Structure and Passivation Effects of Mono- and Dihydrogen Complexes in GaAs$_y$N$_{1-y}$ Alloys

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In GaAs$_y$N$_{1-y}$, the presence of a few percent of N induces a large reduction of the GaAs band gap that vanishes upon hydrogenation. In the present Letter, the energetics of N-H complexes and their effects on the band structure of the GaAs$_{0.97}$N$_{0.03}$ alloy have been investigated by first-principles density functional methods. We find that monohydrogen N-H$^+$ and dihydrogen N-H$_2^*$ complexes are formed depending on doping. Moreover, only N-H$_2^*$ complexes account for the neutralization of nitrogen effects. A model is proposed that clarifies the passivation mechanism of nitrogen by H.

Hydrogen irradiation dramatically affects the electronic properties of semiconductors [1]. Because of a high chemical reactivity, hydrogen binds to and neutralizes dangling bonds in the lattice, thus wiping out nonradiative recombination center, shallow impurity, and deep defect energy levels from the gap of crystalline elemental and compound semiconductors. Much less is known about the effect of hydrogen on isoelectronic impurities, in particular, on substitutional N. In GaAs, when the As anion is substituted by an isoelectronic lighter (heavier) atom, an increase (decrease) of the compound energy gap is expected in a virtual crystal approach, as experimentally observed in the case of P (Sb) substitution. However, this simple "rule of thumb" does not hold in the case of N substitution. A giant reduction in the band-gap energy has been reported indeed for N concentration of the order of a few percent in GaAs$_y$N$_{1-y}$ [2]. Hydrogen irradiation fully neutralizes the N effects in GaAs$_y$N$_{1-y}$ (and In$_x$Ga$_{1-x}$As$_y$N$_{1-y}$) by restoring the band gap of the N-free semiconductor [3,4]. Since N is an isoelectronic impurity, this latter surprising result cannot be explained in terms of a saturation of dangling bonds or neutralization of chemical valence effects, as usually done in the case of shallow and deep impurities. The behavior of N (H) in GaAs (GaAsN) has motivated the present study on the formation of N-H complexes and their role in the H neutralization of the N effects. The achieved results show that the formation of monohydrogen and dihydrogen complexes depends on the position of the Fermi level, as recently found in the case of Ga(PN) [5]. Moreover, monohydrogen complexes do not lead to the neutralization of the N effects, which is achieved instead by forming *dihydrogen* complexes. This is an interesting result showing that H can passivate even the peculiar N effects through an unusual passivation mechanism. A simple model is proposed to account for that mechanism.

In the present Letter, the structure, formation energy, vibrational, and electronic properties of complexes formed by one N and one or two H atoms have been investigated in the GaAs$_{0.97}$N$_{0.03}$ alloy by first-principles local density functional methods in a supercell approach. The main results of this study are summarized here. First, the most stable monohydrogen and dihydrogen N-H complexes are the N-H$_{BC}^+$ complex shown in Fig. 1(a), where a H$^+$ ion is bonded to the N atom and located close to a bond-center (BC) site, and the N-H$_2^*$ complex shown in
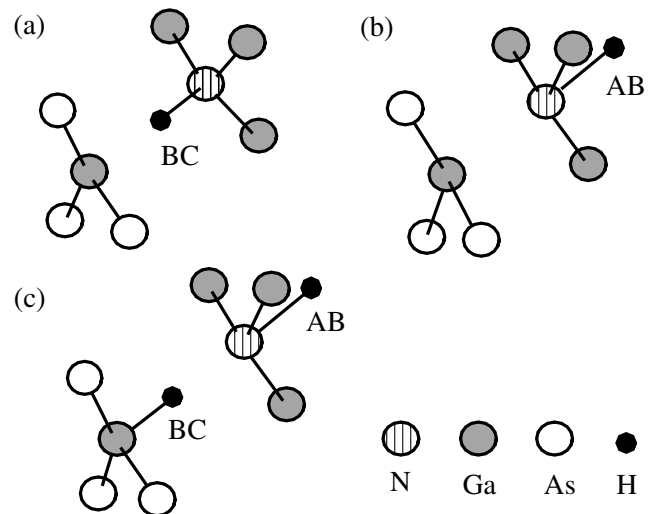

FIG. 1. Atomic configurations of some N-H complexes in GaAs$_y$N$_{1-y}$: (a) N-H$_{BC}$, (b) N-H$_{AB}$, and (c) N-H$_2^*$. BC and AB indicate a bond centered and an antibonding site of H, respectively.

