

Nitrogen passivation induced by atomic hydrogen: The GaP_{1-y}N_y case

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We report on the evolution of the optical properties of GaP_{1-y}N_y epilayers upon hydrogen irradiation for an extended nitrogen concentration range ($y=0.05\%–1.3\%$). For $y\geq 0.6\%$, photoluminescence measurements show that hydrogen leads to an apparent band gap widening and to an ensuing appearance of N cluster states in the forbidden gap of GaP_{1-y}N_y. Hydrogen removal from the samples results in a full recovery of the electronic properties of the as-grown material. For lower N concentration ($y=0.05\%$), hydrogen causes a spectral weight transfer from electronic levels associated with closer N pairs to those associated with more distant N pairs and single N atoms.

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The GaP_{1-y}N_y/GaP system has attracted much interest since the 1960s, when nitrogen incorporation was shown to give rise to efficient light emission by carrier recombination from levels associated with single and multiple nitrogen complexes.¹ This discovery was readily exploited in the fabrication of light emitting diodes in the visible spectral range.² Since then, several experimental and theoretical studies dealt with the role of N in GaP.^{3–8} However, in spite of the fact that hydrogen enters in most of the growth and device making processes based on GaP_{1-y}N_y, almost nothing is known about the effects hydrogen exerts on this material. An infrared study of GaP crystals containing residual hydrogen and nitrogen atoms showed the presence of N-H complexes⁹ whose microscopic structure was later addressed in a theoretical work.¹⁰ The consequences of *ex situ* hydrogen incorporation have been described once, more than ten years ago, for GaP epilayers with a N concentration of about 10^{18} cm^{-3} .¹¹ Therein, a reduction in the luminescence intensity of a few lines related to N pairs was reported.

Recently, it has been shown how hydrogen irradiation on In_xGa_{1-x}As_{1-y}N_y/GaAs heterostructures reverses completely the drastic band gap reduction caused by nitrogen incorporation.¹² In_xGa_{1-x}As_{1-y}N_y and GaP_{1-y}N_y share several common features, among which an anomalous giant decrease in the band gap with increasing nitrogen concentration^{3–6,13–15} and a slowdown in the response of the electronic properties of these materials to external perturbations such as hydrostatic pressure^{13,16} and temperature.^{17,18} Therefore, one might wonder what kind of effects hydrogen produces on the electronic properties of GaP_{1-y}N_y.

Here we describe the effects of hydrogen irradiation on the photoluminescence (PL) properties of GaP_{1-y}N_y epilayers with N concentration varying from $y=0.05\%$ to 1.3% . We find that hydrogen passivates electronically the nitrogen atoms, leading to a fine-tuning of the material optical properties, which evolve with increasing H dose as if the N concentration were gradually decreased. For $y\geq 0.6\%$, H in-

creases the effective band gap of GaP_{1-y}N_y and, as a consequence, exposes in the gap N complex states that were resonant with the continuum of states of the conduction band before hydrogenation. Removal of hydrogen by thermal annealing restores fully the optical properties the material had before hydrogenation, with an activation energy equal to 2.36 eV. In addition, for smaller nitrogen concentration ($y=0.05\%$), hydrogen induces a transfer of spectral weight from closer to more distant N pair and single N levels.

GaP_{1-y}N_y epilayers were grown by gas-source molecular beam epitaxy on (001)-oriented GaP substrates. Nitrogen concentrations as determined by x-ray diffraction measurements are $y=0.05\%$, 0.12% , 0.6% , 0.81% , and 1.3% . The GaP_{1-y}N_y epilayer thickness is 250 nm for all samples, but for the $y=1.3\%$ epilayer, which is 750 nm thick. Hydrogenation was performed by ion-beam irradiation from a Kaufman source with the samples held at 300 °C and using low ion energy (100 eV) and current densities ($\sim 10\ \mu\text{A}/\text{cm}^2$). The H doses (d_H) range between 10^{17} and 10^{19} ions/cm². Hydrogenated samples were annealed at temperatures $T_a=200–550\text{ °C}$ for a duration time equal to 1 h under vacuum (10^{-6} torr). Photoluminescence was excited by the 458-nm line of an Ar⁺ laser, dispersed by a single 1-m monochromator and detected by a cooled photomultiplier with a GaAs cathode used in a single-photon-counting mode.

