetic energy cutoff of 12 Ry. Tests with the (8,8,8) mesh in the 16-atoms cell have given variations in the energy differences up to 0.1 eV, but no qualitative changes have occurred. For a finer mesh there are virtually no vari-
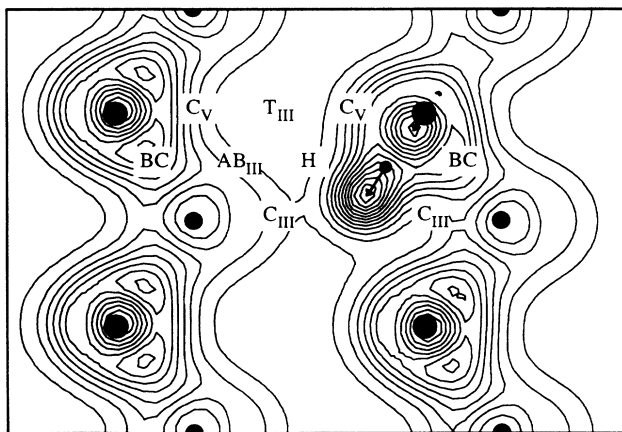

FIG. 1. Contour plot in the (011) plane of the valence-charge density for interstitial neutral hydrogen in relaxed GaAs. The H (indicated in the figure by a small closed circle) was initially placed at the antibonding site with As ions as the nearest neighbor. The new positions of H and of the nearest As ion after the relaxation are indicated by the arrow tip. The unrelaxed atomic positions of the Ga and As ions are indicated by closed circles (the bigger ones are for As). Due to the small relaxation of the As and Ga ions, the relaxed positions have not been indicated. In the figure the other high-symmetry interstitial sites studied are shown too: BC is the bond center site, AB the antibonding site (the subscripts III or V indicate the nearest-neighbor ion), T the tetrahedral site, C the C site defined as the center of the rhombus formed between three adjacent ions and the nearest T site, and H the hexagonal site. The M position does not stay on the (011) plane but lies on a line perpendicular to the Ga—As bond between the BC site and the neighboring hexagonal (H) site.
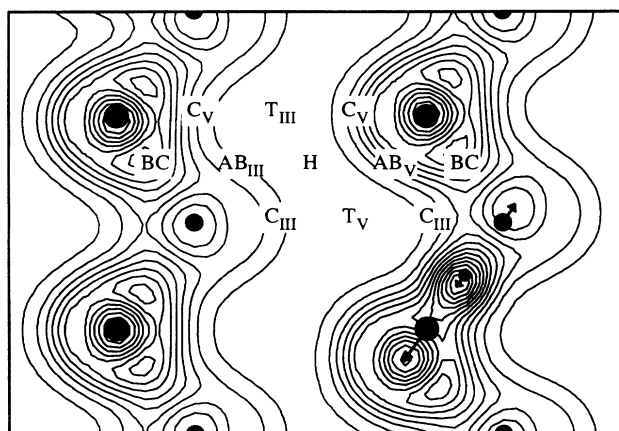

FIG. 2. Contour plot in the (011) plane of the valence-charge density for interstitial neutral hydrogen in relaxed GaAs. The H was initially placed at the bond center. The same notations as in Fig. 1 have been used. The new position of H and of the nearest As and Ga ions after the relaxation is indicated by the arrow tip.

ations. Higher cutoffs tend to lower high-density sites with respect to low-density sites up to 0.1 eV. In the following, the results for energy differences and relaxations have been obtained with the 32-atoms cell; the results for vibration energies and energy barriers have been obtained with the 16-atoms cell. All calculations have been performed with the bulk theoretical equilibrium lattice parameter $a_0 = 5.61$ Å.

In Table I we show our results for the energy differences in the unrelaxed crystal. The favored configurations are those of low charge density: T and H sites. In Table II we show the results for the relaxed crystal. The energy differences among the points become very small. Our results indicate that the AB_V^R configuration has the lowest energy. Its dissociation energy turns out to be about 1.46 eV (this is calculated as the total energy of the AB_V^R configuration, minus the total energy of bulk GaAs, minus the total energy of a supercell of isolated H, all obtained with the same cutoff and k-space mesh).

In Fig. 1 we show the valence-charge density for the AB_V^R site. H is located at 1.56 Å from the neighboring As ion in the direction of the bond towards the T_V site. The neighboring Ga and As ions relax by 0.07 and 0.31 Å, respectively. Other interesting points are the C_{III}^R and M^R sites. When H is placed in the C_{III} site, it moves 0.86 Å in the direction of the low density site T_V. We can distinguish a region close to the T_V site, formed by the AB_V^R, C_{III}^R, and M^R sites, respectively of C_{3v}, C_{2v}, and no symmetry. These points are nearly degenerated in energy, with barriers as low as 0.01 eV along the paths connecting them. A diffusive path connecting neighboring C_{III}^R and AB_V^R through M^R sites around As ions is thus possible. In this region H induces the formation of a deep binding level in the valence band, and of a half-filled level in the lower part of the band gap which behaves as a deep acceptor level.

