

Lattice relaxation by atomic hydrogen irradiation of *III-N-V* semiconductor alloys

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We study the effect of hydrogen incorporation on the lattice properties of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ heterostructures. The band gap widening observed in the photoluminescence spectra of hydrogenated $\text{GaAs}_{1-y}\text{N}_y$ and $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ is accompanied by a lattice expansion along the growth direction, as measured by x-ray diffraction. At the same time, far-infrared spectroscopy reveals that a Ga-N local vibrational mode at $\sim 472\text{ cm}^{-1}$ disappears upon hydrogen irradiation. All these effects are reversed upon hydrogen removal from the hydrogenated samples by thermal annealing. Finally, first-principles calculations indicate that a same dihydrogen complex is responsible for both the band gap reopening and the lattice expansion of hydrogenated $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$.

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I. INTRODUCTION

The electronic passivation of host impurities induced by atomic hydrogen in semiconductors has been widely studied in materials of technological relevance such as Si, Ge, GaAs, InP, GaP,¹ and GaN.² Recently, it has been observed that hydrogen can even tune the band gap of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$,^{3,4} an innovative semiconducting alloy of high potential for telecommunications and solar cell applications.^{5,6} Indeed, the replacement of a tiny fraction ($\sim 1\%$) of arsenic by nitrogen leads to highly nonlinear effects in the electronic properties of the $\text{In}_x\text{Ga}_{1-x}\text{As}$ host lattice.⁷⁻¹⁰ In previous experiments it has been shown that post-growth irradiation of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ with atomic hydrogen leads to a complete reversal of the drastic band gap reduction caused by nitrogen incorporation.^{3,4} The full reversibility of this phenomenon has been demonstrated by thermal annealing experiments in which hydrogen is removed from the samples.⁴ First-principles calculations indicate that a particular complex N-H_2^* accounts for the recovery of the band gap in both hydrogenated $\text{GaAs}_{1-y}\text{N}_y$ (Refs. 11-14) and $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$.¹⁵ In the complex N-H_2^* , two H atoms are necessary to passivate the N electronic properties, contrary to what happens in the passivation of shallow dopants, which is always accounted for by the formation of different monohydrogen impurity complexes.^{1,2}

Here, we study the consequences of nitrogen passivation by hydrogen on the lattice properties of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ alloys with different degree of disorder and opposite sign of strain. We show that the band gap widening observed after irradiation of $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ with hydrogen^{3,4} is accompanied by a dramatic change in the lattice constant of the N-containing layer, which is independent of In content. Indeed, the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ lattice unit cell returns at or very close to that of the N-free material when hydrogen is introduced, both in the In-free and in the more disordered In-

containing alloys. This effect is completely reversible upon hydrogen removal. Finally, first-principle total energy calculations indicate that most likely nitrogen-dihydride N-H_2^* complexes account for the lattice relaxation.

II. EXPERIMENTAL METHODS

Different $\text{GaAs}_{1-y}\text{N}_y$ epilayers ($y=0.0081$ and 0.013 , layer thickness equal to 300 nm) and $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ quantum wells ($x=0.36$, $y=0.052$ and 0.042 , quantum well thickness equal to 8.0 nm) have been grown on undoped GaAs substrates by solid source molecular beam epitaxy. Post-growth incorporation of atomic hydrogen was obtained by ion beam irradiation from a Kaufman source with the samples held at 300°C . The ion energy was about 100 eV and the current density was few tens of $\mu\text{A}/\text{cm}^2$.

X-ray diffraction measurements on $\text{GaAs}_{1-y}\text{N}_y/\text{GaAs}$ epilayers have been performed in the $\theta-2\theta$ geometry by exploiting a molybdenum-rotating anode as x-ray generator and setting the incident wavelength at the $K_{\alpha 1}$ Mo fluorescence line ($0.7092\text{ \AA}$) by means of a Si [111] channel-cut monochromator. The scattered intensity was detected by a NaI(Tl) scintillation detector. Measurements on $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ thin quantum wells were performed by using a copper-rotating anode without monochromator. We referred to the $\text{CuK}_{\alpha 1}$ line ($1.54088\text{ \AA}$) for the determination of lattice parameters; a splitting of the substrate peak due to the $K_{\alpha 2}$ line is visible in the spectra. The x-ray diffraction data have been recorded in the vicinity of the (004) crystal plane reflection. Infrared absorption measurements were performed at liquid He temperature by a Bomem DA3 spectrometer (spectral resolution 1 cm^{-1}) with a Si bolometer.