Figure 1 shows the PL spectra of a GaP_{1-y}N_y epilayer with $y=0.6\%$ after exposure to different hydrogen doses (solid lines). The bottom curve refers to the untreated sample. The middle and top curves are the PL spectra recorded on the $y=0.6\%$ sample after H irradiation with $d_H=10^{17}$ and 1.2×10^{18} ions/cm², respectively. Quite remarkably the spectra of the hydrogenated samples reproduce qualitatively those of the as-grown epilayers with lower N concentration ($y=0.12\%$ and 0.05% : see dashed lines Fig. 1), but for a linewidth broadening at the highest d_H employed (see top curves in Fig. 1). This broadening resembles

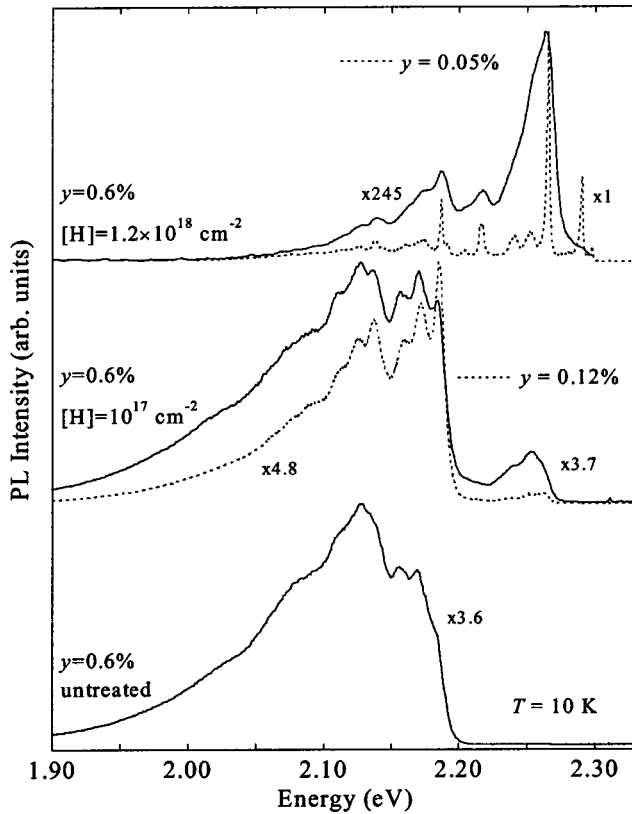


FIG. 1. Peak-normalized photoluminescence (PL) spectra at 10 K of a $\text{GaP}_{1-y}\text{N}_y$ epilayer with $y=0.6\%$ after exposure to different H doses (solid lines). Dashed lines are the PL spectra of $\text{GaP}_{1-y}\text{N}_y$ epilayers having different N concentration. PL normalization factors are given. Laser power density is 10 W/cm^2 .

that found in hydrogenated $\text{In}_x\text{Ga}_{1-x}\text{As}_{1-y}\text{N}_y/\text{GaAs}$ quantum wells.¹² With increasing hydrogen dose, the center of mass of the PL spectra of the hydrogenated $\text{GaP}_{0.994}\text{N}_{0.006}$ blueshifts and a new group of lines appears at about 2.26 eV, namely, in the spectral region where the untreated samples with smaller N concentration show carrier recombination from third-neighbor N pairs and related phonon replica.⁵ Interestingly, in the $y=0.81\%$ sample (not shown here) this H-induced shift of the energy of the PL band corresponds to a change in the color of the light emitted by the sample from red to green, thus suggesting a variety of potential applications. Finally, a reduction in the PL emission intensity is also observed in hydrogenated samples. Similar behaviors are observed in the hydrogenated 1.3% epilayer. The effects now described can be attributed to the formation of nitrogen-dihydrogen N-H_2^* complexes similar to those found to be responsible for the electronic passivation of N by H in $\text{GaAs}_{1-y}\text{N}_y$.¹⁹⁻²¹ Indeed, first-principles total energy calculations have shown that the N-H_2^* complex is stable in $\text{GaP}_{1-y}\text{N}_y$,¹⁰ even if further investigations are needed to assess if this complex is able to passivate N in $\text{GaP}_{1-y}\text{N}_y$, too.

