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Effect of postgrowth hydrogen treatment on defects in GaNP

D. Dagnelund,¹ X. J. Wang,^{2,1} C. W. Tu,³ A. Polimeni,⁴ M. Capizzi,⁴ W. M. Chen,¹ and I. A. Buyanova^{1,a)}

¹Department of Physics, Chemistry and Biology, Linköping University, S-581 83 Linköping, Sweden

²National Laboratory for Infrared Physics, Shanghai Institute of Technical Physics, Chinese Academy of Sciences, 200083 Shanghai, People's Republic of China

³Department of Electrical and Computer Engineering, University of California, La Jolla, California 92093, USA

⁴Dipartimento di Fisica and INFN, Università di Roma "La Sapienza", Piazzale A. Moro 2, I-00185 Roma, Italy

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Effect of postgrowth hydrogen treatment on defects and their role in carrier recombination in GaNP alloys is examined by photoluminescence (PL) and optically detected magnetic resonance. We present direct experimental evidence for effective *activation* of several defects by low-energy subthreshold hydrogen treatment (≤ 100 eV H ions). Among them, two defect complexes are identified to contain a Ga interstitial. Possible mechanisms for the H-induced defect activation and creation are discussed. Carrier recombination via these defects is shown to efficiently compete with the near band-edge PL, explaining the observed degraded optical quality of the alloys after the H treatment. © 2011 American Institute of Physics. [doi:10.1063/1.3576920]

GaN_xP alloys belong to an interesting class of dilute nitrides that have recently attracted great attention owing to their fascinating physical properties, which arise from the large mismatch in atomic size and electronegativity between anion atoms.^{1,2} The pronounced effect of N on the band structure of GaP leads to a huge bowing in band gap energy and N-induced transformation from an indirect to quasidirect band gap,^{3,4} expected to largely intensify light emission. Thus, (In)GaN_xP holds great potential in optoelectronic applications.⁵ Moreover, GaNP with [N]~2% is lattice matched to Si, opening a window for fabrication of optoelectronic integrated circuits on Si wafers.^{6,7} Unfortunately, the presence of N is known to facilitate defect formation leading to efficient nonradiative recombination via defects, detrimental for performance of devices based on dilute nitrides.⁸

Hydrogen is known to have a large impact on the electronic structure and optical properties of GaNAs^{9–11} and GaNP.^{12,13} Here, post growth hydrogenation has been found to reverse alloy properties induced by the N presence, adding to a wealth of fascinating physical properties of dilute nitrides. Unfortunately, effects of hydrogenation on grown-in defects in these materials remain unknown. Due to its high chemical reactivity, H is generally known to efficiently interact with nearly all types of imperfections and impurities present in semiconductors.^{14,15} In most cases this results in *passivation* of defects, whereas H-induced defect activation is only rarely observed.^{16,17} The purpose of this work is to carry out a detailed investigation of the effects of postgrowth H treatment on defects and carrier recombination processes in GaNP epilayers, by employing photoluminescence (PL) and optically detected magnetic resonance (ODMR) techniques.

GaN_xP epilayers with N compositions of 0.6 and 0.8% were studied. They were grown at 520 °C by gas-source molecular beam epitaxy (MBE) on GaP substrates. Post-growth H treatment was performed at 300 °C by ion-beam irradiation from a Kaufmann source using a low H ion en-

ergy (100 eV) and current density of ~ 10 $\mu\text{A}/\text{cm}^2$. Even lower H ion energy of 20 eV was used for one of the GaN_{0.006}P_{0.994} epilayers. The H doses ranged between 2.7×10^{17} and 2×10^{18} ions/cm². To separate effect of H from that of thermal annealing, a piece of the GaN_{0.006}P_{0.994} epilayer was annealed at 300 °C without H treatment. Optical excitation was provided by the 532 nm line of a solid state laser and the resulting PL signal was dispersed by a grating monochromator and detected by a Si photodiode. ODMR experiments were performed at X- and Q-band (i.e., 9.142–9.215 and 34.7 GHz) under optical excitation by the 532 nm line of a solid state laser or the 351 nm line of an Ar⁺ laser. ODMR signals were measured as spin-resonance induced changes in PL intensity. Both PL and ODMR measurements were performed at 5 K.