III. THEORETICAL METHODS

Nitrogen-hydrogen complexes have been investigated in the framework of the density functional theory in the local

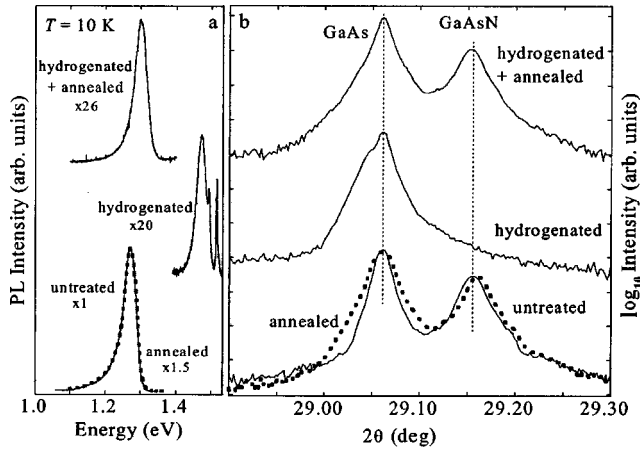


FIG. 1. (a) Photoluminescence (PL) spectra of a 300 nm thick $\text{GaAs}_{0.9919}\text{N}_{0.0081}$ epilayer after different post-growth treatments. Bottom (continuous line): untreated sample. Middle: the same sample after exposure to a hydrogen dose equal to 3.0×10^{18} ions/cm². The narrow bands on the high energy side of the main PL band are due to carrier recombination from GaAs states. Top: a hydrogenated sample with the same H dose of 3.0×10^{18} ions/cm² but annealed at 500 °C for 30 min. The spectrum of a sample subjected to the same heat treatment (temperature 300 °C and duration 6 h) of the hydrogenated sample but in the absence of hydrogen is shown at the bottom by the gray dotted line superimposed to the spectrum of the untreated sample (bottom continuous line). Note that the hydrogenation/annealing process introduces some nonradiative defects responsible for the PL intensity decrease. Normalization factors are given for each PL spectrum. (b) X-ray diffraction curves for the same samples whose PL spectra are displayed in part (a). The x-ray diffraction data have been recorded in the vicinity of the (004) crystal plane reflection. The curves have been vertically offset for clarity.

density approximation. Total energies have been calculated by using supercells, separable *ab initio* pseudopotentials,¹⁶ plane-wave basis sets, the special-points technique for $\mathbf{k}$ -space integration, and the exchange-correlation functional of Ceperley-Alder.¹⁷ Ultrasoft pseudopotentials have been used in the case of nitrogen¹⁸ and nonlinear core corrections have been used in the case of indium. Convergence tests have been done by using plane-wave cutoffs ranging from 18 to 28 Ry, supercells of 32 and 64 atoms, and $\mathbf{k}$ -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) $\mathbf{k}$ -point Monkhorst-Pack mesh, and cutoffs of 22 Ry. In particular, $\text{GaAs}_{1-y}\text{N}_y$ epilayers have been simulated by using a 64-atom supercell of GaAs, which includes one or two N atoms, thus corresponding to y values of 0.03 and 0.06, respectively.

IV. RESULTS AND DISCUSSION

Figure 1(a) shows the photoluminescence (PL) spectra of a $\text{GaAs}_{1-y}\text{N}_y$ epilayer with $y=0.0081$ exposed to different post-growth treatments. Similar results have been reported and described in previous work.^{3,4} We would like to stress here how H insertion [middle curve in Fig. 1(a)] and removal [top curve in Fig. 1(a)] dramatically modify the crystal en-

