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Dual-wavelength excited photoluminescence spectroscopy of deep-level hole traps in Ga(In)NP

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By employing photoluminescence (PL) spectroscopy under dual-wavelength optical excitation, we uncover the presence of deep-level hole traps in Ga(In)NP alloys grown by molecular beam epitaxy (MBE). The energy level positions of the traps are determined to be at 0.56 eV and 0.78 eV above the top of the valance band. We show that photo-excitation of the holes from the traps, by a secondary light source with a photon energy below the bandgap energy, can lead to a strong enhancement (up to 25%) of the PL emissions from the alloys under a primary optical excitation above the bandgap energy. We further demonstrate that the same hole traps can be found in various MBE-grown Ga(In)NP alloys, regardless of their growth temperatures, chemical compositions, and strain. The extent of the PL enhancement induced by the hole de-trapping is shown to vary between different alloys, however, likely reflecting their different trap concentrations. The absence of these traps in the GaNP alloy grown by vapor phase epitaxy suggests that their incorporation could be associated with a contaminant accompanied by the N plasma source employed in the MBE growth, possibly a Cu impurity. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4905274>]

I. INTRODUCTION

Alloying of gallium phosphide (GaP) with nitrogen (N) leads to a giant bandgap bowing^{1–4} and N-induced transformation from an indirect to a quasi-direct bandgap,^{4,5} largely improving radiative efficiency. Further alloying with In, resulting in GaInNP, adds additional freedom in bandgap and strain engineering desirable in exploring hetero- and quantum-structures for high-performance devices. This makes the Ga(In)NP alloys attractive for optoelectronic applications,^{1,2} such as in light-emitting devices that cover the amber spectral range and novel intermediate-band solar cells.^{6,7} The fact that GaNP can be lattice matched to Si further extends the range of potential applications that will integrate superior optoelectronic properties of III-V semiconductors with the mainstream Si microelectronics. Before the full potential of this materials system can be realized, however, a number of key material and physical properties need to be addressed. One of the most important problems is defects (including impurities), which are more profound in this class of highly mismatched materials due to the large disparity in the size and electronegativity between the anion atoms of the alloys as well as the required non-equilibrium growth conditions. Defects in these dilute nitrides are known to often act as efficient non-radiative recombination centers and carrier traps, severely deteriorating optical and transport properties of the materials and hindering them from practical applications.^{8–11} On the other hand, extraordinary room-temperature spin functionalities promising for spintronic applications were also demonstrated by spin engineering of certain defects in Ga(In)NAs alloys^{12–16}—another family of dilute nitrides. A present challenge in development of high-quality Ga(In)NP alloys lies in understanding and control of defects introduced during growth. Previous studies

using the optically detected magnetic resonance (ODMR) technique have identified Ga interstitials commonly found in Ga(In,Al)NP^{9,17–22} and related GaNAsP (Ref. 23) and Ga(In,Al)NAs alloys,^{10,24–26} as well as P-related interfacial/surface defects in GaNP/GaP heterostructures²⁷ and core/shell nanowires (NWs),²⁸ as important defects in carrier recombination that can severely limit efficiencies of optoelectronic and photovoltaic devices. As to carrier traps that are also important in device applications of Ga(In)NP, very little is known so far.¹¹

In this work, we carried out a comprehensive and systematic study of defects in the Ga(In)NP alloys that act as carrier traps and can affect light-emitting efficiency. This was done by means of purely optical and nondestructive techniques of dual-wavelength excited photoluminescence (PL) (DEPL), DEPL excitation, and time-resolved DEPL. These methods are especially suited for detection of carrier traps that are important in light emissions and carrier extraction. This is because PL under a primary optical excitation above the bandgap energy (denoted by P1 below) is directly monitored, see Fig. 1, while a secondary light with a photon energy below the bandgap (denoted by P2 below) excites holes (or electrons) from the traps to the valence band (VB) (or the conduction band (CB)). In this way, only those traps with a significant impact in free carrier concentrations and thus PL are selected in the study.