Figures 1(a) and 1(b) show effects of postgrowth treatment with 100 eV H ions on low temperature PL spectra of the studied GaNP epilayers. In all samples, PL is dominated by excitonic emissions at N-related localized states.¹⁸ Post-

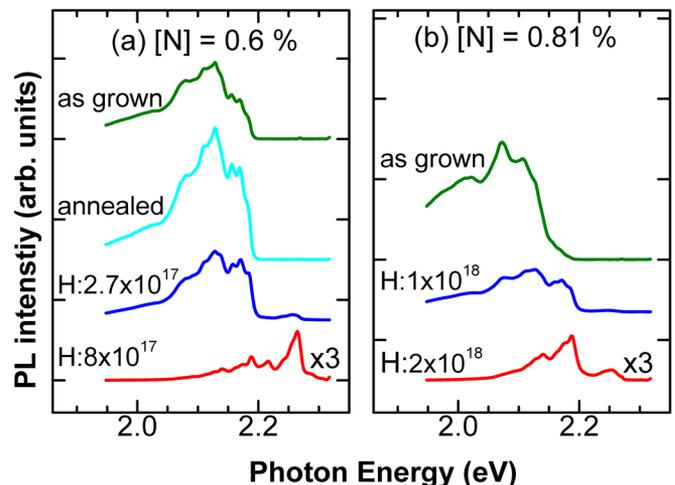


FIG. 1. (Color online) Typical PL spectra measured at 5 K from the studied GaNP epitaxial layers with and without the postgrowth thermal annealing or hydrogen treatment.

^{a)}Electronic mail: irb@ifm.liu.se.

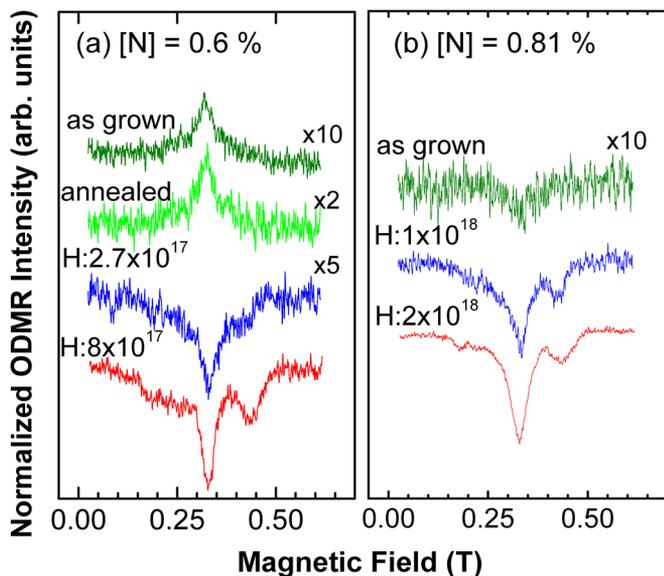


FIG. 2. (Color online) X-band ODMR spectra obtained at 5 K from the GaNP epilayers by monitoring the PL emissions shown in Fig. 1. The magnetic field is parallel to the [001] direction and ODMR intensity is normalized to the PL intensity. The energy of the H ions used in the H treatment is 20 eV in the lowest spectrum in (a), and 100 eV for the others.

growth hydrogen treatment with different H doses induces a monotonic blueshift in the alloy band gap energy, evident from the reappearance of the N-related emissions at the highest energy side of the PL spectra.^{12,13} The observed recovery of the band gap energy can be viewed as a decrease in the effective N concentration, such that the PL from the hydrogenated samples is similar to that of GaNP alloys with a lower N content.^{12,13} In addition to the blueshift, the H treatment also causes a strong decrease in the PL intensity indicating formation of competing recombination channels.

In order to obtain information on defects affecting PL and thus optical quality of the alloy, detailed ODMR studies were conducted. Typical ODMR spectra obtained by monitoring the excitonic emissions are shown in the Fig. 2. Several ODMR signals from different defects can be distinguished. To obtain information on physical properties of these defects, the ODMR spectra were analyzed by using a spin Hamiltonian $H = \mu_B g \mathbf{B} \cdot \mathbf{S} + A \mathbf{S} \cdot \mathbf{I}$. Here, μ_B is the Bohr magneton, \mathbf{B} is the magnetic field. The electronic g-factor and the central hyperfine parameter A are scalars here, since all observed ODMR signals are isotropic. \mathbf{S} and \mathbf{I} denote the electronic and nuclear spin of the studied defect, respectively.

