Ion relaxation and hydrogen LVM in H-irradiated GaAsN

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Abstract

First-principles calculations show that the hydrogen configurations in GaAsN depend on how hydrogen is introduced into the sample. Since proton and neutral H have different ground states, the proton injected into the sample by H-irradiation follows a unique energy pathway to form a charged dihydride, instead of the charge-neutral H_2^* monohydride. The subsequent charge neutralization causes the spontaneous canting of the dihydrides. The resulting canted N–2H structure explains the recent puzzling IR observation, the recoveries of the GaAs band gap and lattice parameter, and the dihydride symmetry determined by the XANES experiment. It may also have broad implications for ion implantation studies in other solids.
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1. Introduction

Large size-mismatched dilute alloys such as GaAsN [1] and ZnSeO [2,3] 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 [4]. On the other hand, H irradiation causes a nearly full recovery of the GaAs band gap [5] and lattice parameter [5] from those of GaAsN. The formed H complexes after H irradiation should be charge neutral due to their large concentration ($> 10^{20}\,cm^{-3}$). First-principles total energy calculations suggested that the lowest-energy charge-neutral H complex is the α-H_2^*(N) complex with characteristic Ga–H and N–H monohydride bonds (Fig. 1a), and that this complex can explain the above experimental observations [6,7]. However, a recent infrared experiment [8] on H-irradiated samples did not observe any Ga–H modes. Instead, two N–H stretch modes were observed at 3195 and 2967 cm^{-1}, as shown in Table 1. Hence, both modes here belong to the N–H bonds. In D-irradiated samples, the two stretch

modes shift to 2216 and 2376 cm^{-1}, respectively. In H/D co-irradiated samples, however, two *additional* D-stretch modes, at 2221 and 2366 cm^{-1} (see Fig. 2a), and one *additional* H-stretch mode, were observed. A second H mode is also expected, but was not observed, which was due possibly 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. A recent XANES study [9] further reveals that the symmetry of the 2 H complexes should be C_{2v}-like, thus further undermining the validity of the C_{3v}-based H_2^* model.

The disagreement between theory and experiment on H configurations in GaAsN suggests that the observed H-complex may not be the ground-state configuration. During H-irradiation, the equilibrium between the injected protons and the electron reservoir of energy E_F is not maintained. Therefore, one cannot assume that protons will take the theoretically predicted ground-state structure for neutral H.

In contrast to the conventional view of H irradiation as simply another convenient mean to enhance H concentration [H] in the solid, in this paper, we will show that the final H configurations can be altered by how the H is

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introduced into the solid. For H irradiation of GaAsN, the relaxation pathway for proton must be considered instead of the neutral H, because H irradiation in large quantity causes the accumulation of positive charges that cannot be easily dissipated. As a result, the injected protons enter the sample and get trapped in the proton-ground-state structure, $N-2H_{BC}^{2+}$, rather than the neutral-H-ground-state structure, $\alpha-H_2^*$. The subsequent charge neutralization results in the formation of metastable canted N–2H complex, which cannot be converted easily to the ground-state structure, $\alpha-H_2^*(N)$, due to a kinetic barrier. The canted N–2H model explains all experimental observations, including IR modes (both in frequency and relative amplitude), dihydride symmetry, and the bandgap and lattice parameter recovery. The good agreement between theory and experiments establishes a new direction to examine ion implantations in semiconductors and solids in general.