ergy gap in a reversible way. The x-ray diffraction data of the same $\text{GaAs}_{1-y}\text{N}_y$ epilayers whose PL spectra are shown in Fig. 1(a) are displayed in Fig. 1(b). In the as-grown $\text{GaAs}_{1-y}\text{N}_y$ sample (bottom solid curve), two diffraction peaks in the rocking curve are observed. The higher and lower intensity peaks originate from the GaAs substrate and $\text{GaAs}_{1-y}\text{N}_y$ epilayer, respectively. The value of the angular separation between the two peaks allows us to measure the N concentration by using the empirical formula reported in Ref. 19. The positive angular shift of the N-containing epilayer peak indicates that it has a smaller lattice constant along the growth direction ($a_{\text{GaAsN}}^{\perp}=5.636$ Å) than it has in the plane where it is lattice matched to the GaAs substrate ($a_{\text{GaAsN}}^{\parallel}=a_{\text{GaAs}}=5.653$ Å). Remarkably, the x-ray diffraction data recorded on the hydrogenated $\text{GaAs}_{1-y}\text{N}_y$ epilayer show a disappearance of the diffraction peak associated with the $\text{GaAs}_{1-y}\text{N}_y$ epilayer [see middle curve of Fig. 1(b)]. In addition, a shoulder can be detected at slightly smaller angles, which indicates the presence of compressive strain in the hydrogenated $\text{GaAs}_{1-y}\text{N}_y$ epilayer. As a result, the value of the lattice constant of the hydrogenated sample can even exceed that of the GaAs. A heat treatment similar to the one the sample is subjected to during the hydrogenation process does not vary the material lattice properties [see gray dotted line, bottom of Fig. 1(b)], reproducing the lack of variation in the optical properties shown at the bottom of Fig. 1(a) by the gray dotted curve. One might wonder if the recovery of the GaAs lattice constant arises from a randomization of the lattice due to H bombardment or from nitrogen diffusion out of the lattice. These possibilities are ruled out by the diffraction data recorded on a same piece of sample which was previously hydrogenated and then annealed until all H was removed: A full restoration of the $\text{GaAs}_{1-y}\text{N}_y$ lattice properties is observed, together with a full recovery of the $\text{GaAs}_{1-y}\text{N}_y$ band gap [see top of Figs. 1(b) and 1(a)]. All these results show that the crystal unit cell of $\text{GaAs}_{1-y}\text{N}_y$ undergoes a large variation of its size upon H insertion and that this processes is reversible. The same results have been observed in the case of a $\text{GaAs}_{1-y}\text{N}_y$ epilayer with $y=0.013$ (not shown here).

In order to strengthen our observations we studied the case of an even more disordered alloy under opposite initial strain conditions, that is, the $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ alloy. The bottom curve in Fig. 2 shows the x-ray diffraction curve of a reference N-free $\text{In}_x\text{Ga}_{1-x}\text{As}$ quantum well (thickness 8.0 nm, $x=0.36$). The substitution of 36% of the Ga atoms with larger In atoms gives rise to compressive strain in the thin quantum well layer ($a_{\text{InGaAs}}^{\perp}=5.929$ Å). This compressive strain can be relieved in part by adding N, as shown in Fig. 2 (middle curve) for an $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ quantum well having the same thickness and In concentration as the N-free reference, but $y=0.052$ ($a_{\text{InGaAsN}}^{\perp}=5.868$ Å). The irradiation of the N-containing sample with H restores the lattice properties of the N-free quantum well (top curve) to such an extent that the diffraction curves of the hydrogenated $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ and of the $\text{In}_x\text{Ga}_{1-x}\text{As}$ samples are hardly distinguishable. Furthermore, the lattice properties of the reference N-free quantum well are left unaffected by the same