Fig. 1(c), respectively. Second, doping significantly affects the formation of the above complexes, since p- and n-type doping favor the mono- and the dihydrogen complexes, respectively. Third, the calculated vibrational frequencies are in very good agreement with the frequencies measured in hydrogenated slightly p-type GaAs and assigned to local vibrational modes (LVM) of hydrogen bonded to N. Finally, only the formation of the N-H_2^* complex leads to the neutralization of the N effects and restores the GaAs energy gap.

By analogy with the case of defect formation energies [6], in a supercell approach the formation energy per H atom $\Omega[N-nH]^q$ of a N-nH complex involving nH atoms and a q charge may be written as

$$\Omega[N-nH]^q = \frac{1}{n}\{E[N-nH]^q - E[N] - n\mu_H + q\mu_e\},$$

where $E[N-nH]^q$ is the total energy of a supercell of GaAs containing one N atom and n H atoms, μ_H is the chemical potential of hydrogen, which is assumed equal to half of the H_2-molecule energy in the vacuum, and q is the positive (negative) charge on the complex, namely, the number of electrons transferred from (to) the complex to (from) an electron reservoir with a chemical potential (or Fermi level) μ_e ($\mu_e = 0$ corresponds to a Fermi level at the top of the valence band).

The effects of N and H on the GaAs energy gap have been investigated here by calculating the transition energy of a defect, that is, the Fermi-energy value $\epsilon^{n/n+1}$ for which the occupation number of a defect electronic state in the energy gap changes from n to $n + 1$. In turn, $\epsilon^{n/n+1}$ can be estimated by the Fermi-energy position where the formation energies of the n and $n + 1$ charge states of the defect are equal [7]. In the present study, the N atoms in the GaAs$_{0.97}$N$_{0.03}$ alloy (i.e., the alloy simulated by 64-atom supercells) as well as the related N-H complexes have been considered as isolated defects and the corresponding $\epsilon^{n/n+1}$ values have been calculated. The $\epsilon^{n/n+1}$ values should be compared with the GaAs energy gap, estimated here by calculating the $\epsilon^{0/-}$ value in the N-free compound material. Although this method gives a rough estimate of the GaAs energy gap, it permits one to compare consistent results obtained within a same approach and to follow the evolution of the gap induced by the incorporation of N or the formation of N-H complexes. This procedure has been successfully used in the case of defects in AlN [8]. In addition, the $\epsilon^{+/0}$ value for the Si shallow donor in GaAs has been calculated here. This donor induces a level close to the bottom of the GaAs conduction band, thus providing a further state of reference to locate the N and N-H levels in the energy gap.

Total energies have been calculated in the local density approximation (LDA) by using supercells, separable *ab initio* pseudopotentials [9], plane-wave basis sets, the special-points technique for **k**-space integration, and the exchange-correlation functional of Ceperley-Alder.

Ultrasoft pseudopotentials have been used in the case of nitrogen [10]. Convergence tests have been done by using plane-wave cutoffs ranging from 18 to 28 Ry, supercells of 32 and 64 atoms, and **k**-point meshes equivalent to a (4,4,4) or (8,8,8) Monkhorst-Pack mesh in the zinc-blende unit cell. The results presented here have been achieved by using 64-atom supercells, the (4,4,4) **k**-point Monkhorst-Pack mesh, and cutoffs of 22 Ry. The stretching frequencies of the hydrogen LVMs have been estimated in the harmonic approximation [11]. Further details on the methods can be found elsewhere [6].