ODMR spectra from as-grown samples are found to be very weak and contain a single line originating from defects with an effective electron spin $S=1/2$ and g-value of ~ 2 . A lack of a resolved hyperfine (hf) structure hampers chemical identification of these defects which, therefore, will not be further discussed in the paper. Thermal annealing alone does not introduce any ODMR signal, see Fig. 2(a). The H treatment, on the other hand, gives rise to several and substantially enhanced ODMR signals for both N compositions. A careful analysis of the spectra obtained at both X- and Q-band revealed that they contain several components originating from different defects (see Fig. 3). The first two components consist of a single ODMR line (denoted as L1 and L2) with their g-values given in Table I. Similar to the ODMR signals in the as-grown samples, chemical identifica-

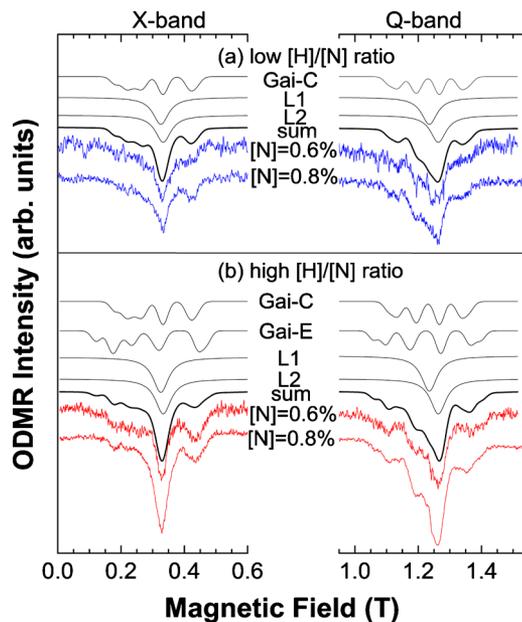


FIG. 3. (Color online) Typical X-band and Q-band ODMR spectra [the lower two curves in (a) and (b)] measured at 5 K and $\mathbf{B} \parallel [001]$ by monitoring the PL emissions shown in Fig. 1, from the H-treated GaNP epilayers with (a) a low and (b) a high $[H]/[N]$ ratio. The simulated ODMR spectra are displayed by the upper four curves in (a) and the upper five curves in (b), using the spin Hamiltonian parameters given in Table I.

tion of the related defects is not possible due to the lack of a resolved hyperfine structure. In addition to these single lines, we observe a rich pattern of lines spreading over a wide field range, with the most prominent peak at around 0.43 T in X-band. These multiple line structures can be attributed to the resolved hf structure arising from the interaction between the electron spin $S=1/2$ and the nuclear spin $I=3/2$ of an interstitial Ga_i atom in the core of the defect.¹⁹

Interestingly, the type of the Ga_i defects introduced by the H treatment is sensitive to the ratio between H and N concentrations, $[H]/[N]$, in the alloys (see Fig. 3). For the lower $[H]/[N]$, only one Ga_i -related defect (denoted as $\text{Ga}_i\text{-C}$) is observed. Its spin Hamiltonian parameters (listed in Table I) coincide with those determined for the defect under the same name revealed in MBE-grown $\text{GaN}_{0.013}\text{As}_{0.0997}$ epilayers subjected to postgrowth annealing at 700–850 °C.^{8,20} Therefore, an equivalent Ga_i -related defect may be involved in both cases. It should be noted that the $\text{Ga}_i\text{-C}$ defect has not been previously observed in GaNP alloys. After further addition of H, however, an additional Ga_i -related ODMR signal [see Fig. 3(b)] $\text{Ga}_i\text{-E}$ is observed with a larger hf splitting by about 30% as compared to that of $\text{Ga}_i\text{-C}$ (see Table I).

