

Stability and electronic structure of hydrogen–nitrogen complexes in GaAs

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We investigate the stability and electronic properties of defects formed by a substitutional nitrogen in GaAs (N_{As}) plus interstitial hydrogen atoms using first-principles total-energy calculations. We find the formation of strong N_{As} –H bond when a single H atom is incorporated in the lowest-energy bond centered (BC) position. This defect induces an electrically active level in the GaAs band gap. When two H atoms are incorporated, we find the stable N_{As} – H_2^* complex as the lowest-energy configuration, with one H atom at the BC position and the second H atom at an antibonding position. The electronic structure of this complex shows the passivation of the gap level restoring the GaAs band gap. © 2002 American Institute of Physics. [DOI: 10.1063/1.1521571]

Hydrogen is a common and unavoidable impurity in all semiconductors which can be found at every stage of devices processing, interacting with broken or weak bonds such as those found at point defects.¹ The result of the chemical interaction of H atoms with such defects is to remove (passivation) or to introduce (activation) energy levels in the band gap, as commonly observed in intrinsic semiconductors. However, the current understanding of the hydrogen interaction with more localized defects and its influence in the band gap of the material is quite poor.

Recently, the effect of atomic hydrogen on the electronic properties of (InGa)(AsN)/GaAs quantum wells has been investigated by photoluminescence spectroscopy.² This work shows an increase in the band gap with the hydrogen incorporation until the band gap is restored to the value of N-free well. This effect is ascribed to the formation of N–H bonds which leads to an electronic passivation of the original N level.³ They also suggest that the N associated wave function maintain a strongly localized impurity-like character for N concentrations as high as $\sim 5\%$.

In a previous work we have investigated the structural and electronic properties of nitrogen occupying an arsenic site in GaAs (GaAs:N).⁴ In this supercell approach the defect system is equivalent to an ordered GaAsN alloy with a N concentration of about 3%. Our main result is the finding of an empty midgap level with a strong localization at the N atom suggesting an impurity-like level. However, the large dispersion observed for this level (~ 0.3 eV), originated due to the proximity of the N atoms of neighboring cells, might be associated to the formation of an impurity band instead of a single bound state which would be responsible for the GaAs band gap reduction. This impurity band has been experimentally observed in heavily doped GaAs:N.^{5–7}

In the present work we study the changes in the structural and electronic properties of the GaAs:N impurity system when hydrogen atoms are added. We investigate the interaction of one and two H atoms with substitutional nitrogen (N_{As}) and its influence in the GaAs band gap. Our results show the formation of a strong N–H bond when one and two H atoms are incorporated. However, the formation of only

single N–H bonds is not enough to clear the band gap, contrary to the initial hypothesis.³ The band gap clearing is only observed for the structure with two H atoms interacting with the N impurity.

Our theoretical approach is performed in the framework of the density functional theory⁸ within the local density approximation (LDA)⁹ and norm-conserving *ab initio* pseudopotentials.¹⁰ Effects due to the Ga 3*d* electrons were included using the nonlinear core correction.¹¹ The Kohn–Sham wave functions are expanded using a plane-wave basis set with an energy cutoff of 45 Ry.¹² We use a fully relaxed 32-atom supercell and two special **k** points for the Brillouin zone sampling.¹³ The final equilibrium structures were completely recalculated using a denser sampling of eight **k** points. The positions of all the atoms in the supercell, plus the interstitials, were relaxed until all the force components were smaller than 0.05 eV/Å.

To find the equilibrium geometry of defects involving hydrogen and substitutional nitrogen in GaAs, we put initially a single H atom in different sites close to N_{As} , before the system is allowed to relax. These sites include the high-symmetry bond centered (BC), in the middle of a Ga–N bond; antibonding (AB_N , AB_{Ga}), opposite to the BC site with respect to the N and Ga atoms, respectively; tetrahedral (*T*) and hexagonal (*H*), interstitial sites of the zinc-blende structures. Other low-symmetry sites were also considered. For the systems containing two H atoms we follow the same procedure considering different sites for a pair of H atoms, in general coupling BC and AB sites. A more detailed description of the initial geometries for the H atoms can be found in Ref. 14.

Figure 1 shows the two lowest-energy equilibrium geometries for the complex involving N_{As} plus one and two interstitial hydrogens. We find that the lowest-energy structures for a single H atom are those where the hydrogen binds with nitrogen in the BC and AB_N configurations, as shown in Figs. 1(a) and 1(b), respectively. Here the BC structure is the most stable one whereas the AB_N structure is 1.17 eV higher in energy. In the BC structure, the N–H bond distance is found to be 1.04 Å, very close to the theoretical value of the N–H bond in the NH_3 molecule (1.03 Å). The distance between the H atom and the neighboring Ga atom is 2.03 Å.