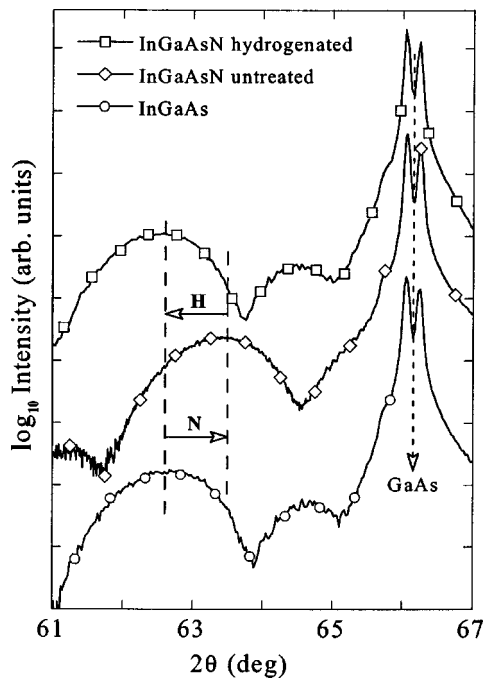


FIG. 2. X-ray diffraction from 8.0 nm thick, In-containing quantum wells. Bottom: $\text{In}_{0.36}\text{Ga}_{0.64}\text{As}$ (no nitrogen). Middle: Untreated $\text{In}_{0.36}\text{Ga}_{0.64}\text{As}_{0.948}\text{N}_{0.052}$. Top: The same $\text{In}_{0.36}\text{Ga}_{0.64}\text{As}_{0.948}\text{N}_{0.052}$ sample now hydrogenated with 3.0×10^{18} H ions/ cm^2 . The vertical dashed lines mark the diffraction peaks due to the quantum well layers. The horizontal arrows depict the effect of N incorporation in $\text{In}_{0.36}\text{Ga}_{0.64}\text{As}$ and H irradiation in $\text{In}_{0.36}\text{Ga}_{0.64}\text{As}_{0.948}\text{N}_{0.052}$. Note the full reversal of the lattice parameter of the hydrogenated $\text{In}_{0.36}\text{Ga}_{0.64}\text{As}_{0.948}\text{N}_{0.052}$ quantum well (top curve) toward that of the N-free reference sample (bottom curve). The double peak at about 66° is due to the GaAs substrate. The x-ray diffraction data have been recorded in the vicinity of the (004) crystal plane reflection. The curves have been vertically offset for clarity.

post-growth H irradiation (not shown here). Similar to the $\text{GaAs}_{1-y}\text{N}_y$ case shown in Fig. 1(a), photoluminescence data recorded on the hydrogenated $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ quantum well showed a full recovery of the band gap to the value of the N-free $\text{In}_x\text{Ga}_{1-x}\text{As}$ quantum well, as reported in Ref. 3. In these $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ quantum wells the H treatment induces a decrease in the photoluminescence intensity higher than that found in In-free materials. This fact shows that defects induced by the hydrogenation process play no major role in the lattice constant recovery. Indeed, the same lattice relaxation upon hydrogenation is observed in both $\text{GaAs}_{1-y}\text{N}_y$ and $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$, although the defect density is quite different in the two cases.

It should be mentioned that similar effects have been observed in hydrogenated Si:B, where a partial relaxation of the Si:B lattice toward that of the undoped Si lattice was observed.²⁰ This effect was attributed to the formation of B-H complexes, i.e., the same complexes responsible for the electrical passivation of B.

Far infrared absorption measurements have been performed in the same $\text{GaAs}_{1-y}\text{N}_y$ samples investigated by x-ray diffraction. Figure 3 shows the infrared spectra of untreated (bottom curve), hydrogenated (middle curve) and hy-

