

H-Induced Dangling Bonds in H-Isoelectronic-Impurity Complexes Formed in GaAs_{1-y}N_y Alloys

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Complexes formed by H and the isoelectronic impurity N in GaAs_{1-y}N_y alloys have been widely investigated because of the significant effects of N on the GaAs properties and their passivation by H represent a unique tool for a defect engineering of semiconductors. However, available results still present a quite puzzling picture. Both the N-H₂^{*} and C_{2v} complexes proposed by theory were challenged indeed by experimental results. In the present Letter, we disclose a *double-faced* behavior of a H atom interacting with an *isoelectronic impurity*: while H, on one side, binds to N and induces the formation of dangling bonds (DB) on its Ga neighbors, on the other side, it saturates these DBs, thus permitting the formation of multiple-H complexes. This peculiar H behavior fully explains the experimental findings and likely represents a general feature of H–isoelectronic-impurity interactions.

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In GaAs_{1-y}N_y alloys, the N isoelectronic impurity (N substituting an As atom, N_{As}) induces an impressive reduction of the GaAs energy gap as well as an appreciable contraction of the GaAs lattice constant [1–5]. The introduction of H recovers the GaAs band gap and induces an overshooting of the lattice constant (i.e., it becomes larger than that of GaAs) [4], thus making H a unique tool for a defect engineering of heterostructures based on N-containing III-V alloys [6]. Many experimental and theoretical studies have investigated the structure and the properties of N-H complexes in order to account for the above H effects [1–4,7]. Theory proposed an N-H₂^{*} complex, where two H atoms are bonded to N and to a neighboring Ga atom, respectively [8–14]. However, this complex was challenged by IR (infrared) measurements supporting a dihydrogen complex with both the H atoms bonded to a single N atom [15]. The C_{2v} complex shown in Fig. 1(a) (i.e., an NH₂ complex with a local C_{2v} symmetry), also proposed by theory [12,16], accounts for the IR results [17,18], for x-ray absorption spectroscopy (XAS) results [16], as well as for the recovery of the GaAs energy gap [12]. This complex (in the canted or asymmetric form shown in Fig. 1(a) [16–18]) was believed to account for all of the H effects. At this point, a recent high resolution x-ray diffraction and photoluminescence spectroscopy study has questioned again previous results by showing that the lattice overshooting observed in the hydrogenated GaAsN is related to a combined effect of N and H, but cannot be attributed to the C_{2v} complex [19]. In fact, measurements during annealing at 250 °C of hydrogenated GaAsN samples show that the lattice overshooting can be gradually reduced until recovering the GaAs lattice constant. At the same time, the C_{2v} complex is not removed because (i) the annealed samples show a full N passivation, and (ii) the C_{2v} vibrational lines disappear at quite higher annealing temperatures (about 500 °C) [15]. Moreover, IR measure-

ments give evidences only of C_{2v} complexes [15]. Thus, all together, the above experimental results draw a puzzling picture about the N-H complexes forming in GaAsN and question once more the theoretical models.

In this Letter, we disclose a peculiar feature of the hydrogen interaction with an isoelectronic impurity, like N_{As}, which can induce the formation of multiple-H complexes and fully explain the structural and electronic effects of H in GaAsN. Such a peculiarity can be exemplified by comparing the isoelectronic N_{As} with the C_{As} shallow acceptor in GaAs. The C_{As} passivation by H can be explained by a simple model where a C_{As} dangling bond (DB) pointing toward a Ga neighbor is saturated by a H atom [20]. This leads to the structure of the C_{As}-H_{BC} ··· Ga(1) complex shown in Fig. 1(b), where a strong C-H bond is formed by a H located close to a bond center (BC) site and the C and Ga(1) chemical valences (four and three, respectively) are fully satisfied. On the contrary, in the present model, we propose that a H interacting with an isoelectronic impurity, like N_{As}, has no saturating effects. H breaks instead a Ga-N bond and forms a strong H-N bond comparable to the H-C bond, but it also induces a DB on the Ga atom involved in the broken bond. This effect is sketched in Fig. 1(a), where two DBs are induced on the Ga atoms of the two broken Ga-N bonds in the C_{2v} complex. This H behavior has relevant consequences, because the H-induced DBs can be saturated by further H atoms, thus leading to multiple-H complexes. A clue on the existence of two unsaturated Ga DBs in the C_{2v} complex is given by the different geometry estimated for the C_{2v}⁰ and C_{2v}⁺² complexes. In the former case, the Ga(1)-Ga(2) distance in Fig. 1(a), 3.24 Å, is significantly shorter than the other Ga-Ga distances, thus indicating that the Ga(1) and Ga(2) atoms form a weak bond. On the contrary, in the C_{2v}⁺² complex (not shown in the figure), the same Ga(1)-Ga(2) distance is much longer, 4.02 Å, since the Ga atoms carrying the