2. Method

Our calculations are based on the density functional theory within the local density approximation (LDA). The electron–ion interactions are described by the ultra-soft pseudopotentials [10], as implemented in the VASP codes [11]. The valence wavefunctions are expanded in a plane-wave basis with a cutoff energy of 348 eV. All calculations were performed using a 64-atom supercell. The vibrational frequencies were calculated based on the dynamical matrix approach [12]. We used the special k-points scheme for Brillouin zone summation and relaxed all the atoms until the forces were less than 0.02 eV/Å.
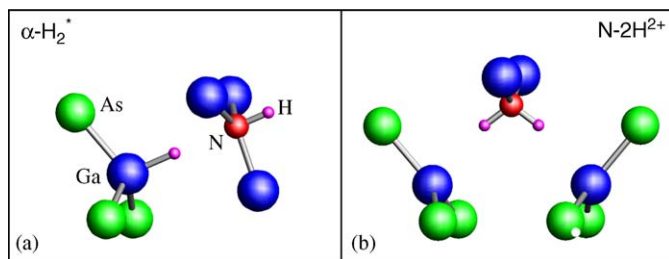

Fig. 1. Ball-stick models for (a) $\alpha-H_2^*$ and (b) $N-2H^{2+}$.

3. Results

Once protons enter the sample, they are unlikely to be neutralized, because the $(+/0)$ level for the diffusing H is near the conduction band minimum of GaAs, which is well above that of GaAsN. It therefore makes sense to study the H^+ instead of H^0 traps in H-irradiated GaAsN.

The most likely proton traps in GaAsN are the N-centered di-proton complexes, among which we found that neither the $\alpha-H_2^{*2+}$ nor the interstitial $H_2^{2+}(Ga)$ (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. Instead, the $N-2H_{BC}^{2+}$ complex is found to be the ground-state for a di-proton complex (see Fig. 1b). Charge neutral $\alpha-H_2^*$ and interstitial $H_2(Ga)$ may occasionally form by simultaneously creating *two* holes near the valence band maximum. Even if this happens, however, our calculation shows that the resulting $\alpha-H_2^{*0}(N) + 2h^+$ and $H_{2,int}^0(Ga) + 2h^+ + N_{As}$ are significantly less stable than the $N-2H_{BC}^{2+}$ (by 0.47 and 0.80 eV/H, respectively). On the other hand, the trapping of two H^+ to form $N-2H_{BC}^{2+}$ lowers the energy by 0.48 eV/H [13]. Each trapped H forms a strong bond with the N (see Fig. 1b) by passing the positive charge to a nearby threefold-coordinated Ga in the $N-2H_{BC}^{2+}$ complex. This could be an important initial step to separate holes from the dihydrides for charge neutralization.
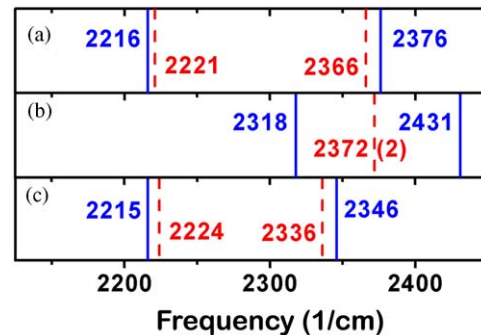

Fig 2. The various D stretch-modes for (a) experiment, (b) $N-2H^{2+}$, and (c) canted N–2H. Solid lines indicate D stretch-modes in fully deuterated samples, whereas dashed lines indicate additional D stretch-modes in H/D flux.

Table 1
Stretch and wag mode frequencies in units of cm^{-1}. N/A stands for not available

	Experiment			$\alpha-H_2^*$		$N-2H^{2+}$			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

Bonapasta et al. proposed that the N–2H$_{BC}^{2+}$ complex accounts for the measured H-modes [14]. However, a sample cannot host a few atomic percent of positively charged H complexes and also the N–2H$_{BC}^{2+}$ complex does not agree with experimental observation of two inequivalent N–H bonds. Thus, the N–2H$_{BC}^{2+}$ complex cannot be the final H configuration after H irradiation. The charge neutralization of the N–2H$_{BC}^{2+}$ must take place as the sample is grounded, but at a later time. This could happen, for example, by capturing electrons (injected from ground by the electrostatic potential between sample and ground) in the conduction band.

