

# Hydrogen pairs and local vibrational frequencies in H-irradiated GaAs<sub>1-y</sub>N<sub>y</sub>

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(Received 31 May 2005; published 4 August 2005)

First-principles total energy calculations show that proton relaxation in H-irradiated GaAs<sub>1-y</sub>N<sub>y</sub> follows an energy pathway to form a charged dihydride, instead of the charge-neutral H<sub>2</sub><sup>\*</sup> monohydride. Charge neutralization will take place later, as the sample is grounded, which will lead to the spontaneous canting of the dihydrides. This canted N-2H model explains the recent puzzling IR observation, the recoveries of the GaAs band gap and lattice parameter, and the dihydride symmetry determined by the x-ray absorption near-edge structure experiment. It may also have broad implications for ion implantation studies in other solids.

DOI: [10.1103/PhysRevB.72.073202](https://doi.org/10.1103/PhysRevB.72.073202)

PACS number(s): 61.72.Vv, 61.72.Bb, 61.72.Ji, 63.20.Pw

Large size-mismatched dilute alloys such as GaAs<sub>1-y</sub>N<sub>y</sub> (Ref. 1) and ZnSeO (Refs. 2 and 3) are promising alloy semiconductors with unique physical properties. For example, with only an atomic percent of N incorporated into GaAs, the band gap decreases by several hundred meV.<sup>4</sup> On the other hand, H irradiation causes a nearly full recovery of the GaAs band gap<sup>5</sup> and lattice parameter<sup>6</sup> from those of GaAs<sub>1-y</sub>N<sub>y</sub>. These intriguing observations have been explained by the  $\alpha$ -H<sub>2</sub><sup>\*</sup>(N) model with characteristic Ga—N and N—H monohydride bonds [Fig. 1(a)].<sup>6,7</sup> However, a recent infrared experiment<sup>8</sup> on H-irradiated samples did not observe any Ga—H modes. Instead, two H stretch modes were observed at 3195 and 2967 cm<sup>-1</sup>, as shown in Table I. The typical Ga—H and As—H stretch modes are near 1800 cm<sup>-1</sup> (Ref. 9) and 2100 cm<sup>-1</sup>.<sup>10</sup> Hence, both modes here belong to the N—H bonds. In D-irradiated samples, the two stretch modes shift to 2216 and 2376 cm<sup>-1</sup>, respectively. In H/D co-irradiated samples, however, two *additional* D-stretch modes, at 2221 and 2366 cm<sup>-1</sup> [see Fig. 2(a)], and one *additional* H-stretch mode, were observed. A second H mode is also expected, but was not observed, which possibly was due to contamination. The observation of the two (instead of one) additional D modes indicates that the H complexes must contain two inequivalent H atoms strongly coupled to each other.

The absence of the Ga—H mode in the IR spectra is a troubling experimental fact for  $\alpha$ -H<sub>2</sub><sup>\*</sup>, despite the fact that the model has the lowest formation energy among all charge-neutral 2H complexes.<sup>7,11</sup> A recent x-ray absorption near-edge structure (XANES) study<sup>12</sup> further reveals that the symmetry of the 2H complexes should be C<sub>2v</sub>-like, thus further undermining the validity of the C<sub>3v</sub>-based H<sub>2</sub><sup>\*</sup> model. Alternatively, an N-2H<sub>BC</sub><sup>2+</sup> complex, first studied by Bonapasta *et al.*,<sup>13</sup> in which both H atoms are on the bond center (BC) site to N [see Fig. 1(b)], is consistent with the XANES result. It also has lower energy than  $\alpha$ -H<sub>2</sub><sup>\*</sup> in p-type GaAsN. However, with a few atomic percent of N-2H<sub>BC</sub><sup>2+</sup>, the sample cannot be p-type. Once it becomes charge neutral, the N-2H<sub>BC</sub> complex is also clearly less stable than the H<sub>2</sub><sup>\*</sup>.<sup>13</sup> In addition, the two BC sites in N-2H<sub>BC</sub><sup>2+</sup> are equivalent [see Fig. 1(b)]. Hence, this model produces only one additional D mode, whereas the IR measurement showed clearly two ad-

ditional D modes. Finally, it has been suggested that N-2H<sub>BC</sub><sup>2+</sup> should lead to no recovery of the GaAs lattice parameter from that of GaAs<sub>1-y</sub>N<sub>y</sub>, in contradiction to the x-ray measurement.<sup>6</sup> The inconsistency between the existing models and the experiments demands a better understanding of the ion implantation experiments in general.