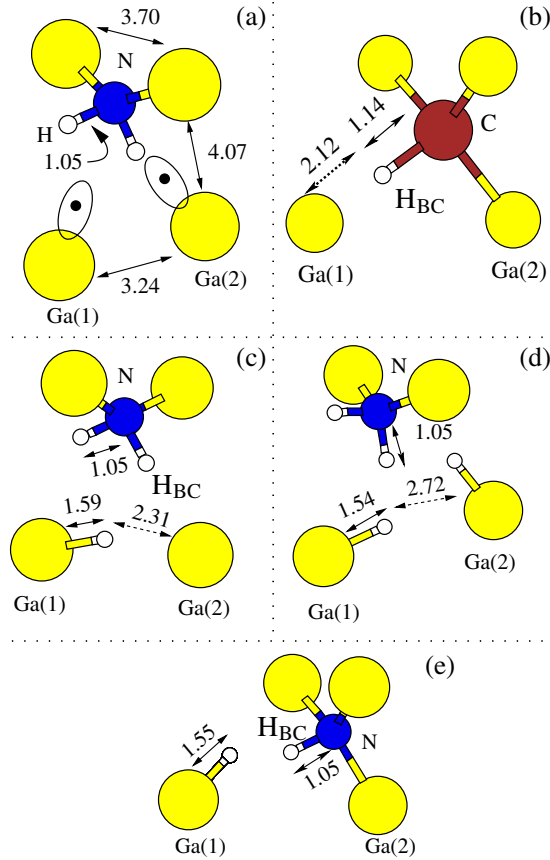


FIG. 1 (color online). Atomic configurations of some N-H and C-H complexes. (a) asymmetric C_{2v} with sketched dangling bonds on Ga(1) and Ga(2), (b) C_{As} - H_{BC} -Ga(1), (c) C_{2v} - H_{Ga} , (d) C_{2v} - $2H_{Ga}$, and (e) $[N-H_{BC}]-H_{Ga}$. BC indicates a bond centered site of H. Atomic distances are given in Å.

DBs have lost their unpaired electron and cannot form any Ga-Ga bond [17].

Total energies have been calculated by using density functional theory methods in a supercell approach, ultra-soft pseudopotentials [21], plane wave basis sets, and the PBE [22] gradient-corrected exchange-correlation functional [23]. Geometry optimizations have been performed by fully relaxing all of the atoms of a supercell. The formation energy per H atom of a N- n H complex involving n H atoms and a q charge is $\Omega_f[N-nH]^q = \frac{1}{n}(E[N-nH]^q - E[N] - n\mu_H + qE_F)$ where $E[N-nH]^q$ is the total energy of a GaAs supercell containing 1 N atom and n H atoms, μ_H is the H chemical potential, and E_F is the Fermi energy [12,24]. Transition energy levels $\epsilon^{n/n+1}$ have been estimated by the E_F position where the formation energies of the n and $n+1$ charge states of the complex are equal [12,24]. The effects of H on the GaAs lattice constant have been calculated by considering the growth of GaAsN on bulk GaAs. Thus, we fixed the planar lattice parameters to that of GaAs but allowed the third one along [001] to relax. Vibrational frequencies have been calculated in the harmonic approximation. Anharmonic corrections have been

estimated similarly to Ref. [25]. IR intensities have been estimated by calculating Born effective charge tensors [26]. Satisfactorily converged results have been achieved by using 64-atom supercells, the (4, 4, 4) \mathbf{k} -point Monkhorst-Pack mesh, and cutoffs of 22 and 30 Ry, which lead to an error bar less than 0.1 eV for the $\epsilon^{+1/0}$ values.