II. SAMPLES AND METHODS

Eight Ga(In)NP/GaP structures grown on (001) GaP substrates and two GaNP/Si structures grown on Si substrates were chosen for this study. They were grown by gas-source or solid-source molecular beam epitaxy, denoted by

FIG. 1. A schematic illustration of the proposed model for the hole trapping and NIR-induced hole de-trapping processes, marked by the thin blue arrows and the thick red arrows, respectively. E_N denotes the N-related localized states that give rise to the PL emissions monitored in this study. E_A and E_B represent two hole trap levels with different energy positions within the bandgap. E_{CB} and E_{VB} denote the conduction band and valence band edge, respectively.

GS-MBE or SS-MBE, using a plasma-assisted nitrogen source. The most important growth parameters of the structures are summarized in Table I. The N compositions of the alloys were determined by high resolution X-ray diffraction measurements. The studied structures can be grouped into five pairs, with each having a specific aim. The first pair comprised two GaNP epilayers with a large difference (28 times) in N concentration, employed to study the effect of N. The second pair was obtained after the first pair was treated by post-growth hydrogenation with a Kaufmann source at 300 °C, using a low H ion energy (100 eV) and with a dose of $[H] = 1 \times 10^{18} \text{ cm}^{-2}$. Details of the hydrogenation can be found elsewhere.²⁶ For the third and fourth pairs, the focus was on alloying with In and doping by shallow donors and acceptors, respectively. The fifth pair of samples consists of a GaNP epilayer grown on a (001) Si substrate and GaNP/GaP shell/core NWs grown on a (111) Si substrate in order to study trap formation in the GaNP alloys grown on Si. A detailed description of the NW growth process can be found in Refs. 29 and 30. To examine whether or not the introduction of the studied carrier traps was directly promoted by the

MBE growth, we also studied an undoped GaNP epilayer grown by vapor phase epitaxy (VPE) as a reference sample. The details of the VPE growth can be found in Ref. 23.

DEPL measurements were performed using either the 532 nm of a solid-state laser or the 632.8 nm line of a He-Ne laser as the primary excitation source, with a photon energy above the bandgap energy of the studied Ga(In)NP alloys. One of the following three near-infrared (NIR) light sources was used for the secondary excitation: the 870–950 nm line from a Ti:Sapphire laser, the 915 nm line from a solid-state laser diode, or 800–2400 nm light from a tungsten halogen lamp which was dispersed through a 0.2-m single grating monochromator (used in DEPL excitation measurements). Laser spots focused onto the sample were typically less than 0.5 mm in diameter. PL signals were dispersed by a 0.8-m double grating monochromator and detected by a Si photodiode. In time-resolved DEPL experiments, an optical chopper and/or a liquid crystal retarder were used for the amplitude modulation of the excitation beams and the resulting DEPL transient signals were recorded by a digital oscilloscope. ODMR measurements were performed at 5 K at a microwave (MW) frequency of 9.21 GHz (X-band). The 532 nm line of a solid-state laser was used as an excitation source. ODMR signals, which represent MW-induced changes of the PL intensity,³¹ were detected by a Si detector when monitoring the PL emissions within the visible spectral range of 570–810 nm.

III. RESULTS AND DISCUSSION

A. PL enhancement induced by the secondary NIR excitation and its origin

Under the above-band-gap optical excitation (P1) alone, all studied Ga(In)NP structures exhibit strong PL emissions in the visible spectral range (the dashed lines in Fig. 2(a)), known to arise from recombination of excitons bound at N-related localized states and their phonon replica.^{32–34} Additional optical excitation with below-bandgap photons (P2) results in a strong increase in the intensity of these PL emissions in the MBE-grown structures (the solid lines in Fig. 2(a)).

TABLE I. List of the Ga(In)NP samples studied in this work, with the main growth parameters and the hydrogen dose used in the post-growth hydrogenation. The numbers 2.5 and 18 in the parenthesis refer to the thicknesses of the $\text{Ga}_{0.45}\text{In}_{0.55}\text{N}_{0.016}\text{P}_{0.984}$ QW and $\text{GaN}_{0.02}\text{P}_{0.98}$ barrier layers in the MQW structure. The maximum values of the PL enhancement factor Q induced by the excitation with below-bandgap light are given in the last row.