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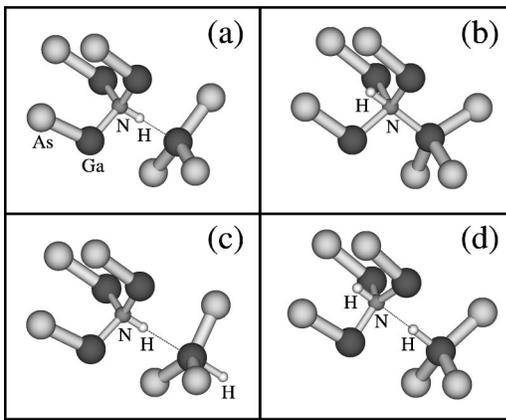


FIG. 1. Equilibrium geometries of complexes involving substitutional nitrogen and interstitial hydrogens in GaAs. (a) and (b) are the two lowest-energy $N_{As}-H$ structures with the H atom in the BC and AB_N configurations, respectively. (c) and (d) are the two lowest-energy $N_{As}-H_2^*$ structures in the BC- AB_{Ga} and BC- AB_N configurations, respectively.

The equilibrium geometries as obtained for T and H sites show the hydrogen in interstitial positions. At these positions the H atom does not interact either with the lattice or with the N_{As} impurity. The H atom at the noninteracting T position is 1.28 eV higher in energy than the BC structure. In fact, this energy is closely related to the binding energy for the H atom in the most stable BC position.

Figures 1(c) and 1(d) show the two lowest-energy equilibrium geometries for two H atoms interacting with the N_{As} defect. This particular hydrogen configuration is known as H_2^* . The lowest-energy equilibrium geometry for the $N_{As}-H_2^*$ complex is the BC- AB_{Ga} structure shown in Fig. 1(c). In Fig. 1(d) is shown the second lowest-energy structure, BC- AB_N , which is 1.09 eV higher in energy than the most stable one. For the BC- AB_{Ga} structure [Fig. 1(c)] the N-H and Ga-H bond distances are 1.02 and 1.59 Å, respectively. The distance between the bond centered H atom and the Ga atom is 1.59 Å, approximately 20% longer than the same distance in the BC structure [Fig. 1(a)].

To determine the stability of the $N_{As}-H_2^*$ complex with respect to the formation of H_2 molecules, we calculate an interstitial H_2 molecule in GaAs:N at the T and H sites. Our results show that the lowest-energy equilibrium position for H_2 is the T sites which is 1.01 eV higher in energy than the most stable $N_{As}-H_2^*$ complex. We also calculate the stability of the $N_{As}-H_2^*$ with respect to the formation of two $N_{As}-H$ defects using the equation: $\Delta E = E_t(N_{As}-H_2^*) + E_t(N_{As}) - 2E_t(N_{As}-H)$. Again we find that $N_{As}-H_2^*$ is the most stable structure by about 1.25 eV. Recently, it has been reported that the $As_{Ga}-H_2^*$ complex in GaAs is stable with respect to the formation of H_2 molecules¹⁵ whereas in perfect GaAs, H_2^* would be unstable.¹⁶ A very recent work has also shown the stability of $N_p-H_2^*$ complex in GaP.¹⁷ These results strongly suggest a general trend for the H_2^* stabilization by the formation of complex with point defects in III-V compounds.

We now examine the electronic structure of the lowest-energy $N_{As}-H$ and $N_{As}-H_2^*$ complexes in GaAs. Figure 2 shows the schematic representation of the single-particle energy levels inside the theoretical GaAs band gap (1.17 eV). In Fig. 2 the dashed line indicates our theoretical results for

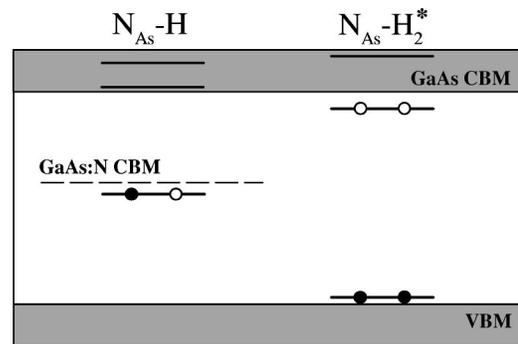


FIG. 2. Schematic representation of the single-particle energy levels in the GaAs band gap as induced by $N_{As}-H$ in the BC configuration and by $N_{As}-H_2^*$ in the BC- AB_{Ga} configuration. The dashed line indicates the bottom of the conduction band of GaAs:N. Filled dots indicate electrons and opened dots indicate holes.

the conduction band minimum (CBM) of heavily doped GaAs:N. According to our (LDA) calculations, the interaction of a single H atom with the N_{As} defect in the BC configuration induces an electrically active a_1 level at 0.61 eV above the valence band maximum (VBM). This a_1 level corresponds to the bottom of the conduction band of GaAs:N which is shifted downward when occupied by the electron of the incoming H atom. The addition of a second H atom forms the $N_{As}-H_2^*$ complex passivating the a_1 level which is lowered close to the top of the valence band. Additionally, we observe an a_1 empty level higher in energy than the bottom of the conduction band of GaAs:N (see Fig. 2). Therefore, the $N_{As}-H_2^*$ defect induces two a_1 levels, a fully occupied and an empty level at 0.04 and 1.08 eV above the VBM, respectively, tending to restore the GaAs band gap.