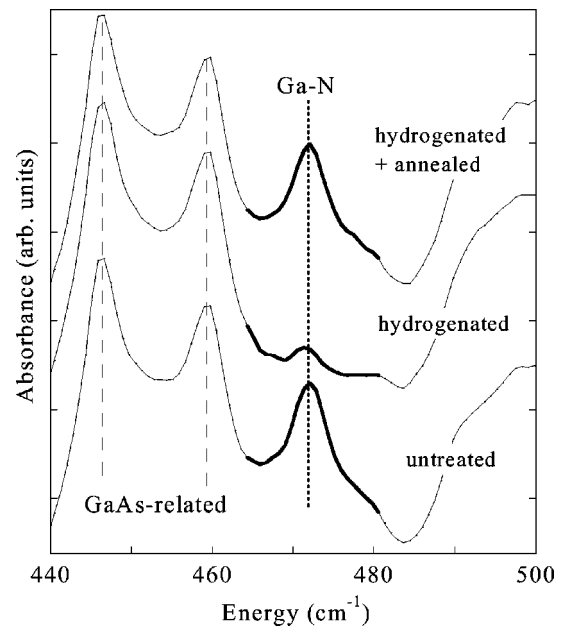


FIG. 3. 4.2 K far infrared absorption spectra of the same samples whose photoluminescence spectra and diffraction curves are shown in Fig. 1. Bottom line: Far infrared absorption spectrum of an untreated $\text{GaAs}_{0.9919}\text{N}_{0.0081}$ epilayer. Middle line: Far infrared absorption spectrum recorded on the same sample after hydrogen irradiation with an impinging dose equal to 3.0×10^{18} ions/ cm^2 . Top line: Far infrared absorption spectrum of a sample hydrogenated with the same H impinging dose 3.0×10^{18} ions/ cm^2 and annealed afterward at 500°C for 30 min. The Ga-N local vibrational mode at 472 cm^{-1} is highlighted by thick lines. The other modes in the spectrum are due to the GaAs substrate.

drogenated plus annealed (top curve) $\text{GaAs}_{0.9919}\text{N}_{0.0081}$ epilayers in the energy region of the local vibrational mode of the Ga-N bond (472 cm^{-1}).²¹ The decrease in the absorption intensity of this mode found in the hydrogenated sample indicates a decrease in the number of Ga-N bonds present in the sample. Subsequent thermal annealing restores the pre-hydrogenation bond number (see top curve in Fig. 3). These data provide further evidence for strong changes in the lattice environment around the N atoms in $\text{GaAs}_{1-y}\text{N}_y$ upon hydrogenation. They show that the microscopic complex responsible for the lattice relaxation has to involve the breaking of Ga-N bonds. In addition, new modes at higher energy appear concomitantly with the disappearance of the Ga-N bonds, as reported previously.²² Infrared absorption measurements in hydrogenated and/or deuterated samples are in progress in order to assess the nature of the new complexes formed upon hydrogenation, in particular their involving one or two H atoms.

To address the microscopic origin of the lattice relaxation in hydrogenated $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ we carried out first-principles total-energy calculations. In previous theoretical works,¹¹⁻¹⁴ it has been shown that the N-H_{BC} and N-H_2^* complexes are respectively the most stable monohydrogen and dihydrogen complexes in $\text{GaAs}_{1-y}\text{N}_y$. In the N-H_{BC} complex there is only a H_{BC} atom bonded to N at a bond center (BC) position between the Ga and N atoms. In the

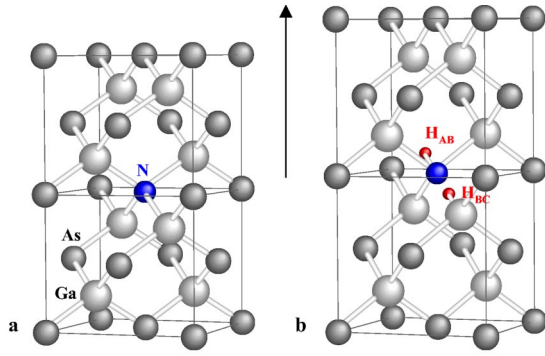


FIG. 4. (Color online) Sketch of the $\text{GaAs}_{1-y}\text{N}_y$ lattice in the vicinity of a nitrogen atom. (a) $\text{GaAs}_{1-y}\text{N}_y$ lattice (no hydrogen). (b) N-H_2^* complex with one hydrogen atom H_{BC} bound to Ga and located at the bond center position between the Ga and N atoms and the other hydrogen atom H_{AB} placed in an antibonding site with respect to the N atom. The lattice difference between the H-containing and the H-free $\text{GaAs}_{1-y}\text{N}_y$ crystals has been exaggerated for clarity. The vertical arrow indicates the growth direction.