N-H complexes having three or more H atoms bonded to an N atom are metastable or unstable. On the contrary, stable complexes with three or four H atoms form when H saturates H-induced DBs; see Fig. 1. The complexes in Figs. 1(c) and 1(d) originate from the complex in Fig. 1(a) when H atoms saturate the Ga(1) DB and both the Ga(1) and Ga(2) DBs, respectively. They will be referred to as C_{2v} - H_{Ga} and C_{2v} - $2H_{Ga}$, respectively. The complex of Fig. 1(e), $[N-H_{BC}]-H_{Ga}$, forms when a H atom saturates the DB of a Ga atom in an N- H_{BC} complex. The formation and stability of the N-H complexes in Fig. 1 have been investigated by considering their formation energies (Ω_f in Table I) and $\epsilon^{+1/0}$ values (see Table III), as well as the energies released in their formation and required for their dissociation (see Table II). The above quantities have to be discussed by taking into account (i) the presence of $\approx 10^{16}$ cm $^{-3}$ acceptors (A) against a 3% ($\approx 10^{21}$ cm $^{-3}$) of N atoms in the slightly p -doped samples used in the experiments [27], and (ii) the negative- U character of H; i.e., H^+ (H^-) ions form in presence of acceptors (donors), H^+ - H^- pairs (and H_2 molecules) form in intrinsic GaAsN [12,13,28]. In detail, at the beginning of hydrogenation, a Fermi energy $E_F < E_g/2$ favors the acceptor compensation by H and the formation of H^+ ions far from the negative acceptors A^- . This implies that E_F is raised to $E_g/2$. However, the diffusing H^+ ions do not reach the A^- acceptors because they are trapped by the predominant N atoms and form stable complexes, e.g., N- H_{BC}^+ ($\Delta E = 1.05$ eV; see Table II). $\epsilon^{+1/0}$ values lower than $E_g/2$ (present estimate, 0.78 eV) and Ω_f values indicate that N- H_{BC} complexes forming in a positive charge state become neutral when $E_F = E_g/2$; see Tables I and III. Even neutral N- H_{BC} complexes are quite stable ($\Delta E = -1.58$ eV; see Table II). Then, the change of charge state of these complexes implies that further H^+ ions form to compensate the acceptors, by satisfying the charge neutrality condition, and react, e.g., with N- H_{BC}^0 complexes to form C_{2v}^{+1} com-

TABLE I. Complex formation energies per H atom, Ω_f , estimated at the values of the Fermi energy, E_F , 0 (i.e., the top of the valence band), $E_g/2$, and E_g (1.56 eV). Ω_f of neutral complexes are given in the last row.

E_F	Complexes			
	N- H_{BC}^+	C_{2v}^{+1}	C_{2v} - H_{Ga}^+	C_{2v} - $2H_{Ga}^+$
0	-0.40	0.01	-0.13	0.12
$E_g/2$	0.38	0.40	0.13	0.31
E_g	1.16	0.80	0.39	0.51
	0.27	0.31	0.12	0.04

TABLE II. For a complex formation, e.g., $N + H_{BC}^+ \rightarrow N-H_{BC}^+$, the corresponding energy difference $\Delta E = E[N] + E[H_{BC}^+] - E[N-H_{BC}^+]$ is given in the upper part of the Table. For a complex dissociation, e.g., $N-H_{BC} \rightarrow N + H_{AB}$, the corresponding $\Delta E = E[N-H_{BC}] - E[N] - E[H_{AB}]$ is given in the lower part. Positive (negative) values indicate exothermic (endothermic) reactions.