Let us now discuss possible mechanisms for the appearance of the Ga_i -related ODMR signals due to the H treatment. Emergence of Ga_i -related ODMR signals could either be due to a direct creation of Ga_i as a result of the H bombardment or H-induced activation of the Ga_i defects already present in the GaNP, or a combined effect of both. In the first case, the maximum energy that can be transferred between a 100 eV H ion and a Ga atom in GaNP is expected to be 5.6 eV in an elastic collision.²¹ This energy is below the threshold displacement energy of a Ga atom: ~ 8.8 eV.²² However, considering the large amount of H implanted and possibility of subthreshold defect formation^{23,24} direct introduction of Ga_i defects by H bombardment could still occur. In order to

TABLE I. Spin Hamiltonian parameters and ODMR line widths obtained from the best fit to the experimental ODMR results.

Defects	L1	L2	Ga _i -C	Ga _i -E
S	1/2	1/2	1/2	1/2
I	0	0	3/2	3/2
g	2.005	1.960	2.000	2.003
A (⁶⁹ Ga) × 10 ⁻⁴ cm ⁻¹	620	830
A (⁷¹ Ga) × 10 ⁻⁴ cm ⁻¹	788	1055
Linewidth (mT)	60	60	35	35

evaluate relevance of this mechanism, one of the samples was hydrogenated with 20 eV H ions. The ODMR spectrum from this sample is shown by the lowest curve in Fig. 2(a) and is identical to that observed after hydrogenation with 100 eV H ions, in spite of five time decrease in the H ion energy. This rules out the bombardment-induced creation of Ga_i.

Alternatively, H treatment could also serve to activate Ga_i defects that were readily present in the epilayers but were inactive in carrier recombination before the treatment. The activation could be accomplished in several ways. It may be related to the H-induced reopening of the alloy band gap, that alters the energy position of the Ga_i-related level with respect to the band edges, e.g., from resonance in the conduction band to within the band gap, making it active or more efficient in carrier recombination. However, judging from the PL spectra (Fig. 1), the band gap energy of the untreated GaN_{0.006}P_{0.994} alloy is similar to that of the GaN_{0.0081}P_{0.9919} after the H treatment with the dose of 1 × 10¹⁸ cm⁻². Yet, the Ga_i-C defect is only detected in the latter sample. This enables us to rule out the band gap reopening alone as the mechanism. Alternatively, H incorporation may affect the Fermi level position in the alloy, changing the charge state of the Ga_i complexes to the spin-active one and, therefore, making possible their detection via ODMR. Another possibility is formation of complexes involving Ga_i and H atoms, facilitated by a high H concentration. This may result in a change in the position of the defect energy level and in the spin-active charge state, thereby activating the defects in carrier recombination monitored by ODMR. The fact that the appearance and type of the Ga_i defects depend on the [H]/[N] ratio could be explained, e.g., if the Ga_i is a part of a defect complex that involves N in a neighboring position. Trapping of H by the N atom could activate the resulting Ga_i defects, such as Ga_i-C at the lower [H]/[N]. Further addition of H should result in bonding of more H atoms at the defects, thereby altering their electronic properties and leading to, e.g., the appearance of Ga_i-E. The formation of the aforementioned complexes could occur as a result of either diffusion of H itself or an increased mobility of the Ga_i (or its partners in the complex) owing to an H-induced decrease in the energy barrier for their migration. The former is believed to be more likely, considering the known high mobility of H in semiconductors.

Now we shall briefly discuss the role of the observed H-induced defects in carrier recombination. Based on the sign of an ODMR signal, one can often distinguish whether the corresponding defect is directly involved in the monitored emission or it participate in competing recombination processes.^{25,26} All hydrogen-induced ODMR signals, which are detected via the near-band-edge PL, have a negative sign, i.e., leads to a decrease in the PL intensity. This unambigu-

ously proves that the defects act as efficient recombination centers that strongly compete with the monitored PL, providing an explanation for the degraded efficiency of the PL emissions observed after the H treatment, Fig. 1.

In conclusion, we have studied effects of postgrowth H treatment on defects and their recombination processes in GaNP epilayers by employing the PL and ODMR techniques. In addition to reopening of the band gap, the H treatment has been found to activate several defects that act as recombination centers and efficiently compete with the near-band-edge light emissions. Two of these defects have been shown to contain a Ga interstitial atom in their cores. Neither of these Ga_i defects has previously been detected in GaNP. Their exact configurations, judging from the characteristic hyperfine splitting, depend on the ratio between H and N contents present in the samples. This may indicate involvement of N and also H atoms within the defect complexes.

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