Series	(1) GaNP/GaP		(2) GaNP:H/GaP		(3) GaInNP/GaP		(4) GaNP:(Mg,S)/GaP		(5) GaNP/Si		(6) VPE-GaNP/GaP
Sample No.	#2666	#L012	#2666+H	#L012+H	#L034	#L0310	#L037	#L038	L001	S200	#15
Growth method	GS-MBE	SS-MBE	GS-MBE	SS-MBE	SS-MBE		SS-MBE		SS-MBE	GS-MBE	VPE
Growth T (°C)	520	590	520	590	460	590	590	590	420	564	610–650
[N] (%)	0.05	1.4	0.05	1.4	1.8	1.6/2	0.6	0.6	1.8	1	0.6
[In] (%)	...	...	...	...	5	55/0	...	...	...	...	...
Structure	epi	epi	epi	epi	epi	MQW	epi	epi	epi	NWs	epi
Thickness (nm)	250	100	250	100	100	(2.5/18) × 3	100	100	1500	1000	100
GaP cap (nm)	...	100	...	100	20	20	20	20	...	...	200
Shallow doping (10^{18} cm^{-3})	...	...	...	...	...	...	p-type Mg:1.2 n-type S:1.8		...	...	...
Post-growth H dose (10^{18} cm^{-3})	...	...	1	1	...	...	...	...	...	...	...
Q (%)	20	20	16	7	25	22	17	2	0	2	0

FIG. 2. (a) Representative PL spectra from three different structures containing the Ga(In)NP alloys, obtained at 5 K under the 532-nm excitation above the bandgap energies (the dashed curves) and under the dual excitation (the solid curves) of both above and below bandgap. (b) The P2-induced enhancement factor Q of the PL emissions shown in (a). The inset shows the evolution of the PL intensity with increasing temperature for the sample #L0310. The power of the below-bandgap excitation P2 was 95 mW for the 0.8–1.0 eV light or 170 mW for the 1.53 eV light. The power of P1 (the 532-nm excitation) was 5 mW.

The PL intensity under the dual excitation, PL_{P1+P2} , was up to 25% higher compared to the PL intensity observed under the P1 excitation alone, PL_{P1} . The magnitude of this effect will be described below by a factor Q in percentages of the PL enhancement, defined by

$$Q = 100 * \left(\frac{PL_{P1+P2}}{PL_{P1}} - 1 \right). \quad (1)$$

From the spectral dependence of Q displayed in Fig. 2(b), the PL enhancement occurs for the entire PL emissions with a somewhat larger Q for the deeply localized N states on the low energy side.

There are in principle several possible physical mechanisms that could lead to this PL enhancement. The first possibility is that P2 with a below-bandgap photon energy could generate free electrons and holes via defect-mediated up-conversion or two-photon nonlinear processes,^{35,36} leading to enhanced PL emissions. This possibility is not plausible here because photo-excitation with only the NIR light P2 did not result in any sizable PL emissions. The second possibility

is that the excitation P2 merely causes an increase in lattice temperature, which in turn affects the PL intensity as it is usually sensitive to temperature. To test this scenario, we studied thermally-induced changes of the PL intensity under the P1 excitation alone. As it can be seen from the inset in Fig. 2(b), the intensity of the monitored PL emissions monotonously decreases with increasing temperature. This safely rules out heating induced by the P2 excitation as the main mechanism for the PL enhancement in the DEPL experiments. We can also exclude the possibility that the observed enhancement was due to increased carrier feeding from the GaP buffer layer or GaP substrate. This is based on the observed significant difference in Q factors between the p- and n-type doped GaNP/GaP structures, despite the fact the GaP buffer layer and substrate of the two structures (the 4th pair of samples in Table I) are identical. This conclusion is further supported by our finding that the P2-induced increase in the PL intensity is also observed when the energy of the P1 excitation is below the bandgap of GaP, e.g., by using the 632.8 nm line of a He-Ne laser for excitation of the $Ga_{0.45}In_{0.55}N_{0.016}P_{0.984}/GaN_{0.02}P_{0.98}$ MQW (not shown here). These experimental findings imply that the process enhancing the PL intensity must take place inside the Ga(In)NP alloys, which is not related to lattice heating by P2. A possible effect of surface depletion (leading to a so-called PL dead layer) that may be altered by NIR excitation can also be safely ruled out because the NIR-induced PL enhancement was observed in the samples with or without a GaP cap layer, as demonstrated by the first pair of the samples given in Table I. This leads us to the most plausible explanation for the observed PL enhancement induced by the secondary NIR excitation, that is, photo-excitation of carriers trapped at defect levels within the Ga(In)NP bandgap.