Complex	Reacting species (products)	ΔE (eV)
$N-H_{BC}^+$	$N + H_{BC}^+$	1.05
C_{2v}^{+1}	$N-H_{BC} + H_{BC}^+$	0.90
$[N-H_{BC}]-H_{Ga}^+$	$N-H_{BC} + H_{BC}^+$	0.60
$C_{2v}-H_{Ga}^+$	$C_{2v} + H_{BC}^+$	1.55
$C_{2v}-H_{Ga}^+$	$[N-H_{BC}]-H_{Ga} + H_{BC}^+$	1.00
$C_{2v}-2H_{Ga}^+$	$C_{2v}-H_{Ga} + H_{BC}^+$	0.61
$[N-H_{BC}]$	$N + H_{AB}$	-1.58
$[N-H_{BC}]-H_{Ga}$	$N-H_{BC} + H_{AB}$	-1.61
C_{2v}	$N-H_{BC} + H_{AB}$	-1.61
$C_{2v}-H_{Ga}$	$C_{2v} + H_{AB}$	-1.13
$C_{2v}-2H_{Ga}$	$C_{2v}-H_{Ga} + H_{AB}$	-1.50
$C_{2v}-2H_{Ga}$	$C_{2v} + H_2$	-1.35

plexes; see Table II. The same holds for all of the investigated N-H complexes; e.g., C_{2v} complexes initially formed in the charge state +1 become neutral before reacting with a further H^+ ion. Such a continuous H^+ formation terminates when the N traps are saturated by H atoms forming complexes with the highest number of H atoms. At this point, further H^+ ions can reach the acceptors and passivate them by forming H-A complexes. GaAsN samples become, therefore, intrinsic semiconductors and further H atoms form H^+H^- pairs and then hydrogen molecules. In agreement with the above mechanism, the ΔE values in the upper part of Table II involve a H^+ ion located at its stable BC site in GaAs [28], H_{BC}^+ , as a reacting species. On the other hand, neutral N-H complexes are involved in the dissociation processes. Reaction products include, therefore, neutral H atoms in their stable antibonding (AB) site in GaAs (H_{AB}) [28]; see Table II.

The ΔE values estimated for the complex formation suggest that diffusing H^+ ions successively form the complexes (see Table II) $N-H_{BC}^+$, C_{2v}^{+1} , $[N-H_{BC}]-H_{Ga}^+$, $C_{2v}-H_{Ga}^+$, and $C_{2v}-2H_{Ga}^+$. These results support the model proposed here for H interacting with N_{As} and suggest that the $C_{2v}-2H_{Ga}$ complex coming from the full saturation of the H-induced DBs in the C_{2v} complex is the predominant neutral complex at the end of the hydrogenation procedure [29].

Regarding the complex dissociation, the negative ΔE values in Table II show that (i) complexes involving three or four H atoms are quite stable, but they have smaller dissociation energies (in absolute value); that is, they should be the first to be removed upon annealing.

(ii) $C_{2v}-H_{Ga}$ complexes dissociate by forming C_{2v} complexes. (iii) $C_{2v}-2H_{Ga}$ complexes dissociate preferably by forming C_{2v} complexes plus H_2 molecules instead of $C_{2v}-H_{Ga}$ complexes. Concerning the passivation and structural effects as well as the vibrational properties, the $[N-H_{BC}]-H_{Ga}$, C_{2v} and $C_{2v}-2H_{Ga}$ complexes induce the N passivation, as shown by the $\epsilon^{0/-1}$ values in Table III, to be compared with the values of 0.84 and 1.56 eV estimated here for the GaAs_{0.97}N_{0.03} and GaAs energy gaps, respectively. A passivation effect of the $C_{2v}-H_{Ga}$ is uncertain, while the $[N-H_{BC}]$ complexes have no passivating effects. Thus, passivation is induced by complexes where the H-induced DBs form a weak Ga-Ga bond (see Fig. 1(a)) or are neutralized by H atoms (see Figs. 1(d) and 1(e)). Table III also reports the $\Delta a/a$ values calculated for the investigated N-H complexes, where a is the lattice constant calculated for bulk GaAs and Δa is the difference ($a^{\perp} - a$), a^{\perp} being the lattice constant along [001]. A $\Delta a/a$ value of 0.48% is the lattice overshooting measured in hydrogenated GaAs_{1-y}N_y samples with $y = 3.20\%$, close to the value $y = 3.12\%$ characterizing our GaAsN supercells [5,19]. The values in Table III show that while the C_{2v} complex fully recovers the GaAs lattice constant, only the $C_{2v}-H_{Ga}$ and $C_{2v}-2H_{Ga}$ complexes induce an appreciable lattice overshooting, comparable to the experiment. A value of -1.08% estimated for the lattice contraction induced by N in GaAs_{0.97}N_{0.03} is also in very good agreement with an experimental value of -1.18% [5,19]. H_2 molecules do not induce any overshooting. Finally, the two stretching and the scissoring N-H frequencies calculated for the three C_{2v} -derived complexes are all in quite good agreement with the experimental IR lines; see Table III. The small differences between the three vibrational frequencies of these three complexes suggest that the C_{2v} -derived complexes, when alternatively present in hydrogenated GaAsN samples, give hardly distinguishable IR signals. In the case of the $C_{2v}-H_{Ga}$ and $C_{2v}-2H_{Ga}$ complexes, further frequencies have been estimated here for