We show now that the effects induced by H on the optical properties of $\text{GaP}_{1-y}\text{N}_y$ are fully reversible. Figure 2 displays the PL spectra of the $\text{GaP}_{0.994}\text{N}_{0.006}$ sample hydrogenated with $d_H=1.2 \times 10^{18}$ ions/cm² after annealing at different temperatures. One can observe that *both* the PL line

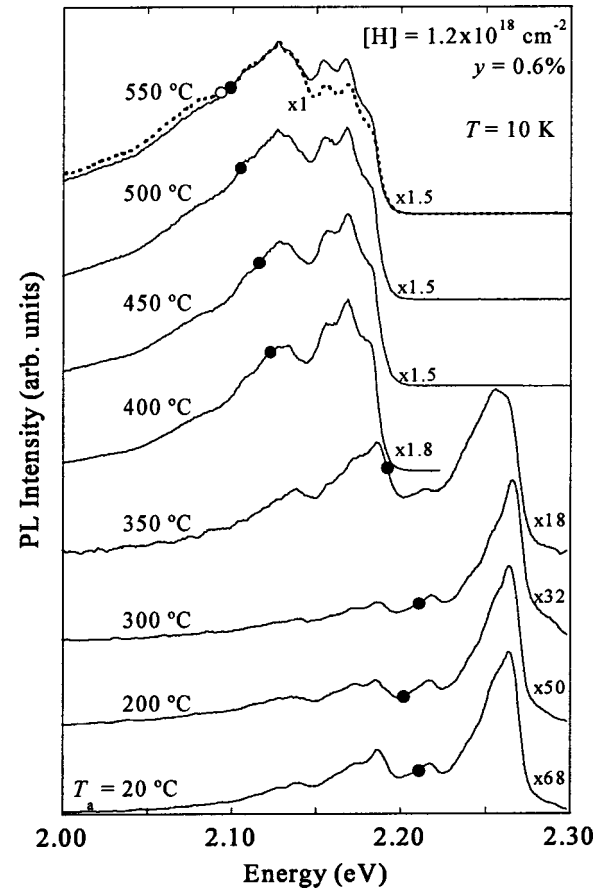


FIG. 2. Peak-normalized photoluminescence (PL) spectra (solid lines) at 10 K of a $\text{GaP}_{0.994}\text{N}_{0.006}$ epilayer hydrogenated with 1.2×10^{18} ions/cm² after 1 h thermal annealing at different temperatures T_a . The thick-dotted line is the PL spectrum of the same sample without hydrogen. The solid (open) dots indicate(s) the energy position of the spectrum center of mass of the annealed (untreated) samples. PL normalization factors are given. Laser power density is 10 W/cm^2 .

shape *and* efficiency change sizably between $T_a=300$ and 400 °C and are almost completely recovered at the highest T_a (550 °C). A quantitative analysis of the dependence of the PL center of mass (see dots in Fig. 2) and integrated intensity on T_a has been done by using the model reported in Ref. 22. It provides the same activation energy for both processes, $E_a=2.36$ eV.²³ This suggests that the decrease in the PL intensity observed upon hydrogenation can be attributed to the double role that hydrogen plays in the host lattice. On the one hand, H forms complexes with N and passivates the electronic activity of the latter, thus accounting for the effective band gap widening observed upon hydrogenation. On the other hand, the N-H complexes may act as nonradiative recombination centers, leading to a decrease in the emission efficiency.

Let us discuss now possible explanations of the striking effects H irradiation has on the optical properties of $\text{GaP}_{1-y}\text{N}_y$. The breaking of the translational symmetry of GaP by the localized N potential has been claimed to produce states at the conduction-band minimum, which result from an admixture of states from different minima in the k

space.⁸ This gives rise to perturbed host states with an increased radiative oscillator strength, whose energy decreases for increasing N concentration and which take in the states associated with N pairs and clusters.⁸ The data described so far show that H affects mainly the energy position of these perturbed host states, with an effective band gap reopening and an ensuing reappearance of the N cluster states in the forbidden gap, in spite of the remnant degree of lattice disorder. We point out that hydrogenation of $\text{GaAs}_{1-y}\text{N}_y$ has been shown to restore the lattice constant of the N-free GaAs host lattice.^{24,25} In turn, one may suppose that the formation of N-H complexes strongly reduces the N-related relaxation of the GaP lattice and that this phenomenon leads to a redistribution of the electronic charge in the whole lattice with a likely decrease in the charge density localized around the N atoms.