In this paper, we develop such a theory by first-principles total energy calculations of the thermal relaxation process of protons, introduced by H irradiation. It was found that most of the protons could only relax to the doubly charged N-2H<sub>BC</sub><sup>2+</sup>, rather than the neutral H<sub>2</sub><sup>\*</sup>. Once trapped in N-2H<sub>BC</sub><sup>2+</sup>, however, the H atoms may not easily escape to form H<sub>2</sub><sup>\*</sup>, even after charge neutralization, due to a large kinetic barrier. Instead, neutralization leads to spontaneous structural transformation of the N-2H<sub>BC</sub><sup>2+</sup> to a canted N-2H. The breaking of the two strained Ga—N bonds and the formation of a weak Ga—Ga bond in the neutral N-2H complex results in the recovery of the GaAs band gap. In addition, the canting of the N-2H dihydride explains the observed two additional D modes in the IR experiment, both in frequency and relative amplitude. Being a dihydride, the model agrees with the XANES result, and also predicts a lattice parameter recovery better than that of the H<sub>2</sub><sup>\*</sup>. The good agreement between theory and experiments establishes a new direction to examine ion implantations in semiconductors and solids in general.

Our calculations are based on the density functional theory within the local density approximation (LDA). The electron-ion interactions are described by the ultrasoft pseudopotentials,<sup>14</sup> as implemented in the VASP codes.<sup>15</sup> The valence wave functions are expanded in a plane-wave basis with a cutoff energy of 348 eV. All calculations were per-

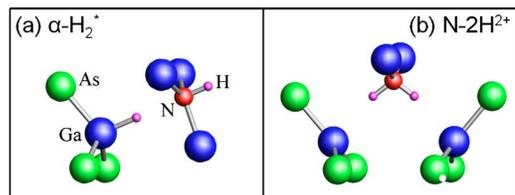


FIG. 1. (Color online) Ball-stick models for (a)  $\alpha$ -H<sub>2</sub><sup>\*</sup> and (b) N-2H<sup>2+</sup>.

TABLE I. Stretch and wag mode frequencies in units of  $\text{cm}^{-1}$ . N/A stands for not available.

	Experiment		$\alpha\text{-H}_2^*$		N-2H $^{2+}$		Canted N-2H				
	Stretch	Wag	Stretch	Wag	Stretch	Wag	Stretch	Wag			
H modes (H-flux)	3195	2967	1447	3140	944	3305	3209	1328	3207	3052	1417
D modes (D-flux)	2376	2216	1076	2290	687	2431	2318	974	2346	2215	1037
Additional modes (H/D flux)	3192	N/A	N/A	None		3260	1164	3204	3056	1257	
	2366	2221	N/A			2372	1164	2336	2224	1238	

formed using a 64-atom supercell. The vibrational frequencies were calculated based on the dynamical matrix approach.<sup>16</sup> We used the special  $k$ -points scheme for Brillouin zone summation and relaxed all the atoms until the forces were less than  $0.02 \text{ eV}/\text{\AA}$ .

Hydrogen irradiation is an effective means of boosting H concentration in semiconductors. Once protons enter the sample, it is generally assumed that the system maintains equilibrium between the injected protons and an electron reservoir of energy  $E_F$ . This assumption is questionable, however, because H irradiation in large quantity causes the accumulation of positive charges that cannot be easily dissipated. A  $\text{H}^+$  may emit a hole into the valence band maximum (VBM) or grab an electron from the conduction band minimum (CBM), if there is any, to become neutralized. However, none of the above is likely because the (+/0) level for the diffusing H is near the CBM of GaAs, which is well above that of  $\text{GaAs}_{1-y}\text{N}_y$ . It therefore makes sense to study the  $\text{H}^+$  instead of  $\text{H}^0$  traps in H-irradiated  $\text{GaAs}_{1-y}\text{N}_y$ . Charge exchange will take place but only at the trap sites at a later time. This could happen, for example, by emission of holes into the VBM, which are then swept away into the ground by the electrostatic potential gradient between the charged sample and the ground.