TABLE III. Transition energy $\epsilon^{n/n+1}$ values (in eV), frequency values (in cm^{-1}), and $\Delta a/a$ values (%) estimated for the investigated N-H complexes. Stretching and scissoring frequencies of the H modes are indicated by ν and δ , respectively. H-1 and H-2 indicate H atoms bonded to N. neg indicates a negative value.

Complex	$\epsilon^{+1/0}$	$\epsilon^{0/-1}$	ν		δ	$\Delta a/a$
			H-1	H-2		
C_{2v}	0.60	1.50	3143	2846	1444	0.00
$C_{2v}-H_{Ga}$	0.75	1.21	3189	2805	1435	0.42
$C_{2v}-2H_{Ga}$	neg	1.69	3167	2884	1439	0.39
$[N-H_{BC}]-H_{Ga}$	neg	1.47	...	2853	...	-0.02
$N-H_{BC}^0$	0.67	0.95	...	2805	...	-0.33
$N-H_{BC}^+$			3213	-1.17
Exp. ^a			3195	2967	1447	0.48

^aExperimental results from Ref. [15].

the stretching modes of the Ga-H_{Ga} bonds, 1487 cm⁻¹ in the former complex, 1856 cm⁻¹ and 2070 cm⁻¹ in the latter one. These vibrational frequencies are not observed. However, the calculated IR intensities of these Ga-H modes are more than 1 order of magnitude smaller than those of the N-H modes, thus supporting a difficult discrimination of the C_{2v}-like complexes on the ground of IR measurements. The results of the above vibrational analysis are not affected by the anharmonicity of the H motion, as shown by estimated anharmonic corrections generally less than 100 cm⁻¹ [29].

The above results indicate a key role of the C_{2v}-2H_{Ga} and C_{2v} complexes. The former complex predominates in hydrogenated *p*-type GaAsN, neutralizes the N electronic effects, and causes a lattice overshooting. A mild annealing induces the dissociation of this complex which forms C_{2v} complexes and H₂ molecules. The C_{2v} complexes recover the GaAs lattice constant and passivate the electronic N effects as well. Annealings at higher temperatures remove the C_{2v} complexes and restore the N effects on the GaAs lattice constant and band structure. Such a picture fully accounts for the passivating effects, the vibrational properties, the evolution of the electronic and structural properties with the temperature observed in hydrogenated GaAsN, and agrees with preliminary XAS results supporting the formation of C_{2v}-2H_{Ga} complexes [30]. Moreover, a difference of 0.22 eV between the dissociation energies of the C_{2v}-2H_{Ga} and C_{2v} complexes (which can be viewed as a lower bound of the activation energy for the complex dissociation) favorably compares with the difference of 0.2–0.3 eV estimated between the corresponding, experimental activation energies [19].

In conclusion, present results disclose a double-faced behavior of H which, on one side, binds to N and induces the formation of Ga DBs, while on the other side, saturates them. Such a behavior increases the number and type of complexes that H may form with an isoelectronic impurity with respect to a shallow dopant and has to be taken into account in order to explain all of the structural and electronic effects induced by hydrogenation. The above model is very simple. It is expected therefore to hold in general for H interacting with isoelectronic impurities in different semiconductors like, e.g., O substituting the anions in II-VI semiconductors. Finally, we see present results as a true stimulation for further experimental investigations by using, e.g., muon spin resonance spectroscopy [31].

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