On the other hand, for H in the low-valence-charge-density region, including the T_V, T_{III}, and H^R sites, the total energy is slightly higher. When H is introduced in these sites, the lattice relaxation is negligible. H induces only deep valence binding levels and no levels in the gap. We remark that the T_V site is unstable: H tends to fall into the region described above.

H in the bond-center site behaves differently than H in the AB_V^R, C_{III}^R, and M^R sites. When H is placed in the bond center, the neighboring Ga and As ions relax strongly (see Fig. 2 and Table I). The relaxation lowers the energy by about 5 eV. A bonding deep valence level and an antibonding half-filled level in the upper part of the band gap are induced. Thus H in the BC^R position behaves as a deep donor. Our calculations for H in the BC^R give a bond relaxation comparable with the experimental results of muonium.[18] Muonium is a light pseudoisotope of H which manifests itself as a normal Mu state and as an "anomalous" muonium Mu* in the interstitial site at the center of the bond.[19] Even though Mu presents a larger zero-point motion and a shorter lifetime than H, the static electronic properties do not depend on the mass or lifetime, and a comparison is thus possible. Mu*, at the bond center, induces a relaxation of $(32\pm7)\%$ in the bond length (we found a relaxation of 40%); the As and Ga ions are displaced 0.65 ± 0.17 and 0.14 ± 0.06 Å away from the bond (our results are 0.66 Å for As and 0.31 Å for Ga). As concerns the stability of H in the BC, we found that if the relaxation is not taken into account the BC is a saddle point for H, whereas with relaxation the BC^R becomes a local minimum: H finds a barrier of about 0.1 eV to move towards the C_{III} site. The dissociation energy for H in the BC^R site is about 1.27 eV.

Our calculations for undoped GaAs can give a hint on the possible mechanisms of hydrogen passivation of dopant through the comparison of the vibrational localized modes of H in the equilibrium positions with the experimentally observed ones. It should be kept in mind, however, that the presence of dopant impurities can alter the vibration frequencies.

For Si-doped GaAs,[6] localized vibrations due to H have been found at 1717 cm^{-1}. This vibration is attributed to the stretching mode of a H-Si$_{Ga}$ complex in which H is in an antibonding position. For comparison we found for the localized vibration of H in the AB_V^R site a stretching mode of about 1600 cm^{-1}. From these results it is possible to infer a mechanism for the hydrogen passivation of n-type GaAs in which deep H-acceptor—donor pairing occurs causing a neutralization of the dopants.

For p-type GaAs,[6] localized vibrational modes of the Be$_{As}$-H complex were found at 2036 cm^{-1} and for the

TABLE I. Total-energy differences for neutral interstitial H in unrelaxed GaAs. The zero of the energy is the global minimum for the relaxed lattice (see Table II). The last two rows give the distances between H and the nearest neighbor (NN) ions. The different columns correspond to the results for H in the different high-symmetry interstitial sites. BC is the bond center, T the tetrahedral site (the subscripts III or V indicate the first-nearest-neighbor ion), AB the antibonding site, C the C sites defined as the center of the rhombus formed between three adjacent ions and the nearest T site, H the hexagonal site, and M the site which lays on a line perpendicular to the Ga—As bond between the BC site and the neighboring hexagonal site.

	BC	C_{III}	C_V	AB$_{III}$	AB$_V$	M	H	T_{III}	T_V
GaAs:H (eV)	5.22	1.24	1.32	2.34	2.34	1.08	0.26	0.33	0.26
$d_{H-Ga_{NN}}$ (Å)	1.21	1.40	1.98	1.21	2.32	1.57	2.32	2.43	2.80
$d_{H-As_{NN}}$ (Å)	1.21	1.98	1.40	2.32	1.21	1.57	2.32	2.80	2.43

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TABLE II. Total-energy differences for neutral interstitial H in GaAs after the relaxation. The last two rows give the distances between H and the nearest-neighbor ions. The different columns correspond to the initial position of H in the different high-symmetry interstitial sites. The notation of the sites as in Table I; the index R indicates that H has moved as well.