B. The photo-excitation threshold of the PL enhancement: Energy level positions of the traps

In order to determine the energy level positions of the carrier traps responsible for the observed strong PL enhancement under the secondary light excitation P2, we measured Q as a function of photon energy of P2. The results from two different Ga(In)NP epilayers are shown in Fig. 3. Two threshold energies, $E_A = 0.56$ and $E_B = 0.78$ eV, which correspond to the energy positions of the relevant defect levels from either the VB edge or the CB edge, are clearly seen and are identical for both samples. This is despite the fact that these two Ga(In)NP epilayers exhibit a large difference in their bandgap energies, evident from the observed large difference in the energies of their PL emissions shown in Fig. 2(a), which is known to be mainly due to their different magnitudes of the CB downshift as a result of different N compositions. Therefore, the observed identical threshold energies E_A and E_B in these two alloys imply that the corresponding photo-excitation processes occur between the two deep-levels and the VB. In other words, there exist two *hole* traps with their energy levels located at 0.56 and 0.78 eV above the VB edge as illustrated in Fig. 1. It should be pointed out that even though E_A and E_B have identical values for these two alloys, the absolute values of Q are different between

FIG. 3. DEPL excitation spectra of two Ga(In)NP alloys, obtained at 5 K by monitoring at 627 nm (for the sample #L034) and 592 nm (for the sample #2666) of the PL emissions. The photo-excitation threshold energies are marked by the vertical dashed lines. The 532 nm laser line was used as P1 with a power of 2 mW. The power range of P2 was about 1–15 mW.

them. As the hole de-trapping rate scales with the trapped hole concentration at a given trap level, the different Q values observed in these two alloys could be taken as an indication for their different concentrations of the hole traps. It is also interesting to note that the ratio between the Q values after reaching each of the two threshold energies is rather similar in these two alloys. This may imply a similar ratio in the product of the photo-excitation cross-section and trap density between the two traps in both alloys. Although this could merely be a coincidence, it could also indicate that the traps in question might have the same origin or are somehow linked to each other as will be further discussed below in connection with possible origins of the defects responsible for the hole traps.

C. Excitation power dependence

The observed PL enhancement by de-trapping of holes from defects is determined by the difference in the steady-state concentrations of VB holes between simultaneous P1 and P2 excitation and P1 excitation alone. It is governed by a detailed balance in the hole trapping and P2-induced de-trapping processes. The hole trapping scales with the number of VB holes that are available to be trapped and the concentration of the unoccupied hole traps that can receive holes from the VB. On the other hand, the P2-induced de-trapping should be proportional to the optical cross-section that is specific for a given trap, the density of optical excitation P2 that releases carriers from the trap, and the concentration of trapped holes at the defect. An increase in excitation power of P2 promotes de-trapping and at the same time increases trapping as the densities of VB holes and the unoccupied hole traps increase due to de-trapping. As a result, the expected dependence of Q on the excitation power of P2 should be highly nonlinear. In order to verify the role of the hole de-trapping processes in the studied Ga(In)NP alloys, we studied excitation power dependence of Q . This

was done by measuring the Q factor as a function of P2 incident power at three different P1 excitation power levels. As shown in Fig. 4, Q is found to be a strong function of the P2/P1 ratio. It first increases when P2/P1 increases over three orders of magnitude within the range $P2/P1 < 10$. As expected, the observed increase is nonlinear for all three excitation powers of P1. With a further increase in P2/P1 over the range of $10 < P2/P1 < 100$, Q starts to saturate. This can be attributed to the situation when the re-trapping of holes from the VB to the traps has increased to such a level that it completely compensates the P2-induced de-trapping as more and more trapped holes have been released from the defects to the VB by increasing P2. The saturation Q value is thus determined by the maximum concentration of holes that can be photo-excited by P2 from the defects in the steady-state condition under both P1 and P2 excitation.