In order to understand the origin of the a_1 gap levels of $N_{As}-H$ and $N_{As}-H_2^*$, we plot the electronic charge density (or squared wave function) for these energy levels through the (100) plane of the lattice as shown in Fig. 3. The total charge density of the BC configuration [Fig. 3(a)], shows that hydrogen forms a strong bond with nitrogen favored by the high electronegativity of nitrogen. This structure re-

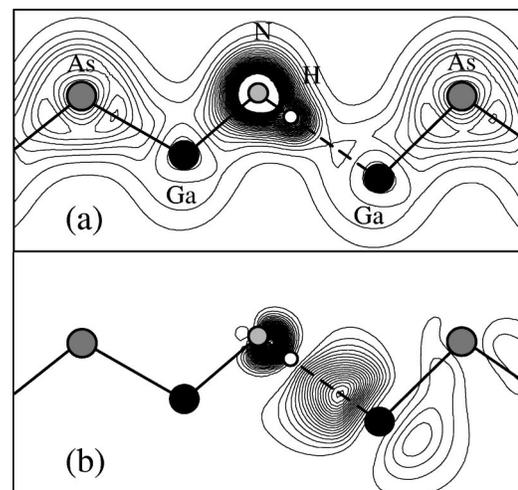


FIG. 3. Wave function squared plots through the (110) plane for the $N_{As}-H$ complex in GaAs with the H atom in the lowest-energy BC configuration. (a) For all the occupied single-particle energy levels. (b) For the half-occupied gap level.

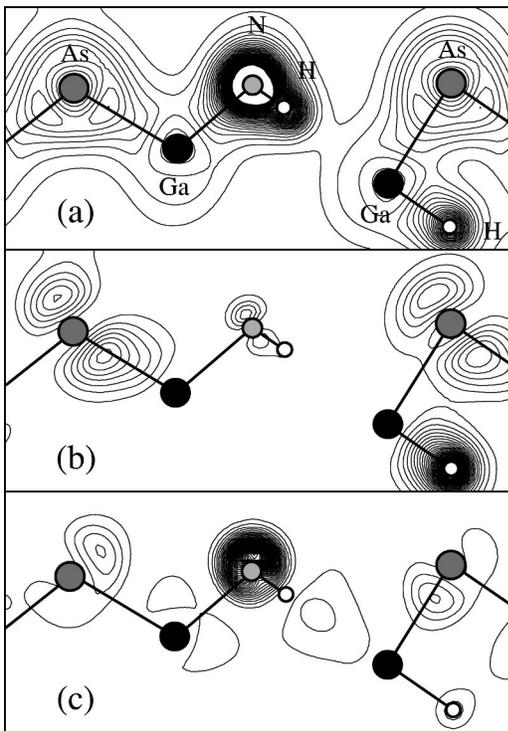


FIG. 4. Wave function squared plots through the (110) plane for the $N_{As}-H_2^*$ complex in GaAs with the H atoms in the lowest-energy BC- AB_{Ga} configuration. (a) For all occupied single-particle energy levels. (b) for the occupied level in the band gap. (c) For the empty level in the band gap.

sembles a NH molecule occupying an As site in GaAs. In fact, the N-H bond length has quite the value found in ammonia. According to Fig. 3, the formation of the N-H bond saturates the nitrogen orbital resulting in a very weak H-Ga bond. The charge density plot of the half-occupied gap level [Fig. 3(b)], shows a strong charge localization at the N-H bond suggesting a nitrogen-like character. This level would be the GaAs:N CBM as perturbed by the H atom. We also observe a charge density in the neighborhood of the Ga atom which can be associated to a dangling bond of the Ga atom emerging when the H atom binds with the N atom.

Figure 4 shows the electronic charge density plots for $N_{As}-H_2^*$ complex in the BC- AB_{Ga} configuration. The total charge density [Fig. 4(a)] shows that one H atom forms a strong N-H bond preserving the molecular character observed in the $N_{As}-H$ defect. The second H atom binds with the Ga atom saturating its dangling bond. The charge density

of the fully-occupied gap level [Fig. 4(b)] shows a delocalized band-like character as perturbed by the second H atom. For the empty level in the gap [Fig. 4(c)], we observe a quite delocalized level with a nitrogen-like character similar to those found for the CBM of GaAs:N.

According to our results the formation of a strong N-H bond induced by the high electronegativity of the N atom would be responsible for the electrically active gap level. The H atom essentially saturates a bond with nitrogen in the BC configuration breaking the initial N-Ga bond. Therefore, the unpaired electron would have originated in the Ga-atom dangling bond. When a second H atom is incorporated, it binds with the Ga atom passivating the gap level and increasing the GaAs:N band gap. These results would explain recent photoluminescence measures which report the restoring of the (InGa)As band gap induced by H atoms in the InGaAsN quantum well.² The same behavior would be expected to occur in hydrogenated GaAsN alloys.

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