N-H_2^* complex, two strong Ga-H_{BC} and N-H_{AB} bonds are formed, which involve, respectively, a H_{BC} atom in bond center position between the Ga and N atoms and a H_{AB} atom in opposite position with respect to the same nitrogen atom; see Fig. 4(b). In the present study, total energy calculations have been performed in order to evaluate the change in $a_{\text{GaAsN}}^\perp$ induced by the formation of those two complexes in $\text{GaAs}_{1-y}\text{N}_y$ epilayers with $y=0.03$ and 0.06 grown on a GaAs substrate. The value of the lattice parameter in the growth plane was fixed to that calculated for GaAs ($5.557 \text{ \AA}$) while the value of the lattice parameter along the growth direction, c , was allowed to range from 5.292 to $5.662 \text{ \AA}$. For each c value considered, the supercell geometry has been fully optimized. The c value corresponding to the total-energy minimum (i.e., $a_{\text{GaAsN}}^\perp$) has been evaluated through a Murnaghan fit²³ of the total energy values corresponding to the sampled values of c . For $y=0.06$, we calculate values of $a_{\text{GaAsN}}^\perp$ equal to $5.406 \text{ \AA}$ for H-free material, $5.371 \text{ \AA}$ for a lattice containing N-H_{BC} complexes, and $5.512 \text{ \AA}$ for a lattice containing N-H_2^* complexes. The first value corresponds to a contraction of the $\text{GaAs}_{0.94}\text{N}_{0.06}$ alloy lattice along the growth direction, which follows the Vegard's law (the evaluated GaAs lattice constant is $5.557 \text{ \AA}$). The lattice undergoes a further slight contraction in the case of N-H_{BC} complex, while 99.2% of the GaAs lattice constant is recovered in presence of the N-H_2^* complexes (that is, 70% of the change produced by N introduction is recovered by H). For $y=0.03$, similar results have been obtained and 99.6% of the GaAs lattice constant is recovered by the formation of the N-H_2^* complex. Thus, that same dihydrogen N-H_2^* complex that accounts for N electronic passivation^{11–13} induces also a lattice relaxation like that observed after hydrogenation, as schematically shown in Fig. 4.

It is worth highlighting some important difference with respect to the case of hydrogenated Si:B.²⁰ Therein a H atom

located at the BC site of a Si-B bond induces an outward relaxation of its Si and B neighbors which, in turn, leads to a partial recovery of the undoped Si lattice constant. The present results show, instead, that a H atom located at the BC site of a Ga-N bond in $\text{GaAs}_{1-y}\text{N}_y$ does not lead to a recovery of the GaAs lattice constant nor to N passivation, which are obtained only when N-H_2^* complexes are formed. Indeed, the cases of a single H_{BC} atom in Si:B and in $\text{GaAs}_{1-y}\text{N}_y$ are different because of the different chemical bonding occurring. In the former case, H_{BC} saturates the Si dangling bond thus leaving the chemical valence of both Si and B fully satisfied. In $\text{GaAs}_{1-y}\text{N}_y$, H_{BC} too induces an outward local relaxation of the Ga and N atoms.¹³ However, the H atom is now bonded to the N atom and this leaves an unsaturated dangling bond on the Ga atom. A detailed analysis of the chemical bonding of the N-H_{BC} complex shows that the Ga dangling bond induces a Ga-H bonding interaction, which lowers the total energy of the system when the $\text{GaAs}_{1-y}\text{N}_y$ lattice constant is reduced.²⁴ Therefore, the formation of the N-H_{BC} -Ga complex does not lead to a dilation of the $\text{GaAs}_{1-y}\text{N}_y$ lattice toward that of the GaAs lattice, rather it leads to a lattice contraction. On the ground of the above considerations, one can conclude that the different chemical behavior of a dopant impurity, similar to B in Si, and of an isoelectronic impurity, similar to N in GaAs, accounts for the different effects H-containing complexes induce in Si:B and $\text{GaAs}_{1-y}\text{N}_y$ lattices.

V. CONCLUSIONS

We have shown that hydrogen irradiation of both tensilely strained $\text{GaAs}_{1-y}\text{N}_y$ and compressively strained $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y$ leads to the breaking of Ga-N bonds and to an ensuing expansion of the lattice unit cell at (or slightly greater than) that of the N-free material. We believe this is a quite general phenomenon that can be observed also in other $\text{AB}_{1-y}\text{C}_y$ alloys, where the C atoms have atomic size and electronegativity largely different from those of the B atoms (e.g., $\text{GaP}_{1-y}\text{N}_y$). Total energy minimization methods indicate that a complex involving two hydrogen atoms in the neighborhood of a nitrogen atom accounts for both the lattice relaxation and the N passivation in $\text{GaAs}_{1-y}\text{N}_y$. We believe our results are of relevance also from the application standpoint. Indeed, hydrogen is largely present as a carrier gas in the growth techniques used for large scale semiconductor production such as those based on vapor deposition, in which the incorporation of hydrogen in the grown material is a likely occurrence.

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