Different configurations of mono- and dihydrogen complexes have been investigated, which include positive, negative, and neutral states of complexes where one or two H atoms (ions) are located at an antibonding (AB) or BC sites close to the N or the Ga atoms of a Ga-N bond (see Fig. 1). Less symmetric geometries have been also considered in order to avoid spurious effects due to the symmetry of the atomic forces. The calculated total and formation energies have been then used to identify the stable and metastable configurations of the N-H complexes for different positions of the Fermi level. In the most interesting monohydrogen complexes, a H^+ ion is bonded to the N atom and located at the BC or at an AB site (see Fig. 1). In the dihydrogen complexes, the H atoms are located at BC and AB sites close to N or to one of its Ga neighbors; see, e.g., the geometry of the N-H_2^* complex shown in Fig. 1(c). Only the properties of the N-H_{BC}^+ and N-H_2^* complexes shown in Fig. 1 will be discussed here because they are the most stable mono- and dihydrogen complexes (i.e., with the smallest formation energies), respectively. The results achieved for all the investigated complexes will be reported elsewhere. The geometry of the N-H_{BC}^+ complex is characterized by an online Ga—H_{BC}^+-N configuration where the Ga and N atoms relax outward with displacements of 0.63 and 0.45 Å, respectively. The N-H_{BC}^+ and Ga-H_{BC}^+ distances are equal to 1.06 and 2.43 Å, respectively. The same distances are equal to 1.07 and 1.58 Å, respectively, when estimated by the sum of the atomic covalent radii. The comparison of the two sets of values suggests the formation of a strong N-H bond and the existence of a weak Ga-H interaction. In the neutral N-H_2^* complex, the involved Ga and N atoms displace outward of 0.16 and 1.04 Å, respectively. The N-H_{AB} and Ga-H_{BC} bond lengths are equal to 1.07 and 1.54 Å, respectively. The N-H_{BC} distance is 2.06 Å, that is, much larger than the 1.07 Å value estimated from the atomic covalent radii. This complex is therefore characterized by the formation of strong Ga-H_{BC} and N-H_{AB} bonds and by a negligible N-H_{BC} interaction. The chemical bonding in the above complexes is confirmed by plots of the electronic charge density (not reported here). The formation energies of the above N-H complexes are given in Table I for different values of μ_e. Present results clearly show that p-type and n-type doping favor the formation of the N-H_{BC}^+ and N-H_2^* complexes, respectively, while the

TABLE I. Formation energies (in eV) of several N-H complexes in $GaAs_{0.97}N_{0.03}$ calculated for Fermi-energy (μ_e) values equal to 0 (top of the valence band), $E_g/2$, and E_g, where E_g is the experimental GaAs energy gap (1.52 eV).

Complex	0	$E_g/2$	E_g
$[N\text{-}H_{BC}^+]$	−0.68	0.08	0.84
$[N\text{-}H_{AB}^+]$	−0.44	0.32	1.08
$[N\text{-}H_2^*]$	−0.28	−0.28	−0.28

two complexes may coexist in semi-intrinsic GaAsN. This indication is supported by the stretching frequencies calculated here for the hydrogen LVMs. A frequency value of 3172 cm^{-1} calculated for the $N\text{-}H_{BC}^+$ complex is in very good agreement with the value of 3195 cm^{-1} measured in hydrogenated slightly p-type samples of $GaAs_{0.99}N_{0.01}$ epilayers [12].