It is interesting to note that the P2/P1 ratio required to reach the saturation of Q , as well as the overall dependence of Q on P2/P1, is nearly identical at all P1 values that varied by more than 20 times. We suggest that this is because the share of photo-excited holes between those participating in the monitored PL and those being trapped by the defects (depending on the defect concentrations) is nearly fixed at all excitation power values of P1 for a given sample. Stronger P1 means a higher density of the trapped holes, which subsequently requires proportionally stronger P2 to de-trap the holes from the defects to reach the same degree of PL enhancement. The saturation value of Q should then somewhat reflect the extent of holes that were trapped by the defects with respect to the total number of photo-generated holes by P1, which is $\sim 25\%$ in the sample shown in Fig. 4. The saturation values are found to vary among different Ga(In)NP alloys, see Table I, which indicates different concentrations of the studied hole traps. When $P2/P1 > 100$ for the sample shown in Fig. 4, Q at the lowest P1 seems to start to decrease. We suggest that this is due to increasing importance of other competing processes under the same below-bandgap excitation P2 when the absolute number of the

FIG. 4. (a) The measured Q values as a function of the P2/P1 ratio (the symbols) at three different P1 as specified, obtained at 5 K with a P2 wavelength of 870 nm.

trapped holes at the studied defects has significantly decreased. A plausible competing channel could be photo-excitation of the electrons from N-related states that gives rise to the monitored PL emissions, thereby reducing the PL intensity.³⁷

D. Dynamics of the trapping and photo-induced de-trapping processes

In order to shed light on the dynamics of the trapping and de-trapping processes, we carried out a detailed time-resolved DEPL study. Fig. 5 shows the measured time variations of the PL intensity under various combinations of pulsed P1 and P2 excitation. As it can clearly be seen from the region III of the experimental curve (the top curve in Fig. 5), both rise and decay of the PL intensity under the pulsed P1 excitation alone are faster than the experimental resolution of $\sim 100 \mu\text{s}$. This is in agreement with our earlier time-resolved PL study of GaNP alloys by using ultrafast laser spectroscopy, from which the rise and decay times were determined to be in the range of 1 and 150 ns, respectively.⁵ Equally fast rise and decay were also observed when P1 is switched on and off in the presence of cw P2 excitation, see the region I of the experimental curve in Fig. 5. All these observations can be attributed to fast photo-generation of excitons at the light-emitting N-related centers by P1 and short lifetimes of these excitons. The observed slow decrease in the PL intensity during the P1 pulse seen in region I can be explained as follows. At the instant when P1 is switched on, the number of VB holes provided by P2-induced de-trapping is determined by the steady-state value under the P2 excitation alone. This value is higher than the steady-state value under both P1 and P2 excitation (represented by the saturation value of $\text{PL}_{\text{P1+P2}}$ shown in the region II of Fig. 5), as P1 provides more VB holes that enhance the hole trapping. As a result, the PL intensity undergoes a gradual transition between the two values during the P1 pulse, of which the transition speed is governed by the hole trapping rate that is supported by the experimental decay curve due to the hole

FIG. 5. The topmost curve is the time variation of the PL intensity (detected at the emission energy of 2.1 eV) under various combinations of the pulsed P1 and P2 excitation, measured at 5 K from the Mg-doped $\text{Ga}_{0.006}\text{P}_{0.994}$ alloy. The lowest two curves show the pulse sequences of the P2 (at 1.355 eV) and P1 (at 2.33 eV) excitation beams. The PL intensities PL_{P1} and $\text{PL}_{\text{P1+P2}}$ are defined in the figure.

trapping shown in the region II of Fig. 5. We should point out that photo-excitation with only the P2 light did not result in any sizable PL emissions, as shown in the region I of Fig. 5, confirming our results from the cw PL experiments presented above.