The data displayed in Figs. 1 and 2 show also that the N cluster states are pinned at fixed energy regardless of the mechanism (either N incorporation or H irradiation) that exposes them in the forbidden gap of the host lattice. To better investigate the effect of H on the N cluster states, we now consider a sample having $y=0.05\%$ where the emission lines due to carrier recombination in different N complexes are spectrally well distinguished. Figure 3 shows the PL spectra of the as-grown (lower curve) and hydrogenated (upper curve) $y=0.05\%$ epilayer.²⁶ An attribution of the different lines to given N complexes has been reported in previous works⁵ and we will not enter into further details. Here we want to stress two important consequences of hydrogenation: (i) a clear passivation of the background signal underlying the narrow lines and most likely due to distorted bonds in the sample arising from lattice relaxation around N atoms and (ii) a shift in the spectral weight from below to above 2.3 eV in agreement with the H-induced blueshift of the perturbed host states. This is different from what we found in $\text{GaAs}_{1-y}\text{N}_y$ where all N-related lines were fully passivated by H.²² In particular, the emission line due to carrier recombination from a single nitrogen atom, N_A^0 , increases its absolute integrated intensity with respect to that found in the not-hydrogenated sample by more than two orders of magnitude, as shown in the inset of Fig. 3. This finding can be attributed to changes in the carrier relaxation processes ensuing the band gap blueshift. Alternatively, one can hypothesize that N pairs are passivated by the interaction of one N atom with hydrogen, which leaves the other N atom of the pair acting from an electronic point of view as a single N. In general, the comparison of the PL spectra before and after hydrogenation indicates that H binds more effectively to deeper N complexes and closer N pairs (as suggested also in Ref. 11) and that H may cure the lattice distortion of GaP subsequent to the incorporation of the small N atoms.

In conclusion, we have shown that the $\text{GaP}_{1-y}\text{N}_y$ band gap widens and localized states associated with N complexes appear in the gap with increasing H dose. Therefore, H counteracts the mixing of k -space states induced in GaP by the

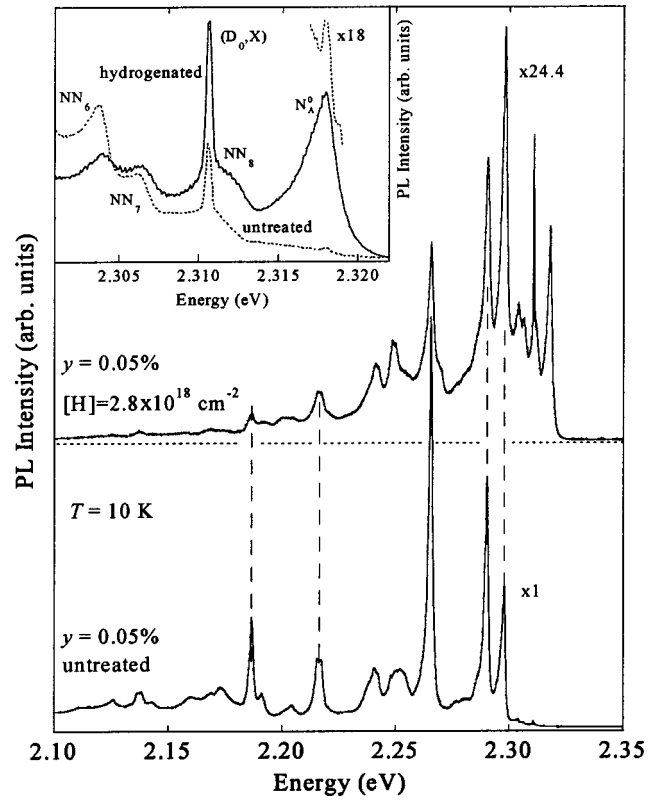


FIG. 3. Peak-normalized photoluminescence (PL) spectra at 10 K of a $\text{GaP}_{1-y}\text{N}_y$ epilayer with $y=0.05\%$ before (lower curve) and after H irradiation with a dose equal to 2.8×10^{18} ions/cm² (upper curve). In the latter case the horizontal dashed line sets the spectrum baseline. The vertical dashed lines highlight some lines whose relative intensity has changed after hydrogenation. PL normalization factors are given. Laser power density is 10 W/cm². Inset: enlarged part of the spectra shown in the main part of the figure. The intensity of the PL signals can be compared directly. N_A^0 is the recombination line associated with a single N level, (D_0,X) indicates the line due to a sulfur-bound exciton recombination (Ref. 26), and NN_i are the levels of the i th nearest-neighbor N pairs (Ref. 5).

strongly localized potential associated with N atoms, without fully restoring, however, the translational symmetry of the GaP lattice. We speculate that the incorporation of H reduces the relaxation of the GaP lattice subsequent to N incorporation and leads to a major charge redistribution in the lattice as well as to a restoring of the GaP band gap. Finally, from an application standpoint the effects here described would allow post-growth treatments to convert the $\text{GaP}_{1-y}\text{N}_y$ band edge emission from red to green continuously on a same chip.

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