Let us consider now hydrogen neutralization of N effects on the GaAs energy gap. The $\epsilon^{0/-}[GaAs]$ value calculated for pure GaAs (i.e., the present estimate of the GaAs energy gap) is 1.85 eV, 22% higher than the experimental value (1.52 eV). The $\epsilon^{0/-}[N]$ value calculated for an isolated N atom in GaAs is 1.2 eV from the top of the valence band. This value is assumed as the energy gap of the $GaAs_{0.97}N_{0.03}$ alloy, thus corresponding to a reduction of 650 meV of the GaAs energy gap (see Fig. 2) not much larger than the experimental value of 400 meV [13]. The formation energies of the $N\text{-}H_{BC}^+$ and $N\text{-}H_2^*$ complexes as a function of the Fermi level are reported in Fig. 2. The crossing points of the formation energies corresponding to different charge states of the complexes permit one to estimate the transition energy values. Figure 2 shows that
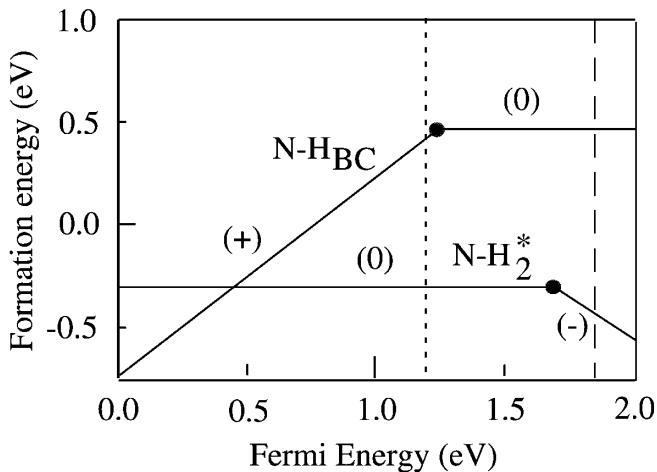

FIG. 2. Formation energy as a function of the Fermi energy μ_e for the $N\text{-}H_{BC}$ and $N\text{-}H_2^*$ complexes in $GaAs_{0.97}N_{0.03}$. The vertical short-dashed and long-dashed lines correspond to the $\epsilon^{0/-}[N]$ and $\epsilon^{0/-}[GaAs]$ values, respectively, namely, to the energy gaps of $GaAs_{0.97}N_{0.03}$ and GaAs (1.20 and 1.85 eV, respectively). The line segments represent the charge states of the complexes and the dots indicate the transition energies.