Upon the N–2H$_{BC}^{2+}$ neutralization, two important things happen spontaneously to N–2H$_{BC}^{2+}$: (1) the formation of the Ga–Ga bond in Fig. 3a and (2) the canting of the dihydride in Fig. 3b. 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. We note that such a canting occurs only when the weak Ga–Ga bond forms due to the Coulomb attraction between the electron-rich Ga–Ga bond and the electron-depleted H bonded to N.

Table 1 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 α-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 details 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 to one of the minima and contributes 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 relative IR intensities (I) for the D modes in Fig. 2c. The ratio of IR intensities originated from the same defect can be approximated to the first-order by the ratio of $|d\mathbf{p}/dQ_i|$ [2,15,16], where $\mathbf{p}$ is the dipole moment of the system and Q_i is the ith normal-mode coordinate. We calculated the dipole moment change $\Delta\mathbf{p}$ for each mode after taking same distance ($|\Delta Q|$) of atomic displacements along each normal-mode coordinate (Q_i). Then the ratio of any two IR intensities here is simply the ratio of $|\Delta\mathbf{p}|^2$ resulted from atomic displacement of same $|\Delta Q|$ in two normal-mode coordinates. 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 α-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 α-H$_2^*$ is calculated to be 0.8 eV. In addition, because of the large mass differences between H and Ga and between H and N, the actual barrier to convert a canted N–2H to α-H$_2$* could be significantly higher than the calculated 0.8 eV [17]. Note that the kinetic energy carried by proton should not help the N–2H overcome the energy barrier to become α-H$_2^*$, because it dissipates quickly after protons enter the sample by a distance of only a few nm [18], which is two orders of magnitudes smaller than GaAsN film thickness of 300 nm studied in Ref. [8]. Also, a GaAs capping layer of 100-nm thickness is usually applied to eliminate direct damages by the energetic protons [19,20]. Hence, protons enter most of GaAsN layer by thermal diffusion. Thus, one can safely ignore any effect of energetic protons and local heating on the relaxation of the metastable H complexes.

Despite the kinetic barrier, there is a finite probability that α-H$_2^*$(N) may form. However, even if this happens, the H at α-H$_2^*$(N) can be etched away by diffusing protons. Our calculations show that, an H$^+$(As), which has roughly a 0.2-eV diffusion barrier in GaAsN, can spontaneously transform any α-H$_2^*$(N) into an interstitial H$_2$(Ga) plus an 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,
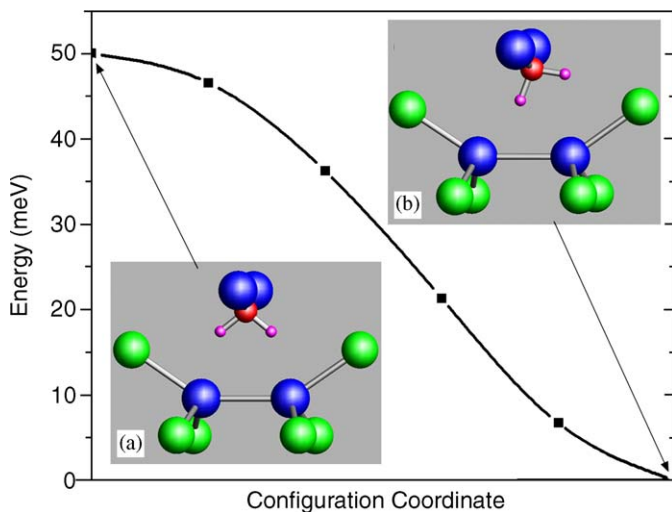

Fig 3. Calculated canting pathway, indicating that the uncanted N–2H is unstable against the canting. The structures of uncanted and canted N–2H complexes are shown in insets (a) and (b), respectively.

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 [0 0 1] 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 α-$H_2^*(N)$, and 100.23% for $H_2(Ga)$. The canted N–2H may take two distinct orientations with respect to the [0 0 1] 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 α-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.

4. Summary

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 GaAsN: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.

Acknowledgements

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