When the samples were exposed to a constant P1 excitation, an excitation pulse of P2 yields a noticeably slower rise and decay of the PL intensity as seen from the region II of Fig. 5. The observed rise of the PL intensity from PL_{P1} to $\text{PL}_{\text{P1+P2}}$ should directly reflect the dynamics of the hole de-trapping when P2 is switched on, whereas the fall from $\text{PL}_{\text{P1+P2}}$ back to PL_{P1} when P2 is switched off stems from the hole re-trapping by the defects. Unlike that under above-bandgap excitation P1, the rise and decay of the PL intensity due to an additional below-bandgap excitation pulse P2 occur in the range of milliseconds to tens of milliseconds, which are about five to six orders of magnitude slower than that observed under only the pulsed P1 excitation. The observed decay dynamics is identical to the PL decay during the P1 pulse in the region I of Fig. 5, supporting our conclusion that both are related to the hole trapping process.

To understand the detailed dynamics of the hole de-trapping and re-trapping processes, we studied the rise and decay of the PL intensity as a function of powers of both P1 and P2 excitation. The results are shown in Fig. 6. The rise can approximately be described by a simple single exponential function, shown by the solid curves in Figs. 6(a) and 6(b). The determined rise time is found to be nearly unaffected by the P1 excitation power (Figs. 6(a) and 6(c)). In sharp contrast, it speeds up at higher excitation powers of the below-gap excitation P2 (Figs. 6(b) and 6(d)), approximately as a function of $P2^{-0.5}$. The de-trapping rate of holes from

FIG. 6. (a) and (b) Typical temporal evolutions of the PL emission when the P2 excitation (915 nm) is switched on at $t \sim 0.07$ s and switched off at $t \sim 0.6$ s. The solid lines are the fittings of the PL rise (by a single exponential function) and decay transients (by a stretched exponential function). The rise and decay time constants are displayed as a function of (c) P1 and (d) P2. All measurements are done on the Mg-doped GaNP structure (#L037).

the defects by P2, which is inverse to the rise time, should be directly proportional to the photon flux of the excitation light P2 and the density of the trapped holes. This explains the observed strong effect of P2 on the rise time. P1 can indirectly affect the rise time as it plays a key role in the number of photo-excited holes that are subject to trapping by the defects. In contrast to the rising, the decay caused by the hole re-trapping clearly does not follow a simple exponential law, a rather common feature for earlier persistent photoconductivity and DEPL experiments in other semiconductors.³⁸ This can be understood by the fact that the re-trapping rate scales with the density of the empty traps, which continuously decreases during the hole re-trapping process. To obtain an approximate quantitative description of the decay time such that it can be compared under different excitation conditions, we modeled the decay by assuming a stretched-exponential function

$$PL(t) = (PL_{P1+P2} - PL_{P1}) e^{-(\frac{t}{\tau})^b}. \quad (2)$$

Here, τ is the DEPL decay time, and b is the stretching exponent, with $0.48 < b < 1$ reflecting dispersive properties of the trapping rates. As shown in Fig. 6, the decay accelerates by increasing P1 and P2 excitation power. It has a somewhat stronger dependence on P1, however. This is consistent with the fact that the density of the empty traps is determined by both the P1 and P2, namely, the former determines the number of defects available to trap holes and the latter decides how many of these available traps are empty.

E. Temperature dependence

The effect of lattice temperature on the observed PL enhancement due to hole de-trapping was investigated by measuring the Q values as a function of sample temperatures ranging from 5 to 160 K, as shown in Fig. 7(a) for two different GaNP alloys. Q was found to be nearly constant below 100 K, followed by a rapid decrease at temperatures above 100 K. Above 160 K, Q became negligibly small. We suggest that this is probably caused by a thermally activated acceleration of the hole trapping and thermal emission of holes from the traps, which are known for other semiconductors to exponentially increase with increasing temperature. These

FIG. 7. Temperature dependence of (a) the Q values and (b) the rise and decay times. The solid line is just a guide to the eye. The power of P1 and P2 was 50 and 300 mW, respectively.

processes could eventually become more efficient than the P2-induced de-trapping process, thereby overshadowing the effect of the latter. This suggestion seems to be consistent with a drastic shortening of the hole trapping time (i.e., the decay time) over the sample temperature range, see Fig. 7(b), which is much more pronounced as compared with the thermal variation of the P2-induced de-trapping time. We cannot completely rule out other processes that could also possibly contribute to the observed decrease in the Q factor with rising temperature. One of such processes is thermally activated emission of electrons from the N-centers to the conduction band where they become more mobile at high temperatures and could recombine with the holes trapped at the defects.