The most likely proton traps in  $\text{GaAs}_{1-y}\text{N}_y$  are the N-centered diproton complexes, among which we found that neither the  $\alpha\text{-H}_2^{*2+}$  nor the interstitial  $\text{H}_2^{2+}(\text{Ga})$  (namely, a charged molecule at the tetrahedral interstitial site next to a

Ga) is a good candidate for the proton trap, because a positive charge completely destabilizes the respective atomic structure. Charge-neutral  $\alpha\text{-H}_2^*$  and interstitial  $\text{H}_2(\text{Ga})$  may occasionally form by simultaneously creating *two* holes near the VBM. Even if this happens, however, our calculation shows that the resulting  $\alpha\text{-H}_2^{*0}(\text{N})+2h^+$  and  $\text{H}_{2,\text{int}}^0(\text{Ga})+2h^++\text{N}_{\text{As}}$  are significantly less stable than the  $\text{N-2H}_{\text{BC}}^{2+}$  (by  $0.47$  and  $0.80 \text{ eV}/\text{H}$ , respectively). The trapping of two  $\text{H}^+$  to form  $\text{N-2H}_{\text{BC}}^{2+}$ , on the other hand, lowers the energy by  $0.48 \text{ eV}/\text{H}$ .<sup>17</sup> Each trapped H forms a strong bond with the N [see Fig. 1(b)] by passing the positive charge to a nearby threefold-coordinated Ga in the  $\text{N-2H}_{\text{BC}}^{2+}$  complex. This could be an important initial step to separate holes from the dihydrides for charge neutralization.

Upon neutralization, two important things happen spontaneously to  $\text{N-2H}_{\text{BC}}^{2+}$ : (1) the formation of the Ga—Ga bond in Fig. 3(a), and (2) the canting of the dihydride in Fig. 3(b). The former eliminates electronic states from within the original GaAs band gap, in agreement with the gap recovery experiment. The latter qualitatively alters the H/D vibrational properties. Because of its importance, we have calculated not only the initial and final positions of canting, but also four intermediate ones along the pathway. The smoothness of the curve in Fig. 3 suggests that the results are numerically highly accurate. Canting caused by a steric repulsion has been reported for dihydrides on Si (001) surfaces in the ex-

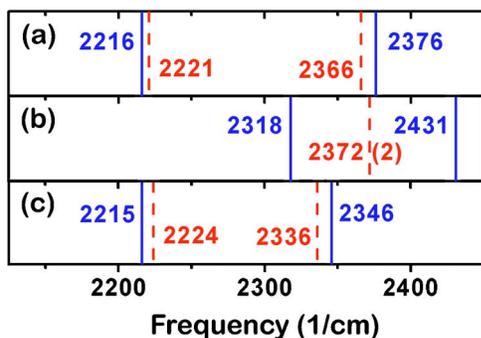


FIG. 2. (Color online) The various D-stretch modes for (a) experiment; (b)  $\text{N-2H}^{2+}$ ; and (c) canted  $\text{N-2H}$ . Solid lines indicate D-stretch modes in fully deuterated samples, whereas dashed lines indicate additional D-stretch modes in H/D flux.

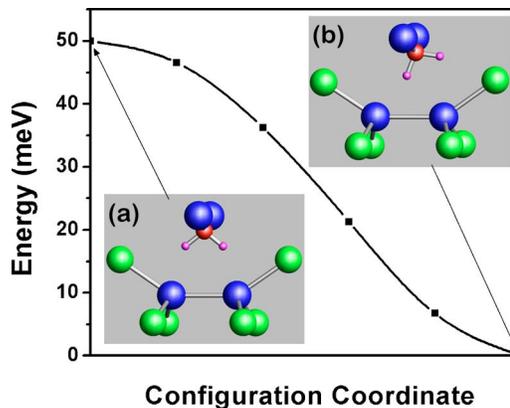


FIG. 3. (Color online) Calculated canting pathway, indicating that the uncanted  $\text{N-2H}$  is unstable against the canting. The structures of uncanted and canted  $\text{N-2H}$  complexes are shown in insets (a) and (b), respectively.

trema H-rich condition.<sup>18</sup> However, to our knowledge, it has never been reported for defects in bulk semiconductors and in the absence of steric repulsion between H atoms. On the other hand, we note that such a canting occurs only when the weak Ga—Ga bond forms. A similar three-center interaction has recently been proposed for carbon nanotube adsorption on semiconductor surfaces.<sup>19</sup>

Table I tabulates the calculated H and D frequencies. When compared with experiment, the dihydride  $N-2H_{BC}^{2+}$  and canted N-2H models produce better results for the H wag mode, 1328 and 1417  $cm^{-1}$ , respectively, than the monohydride  $\alpha-H_2^*$  model does, 944  $cm^{-1}$ . This is another indication that the defect responsible for the IR signals cannot be a monohydride. Because the two additional D modes in the mixed H/D flux are key IR results, they are examined in greater detail in Fig. 2: The canting of the dihydride leads to two additional modes versus one additional mode of the uncanted  $N-2H_{BC}^{2+}$ . Only the former agrees with the IR experiment. The canting of the dihydride also results in two equivalent minima in the energy landscape, which become vibrationally different when one H is replaced by D. The barrier in Fig. 3 is only 50 meV. Hence, we expect that, at low  $T$ , each N-DH complex should be trapped in one of the minima and contribute only to one of the additional D modes. At higher  $T$ , however, there will be no such trapping so that each N-DH complex contributes to both additional D modes, possibly in a 1:1 ratio.