	BC^R	C_{III}^R	C_V^R	AB_{III}^R	AB_V^R	M^R	H^R	T_{III}	T_V
GaAs:H (eV)	0.19	0.11	0.21	0.23	0.00	0.11	0.25	0.29	0.22
$d_{\text{H-Ga}_{NN}}$ (Å)	1.68	2.40	2.09	1.83	2.24	2.84	2.33	2.38	2.78
$d_{\text{H-As}_{NN}}$ (Å)	1.72	2.16	2.21	2.98	1.56	1.98	2.32	2.84	2.43

Zn_{Ga}-H complex at 2147 cm^{-1} which were assigned to the stretching mode of the complex with H in the BC position. The BC site could be occupied during the diffusion (usually H diffusion is performed at sample temperatures of 250–300 °C).[1] H could move quite freely in GaAs, bind to the BC site during the diffusion and, eventually, be trapped into the BC site after the cooling down of the sample. We found a localized stretching vibration mode of about 2400 cm^{-1} for H in the BC^R. Thus in p-type GaAs, if H reaches the BC^R sites it behaves as a deep donor and the acceptors could be passivated by neutralization. Let us note that the thermal motion of H from bond-center site to bond-center site about the Be acceptor has been observed[20] and it was found that the motion is thermally activated with an energy of 0.37 eV (to be compared with the barrier of 0.1 eV that we found).

In conclusion, we have presented a detailed microscopic calculation for H⁰ in GaAs. Our results suggest that H in GaAs behaves as a deep donor or a deep acceptor depending on its lattice position. The passivation of dopant ions results from neutralization which follows the pairing between the H and the impurity. For n-type doped GaAs, the complexing between H and the dopant occurs without a bond breaking, whereas for p-type doped GaAs the acceptor neutralization follows a bond rearrangement as H gets into the bond.

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

[2] W.C. Dautremont-Smith, in *Defects in Electronics Materials*, edited by M. Stavola, S.J. Pearton, and G. Davies (MRS, Pittsburgh, PA, 1988), Vol. 104, p. 313.

[3] E. M. Omel'yanovskii, A. V. Pakhomov, A. Y. Polyakov, and L. V. Kulikova, Fiz. Tekh.—Semicond. **21**, 1762 (1987) [Sov. Phys. Semicond. **21**, 1068 (1987)].

[4] R. A. Morrow, J. Appl. Phys. **66**, 2973 (1989).

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

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

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

[8] K. J. Chang and D. J. Chadi, Phys. Rev. B **40**, 11 644 (1989).

[9] F. Buda, G. L. Chiarotti, R. Car, and M. Parrinello, Phys. Rev. Lett. **63**, 294 (1989).

[10] S. T. Pantelides, Appl. Phys. Lett. **50**, 995 (1987).

[11] Dj. M. Maric, S. Vogel, P. F. Meier, and S. K. Estreicher, Phys. Rev. B **40**, 8545 (1989).

[12] P. Briddon and R. Jones, in Ref. 6, p. 459.

[13] The pseudopotentials for Ga and As are those used by W. Andreoni, G. Pastore, R. Car, M. Parrinello, and P. Giannozzi, in *Band Structure Engineering in Semiconductor Microstructures*, Vol. 189 of *NATO Advanced Study Institute, Series B: Physics*, edited by R.A. Abram and M. Jaros (Plenum, New York, 1989), p. 129, with the d potential of Ga so modified: $R_2 = 1.12$; $a_2 = 0.21826$; $b_2 = 1.015$. For H a pseudopotential of the same form has been used: $Z_v = 1$; $R_c = 0.25$; $R_0 = 0.284$; $a_0 = -1.9287$; $b_0 = 0.3374$.

[14] D.M. Ceperley and B.J. Alder, Phys. Rev. Lett. **45**, 566 (1980); J. Perdew and A. Zunger, Phys. Rev. B **23**, 5048 (1981).

[15] C.L. Fu and K. M. Ho, Phys. Rev. B **28**, 5480 (1983).

[16] H. Hellmann, *Einführung in die Quantenchemie* (Deuticke, Leipzig, 1937); R.P. Feynman, Phys. Rev. **56**, 340 (1939).

[17] Obtained through a Broyden-Fletcher-Goldfarb-Shanno formula: see W. H. Press, B. P. Flannery, S. A. Teukolsky, and W. T. Ketterlin, *Numerical Recipes* (Cambridge University Press, Cambridge, 1986), Chap. 10.

[18] R. F. Kiefl, M. Celio, T. L. Estle, G. M. Luke, S. R. Kreitzman, J. H. Brewer, D. R. Noaks, E. J. Ansaldo, and K. Nishiyama, Phys. Rev. Lett. **58**, 1780 (1987).

[19] S. F. J. Cox, J. Phys. C **20**, 3187 (1987).

[20] M. Stavola, S. J. Pearton, J. Lopata, C. R. Abernathy, and K. Bergman, Phys. Rev. B **39**, 8051 (1989).