F. Formation and possible nature of the hole traps

In an attempt to understand formation and possible chemical identity of the defects responsible for the observed hole traps, effects of growth temperature, alloying with N and In, shallow doping, and post-growth treatments on Q were studied and are summarized in Table I. No clear correlation was found between Q and growth temperature, the N and In compositions, or strain, even for the highly strained $\text{Ga}_{0.45}\text{In}_{0.55}\text{N}_{0.016}\text{P}_{0.984}/\text{GaN}_{0.02}\text{P}_{0.98}$ MQW structure. This implies that Q is largely insensitive to these growth and material parameters, indicating that the observed traps are common grown-in defects in these MBE-grown Ga(In)NP alloys.

Post-growth treatments, such as rapid thermal annealing (RTA) and post-growth hydrogenation, are commonly used to passivate various defects and traps in semiconductors. Both RTA (1 min at 700 °C) and post-growth H treatments were found to reduce the Q values, but they do not completely quench the effect of the PL enhancement (see Table I). The difference in the degree of reduction of Q between the two hydrogenated samples is due to their difference in the extent of hydrogen passivation of the hole traps. This could be attributed to consumption of hydrogen by other defects in each sample. Since the two hydrogenated samples were grown at different temperatures, with different N compositions, and by different MBE methods, namely, solid-source MBE vs. gas-source MBE, grown-in defects or residual impurities in these two samples are likely different in terms of both types and concentrations. On the other hand, Q was negligibly small in the structures which were either (i) n-type doped or (ii) grown on Si substrates (see Table I and Fig. 8). The presence of shallow n-type dopants could influence the studied PL enhancement effect by charge compensation via electron transfer³⁹ that annihilates with the holes trapped at the defects. By annihilating electron-hole pairs, this transfer process also acts as a competing non-radiative recombination channel³⁹ that could provide an explanation for the observed weaker PL intensity in the n-type sample. For the structures grown on Si substrates, on the other hand, the GaNP alloys could possibly be unintentionally n-type doped as a result of diffusion of Si atoms from the substrate. In view of charge compensation, the p-type doping by

FIG. 8. (a) Representative PL spectra taken at 5 K from the $\text{GaN}_{0.006}\text{P}_{0.994}$ alloys doped with either S (the thin line) or Mg (the thick line). (b) Spectral dependence of the Q factors for the two samples.

shallow acceptors should not destroy the PL enhancement effect induced by the hole traps. On the contrary, it may even promote the effect as it can increase the number of holes at the traps via hole transfer from the shallow acceptors.

In order to shed light on possible defects present in the alloys, we resorted to magnetic resonance techniques, in particular, the ODMR technique that has the required sensitivity for studies of defects in thin films and quantum structures.^{27,31,40,41} Previous ODMR studies^{9,17–22} have shown that two different species of Ga self-interstitials ($\text{Ga}_i\text{-A}$ and $\text{Ga}_i\text{-B}$) are commonly found in $\text{Ga}(\text{In})\text{NP}$, and dominate in their ODMR spectra. If the studied traps give rise to an ODMR signal in one of the charge states before or after the P2-induced excitation of the trapped holes, a change in their ODMR spectra would be observed when the P2 excitation is added to the primary P1 excitation. This hypothesis was tested and the results are depicted in Fig. 9, for a representative case of the $\text{Ga}_{0.45}\text{In}_{0.55}\text{N}_{0.016}\text{P}_{0.984}/\text{GaN}_{0.02}\text{P}_{0.98}$ MQW structure. Unfortunately, no difference in the ODMR spectra was observed upon additional P2 excitation. This finding indicates that neither $\text{Ga}_i\text{-A}$ nor $\text{Ga}_i\text{-B}$ is taking part in the studied hole trapping and de-trapping processes. It also implies that the trapping, photo-induced de-trapping, and recombination processes associated with the hole traps are not spin dependent, such that the involved defects eluded detection by ODMR.