We have also calculated the IR intensities ( $I$ ) for the D modes in Fig. 2(c). Our derivation shows that the relative IR intensities can be approximated by the ratio of  $|d\vec{p}/dQ_i|^2$ , where  $\vec{p}$  is the dipole moment of the system and  $Q_i$  is the  $i$ th normal coordinate. This yields  $I_{2215}:I_{2224}:I_{2336}:I_{2346} = 1:0.84:0.44:0.21$ , where the subscripts are the mode frequencies ( $cm^{-1}$ ). These results can be compared to the measured IR intensities, estimated from reading Fig. 2 in Ref. 8,  $I_{2216}:I_{2221}:I_{2366}:I_{2376} \approx 1:0.43:0.33:0.29$ . By reproducing the qualitative experimental trend, these calculations provide further support to the canted N-2H model.

Once the H atoms are trapped in a neutral canted N-2H complex, they may not escape easily to form  $\alpha-H_2^*$ , despite that the latter is 0.2 eV/H lower in energy. The minimum-energy barrier for converting a canted N-2H to  $\alpha-H_2^*$  is calculated to be 0.8 eV. In addition, there are significant mass differences between H ( $m=1$ ) and Ga ( $m=69$ ) and between H and N ( $m=14$ ). It is thus difficult for the much heavier Ga and N atoms to respond in harmony to the movement of the H. As a result, the actual barrier to convert a canted N-2H to

$\alpha-H_2^*$  could be significantly higher than the 0.8 eV. On the other hand, a  $H^+(As)$ , which has roughly a 0.2-eV diffusion barrier in  $GaAs_{1-y}N_y$ , should spontaneously transform any  $\alpha-H_2^*(N)$  into an interstitial  $H_2(Ga)$  plus a  $H^+(N)$ . This reaction is not only exothermic with energy lowering by 0.61 and 0.48 eV for  $H^0$  and  $H^+$ , respectively, but also barrierless other than the diffusion one. These, combined with the proposed proton relaxation pathway, explain why a metastable dihydride  $C_{2v}$  symmetry was observed by the recent XANES study, instead of the global minimum-energy monohydride  $C_{3v}$  symmetry.

Finally, we studied the recovery of the GaAs lattice parameter upon H irradiation. To mimic the epitaxial growth, we fixed the planar lattice parameters to that of bulk GaAs, but allowed the third one along [001] to relax. Assuming the lattice parameter of bulk GaAs is 100%, we obtain 98.69% for  $N_{As}$ , 98.81% for  $H_{BC}^+(N)$ , 99.59% for  $\alpha-H_2^*(N)$ , and 100.23% for  $H_2(Ga)$ . The canted N-2H may take two distinct orientations with respect to the [001] direction with degeneracy of 2 and 4, respectively. The corresponding lattice parameters are 100.55% and 99.37%, so the weighted average is 99.76%. This result is slightly better than that of  $\alpha-H_2^*$ , but could be expected, because for  $H_2^*$ , two H atoms cut only one strained N—Ga bond, whereas for canted N-2H, the two H atoms cut two N—Ga bonds, instead, leaving more rooms for the lattice recovery.

In summary, we have developed a model for ion relaxation following the initial implantation. The theory is qualitatively different from the ordinary equilibrium defect theory and may have implications for a broad range of ion implantation experiments. Application of this theory to  $GaAs_{1-y}N_y:H$  reveals a canted N-2H complex, which simultaneously accounts for all major experimental observations including the puzzling IR frequencies and amplitudes, the dihydride symmetry by XANES, the recovery of the GaAs band gap by optical measurement, and the recovery of the GaAs lattice parameter by x-ray diffraction.

We thank M. Capizzi for many valuable discussions and for kindly providing the preprint of Ref. 12. We also thank A. Janotti, S. Asher, B. Keyes, S. Kurtz, S.-H. Wei, and P. Zhang for suggestions. This work was supported by the U.S. DOE/BES and DOE/EERE under Contract No. DE-AC36-99GO10337 and by the NERSC for MPP time. The work in Thailand was supported by the Thailand Research Fund under Contract No. BRG4680003.

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- <sup>17</sup>Here, we compare the energy with  $\text{H}^+(\text{N})+\text{H}^+(\text{As})$ , because in these H-irradiation experiments,  $[\text{H}]$  is greater than  $[\text{N}]$ .
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