the $\epsilon^{+/0}[N\text{-}H_{BC}^+]$ almost coincides with the energy gap estimated for the $GaAs_{0.97}N_{0.03}$ alloy. On the contrary, the $\epsilon^{0/-}[N\text{-}H_2^*]$ value is close to the energy gap estimated for pure GaAs. Although the calculated $\epsilon^{n/n+1}$ values are affected by the well-known LDA band-gap error, the qualitative result is clear: The effects of N in GaAs can be neutralized by the formation of the $N\text{-}H_2^*$ complex, while monohydrogen complexes do not restore the GaAs gap. As a further confirmation, an $\epsilon^{+/0}$ value of 1.72 eV has been estimated for the Si donor in GaAs, in agreement with the shallow character of this dopant. An analysis of the bonding and antibonding states corresponding to the $N\text{-}H_{BC}^+$ and $N\text{-}H_2^*$ complexes leads to the same conclusions and clarifies the above results. Contour plots in the (110) plane of the charge densities $|\Psi_{n,0}|^2$ corresponding to the lowest *unoccupied* molecular orbitals (LUMO) induced by isolated N and N-H complexes are shown in Fig. 3. The LUMO of the isolated N is characterized by a strong localization of the electronic charge on the N atom [see Fig. 3(a)]. The formation of the $N\text{-}H_{BC}^+$ complex gives rise to a state in valence band corresponding to the formation of a strong N-H bond and to the LUMO of Fig. 3(b). In this state, the electronic charge is still localized on the N atom although polarized toward the H^+ ion. The figure also shows a dangling bond of the Ga neighboring the H ion that points toward the H itself. A simple picture may explain the characteristics of the bonding and antibonding states related to the $N\text{-}H_{BC}^+$ complex. The H^+ ion takes the place of the Ga atom no longer bonded to the N atom which, however, still keeps its five electrons to form four chemical bonds. Thus, the H^+ insertion in the Ga-N bond does not affect the main characteristic of the original nitrogen LUMO, that is, the strong charge localization on N. This accounts for the closeness of $\epsilon^{0/-}[N]$ and $\epsilon^{+/0}[N\text{-}H_{BC}^+]$ values. On the other hand, in the $N\text{-}H_2^*$ complex, a new occupied level, related to the formation of the Ga-H and N-H bonds, appears close to the top of the valence band. This bonding state leads to a quite different N bonding where the N atom forms a N-H bond *not perturbed* by the dangling bond of the Ga neighbor, now fully saturated by the second H atom. The new bonding state has its antibonding counterpart in the LUMO shown in Fig. 3(c). In the latter state, the charge is still localized on the N atom but polarized towards the H atom that is bonded to the Ga atom. Furthermore, there is some charge localization between the same two (nonbonded) H and N atoms. The strong antibonding character of this charge localization makes this LUMO very different from the previous ones, thus accounting for an $\epsilon^{0/-}[N\text{-}H_2^*]$ higher than $\epsilon^{0/-}[N]$ and $\epsilon^{+/0}[N\text{-}H_{BC}^+]$ and close to the value estimated for the bottom of the GaAs conduction band. The above analysis and transition energies provide therefore a theoretical framework for understanding the observed hydrogen passivation of N in GaAs.
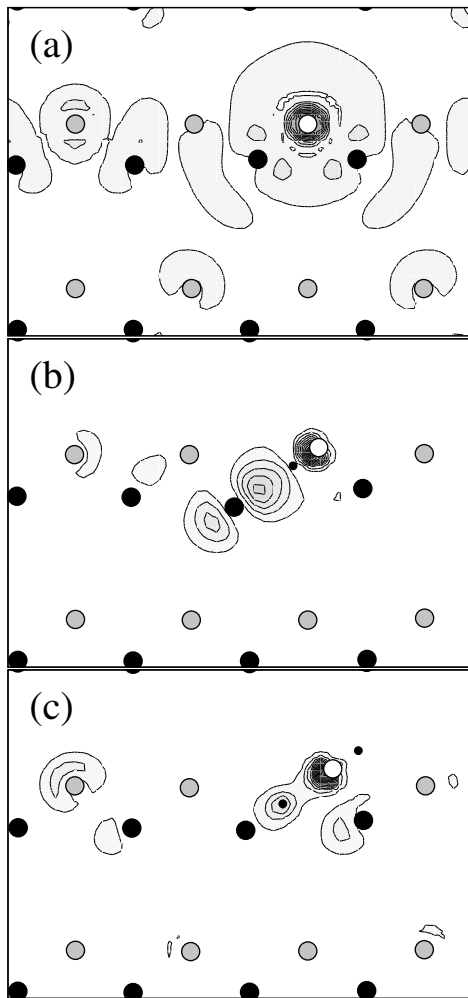
FIG. 3. Contour plots in the (110) plane of the charge density $|\Psi_{n,\mathbf{0}}|^2$ corresponding to the lowest unoccupied molecular orbital (LUMO) of (a) an isolated N atom, (b) the N-H_{BC}^+ complex, and (c) the N-H_2^* complex, in GaAs$_{0.97}$N$_{0.03}$. The Ga, As, and N atoms are indicated by black, grey, and white full dots, respectively. Small dots represent the H atoms.

In conclusion, N-H_{BC}^+ and N-H_2^* complexes are favored by p- and n-type doping, respectively. Notwithstanding, we predict the formation of both complexes in p-type materials because the formation of N-H_{BC}^+ complexes is accompanied by the H passivation of shallow acceptors that raises the Fermi level, thus favoring the formation of

N-H_2^* complexes. As a matter of fact, two additional N and H related LVMs have been recently observed at 2967 and 2015 cm^{-1} in the same samples where the above 3195 cm^{-1} LVM has been measured [12]. Thus, although only N-H_2^* complexes lead to the neutralization of nitrogen effects, N passivation is expected both in n- and p-type GaAsN. For what concerns the interaction of hydrogen with isoelectronic impurities, present results show that hydrogen neutralizes the N effects as it generally does in the case of shallow acceptors and defects. However, the passivation mechanisms are unusual and more complex by involving, e.g., the formation of dihydrogen complexes. Similar conclusions have been achieved in the case of the In$_{0.25}$Ga$_{0.75}$As$_{0.97}$N$_{0.03}$ alloy.

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