Though no positive experimental identification on the origin of the studied hole traps can be obtained in the present study, a comparison of our results with reported defects in

FIG. 9. ODMR spectra from the $\text{Ga}_{0.45}\text{In}_{0.55}\text{N}_{0.016}\text{P}_{0.984}/\text{GaN}_{0.02}\text{P}_{0.98}$ MQW structure, obtained by detecting the visible PL and using only above bandgap excitation P1 with the wavelength of 532 nm (the solid curve) and the dual excitation with 532 and 870 nm (the dashed curve). The ODMR intensity is normalized by the PL intensity.

the literature yielded useful information on possible candidates. Several traps have been observed and identified in GaP:N .⁴² N-related traps are commonly observed with photo-ionization energies in the range of 0.36–0.46 eV. It should be noted that the nitrogen-related defects are known to give rise to *electron* traps. Moreover, their photo-ionization energies greatly deviate from the values of 0.56 eV and 0.78 eV determined for the hole traps in our case. The N-related centers can therefore be excluded here. Oxygen in GaP, substituting phosphorus in the group-V sublattice, yields two deep-levels with the bandgap.⁴² Though the absolute values of their photo-ionization threshold energies are close to that of the studied hole traps, the O_P donor is a deep donor in GaP yielding two electron trap levels of which the photo-ionization threshold energies are measured from the CB. Therefore oxygen can also be ruled out. This conclusion is further justified by secondary ion mass spectroscopy (SIMS) of the studied structures, which shows that the concentration of O in the #2666 sample is two orders of magnitude higher than that in the rest of the samples, which is not correlated with the observed Q values.

In copper-diffused GaP, Cu introduces *two* levels in the GaP band gap, namely, the B level with the energy of ~ 0.7 eV and the A level with the energy of ~ 0.5 eV relative to the *VB top*.⁴³ These energy values match well with the optical threshold energies of the hole traps in our studied $\text{Ga}(\text{In})\text{NP}$ alloys. In addition, the total charge in the VB associated with the trap A and trap B was found to be roughly the *same*.⁴² This is in line with the observation of a similar increase in Q after reaching each of the two optical thresholds, i.e., about the same number of carriers is photo-ionized from each trap. Furthermore, doping with S shallow donors was observed to reduce the photo-ionization of the trap B by one order of magnitude, in line with our observation of a reduced Q-value upon doping with S. Thus, based on the observed stark similarities between Cu in GaP and the hole

traps in our studied Ga(In)NP alloys in (i) the two hole trap levels, (ii) the photo-excitation threshold energies, (iii) a fixed ratio of photo-excited holes from the traps, and (iv) suppressed photo-excitation of the trapped holes upon doping with S, the observed traps are tentatively assigned to a defect center involving copper.

Though Cu impurities are not commonly observed in MBE-grown N-free GaP, they have been reported in MBE-grown GaNAs in concentrations $>5 \times 10^{15}/\text{cm}^3$.⁴⁴ Based on a depth-resolved distribution of these hole traps, the introduction of Cu impurities was shown to be connected with the operation of the nitrogen plasma cell during GaNAs growth. We believe that this could apply as well to our case of the MBE-grown Ga(In)NP alloys. This suggestion is supported by a parallel study of a GaNP epilayer grown by VPE that did not involve an N plasma source, where no PL enhancement was observed (see Table I). We should point out that this VPE sample is undoped, similar to the MBE-grown undoped GaNP/GaP samples (the first pair in Table I). The observed stark contrast between the VPE and MBE samples in the Q value can therefore be taken as clear evidence for the absence of the hole traps in the former.

IV. CONCLUSION

To summarize, we have shown that a strong enhancement (up to 25%) of the PL emissions in the visible spectral range is observed in the MBE-grown Ga(In)NP/GaP alloys upon illumination by a secondary NIR light below the bandgap energy of the alloys. Based on a combined study of DEPL, DEPL excitation, time-resolved DEPL and ODMR, we uncovered two deep-level hole traps at 0.56 and 0.78 eV above the VB top to be responsible for the observed NIR-induced PL enhancement of the Ga(In)NP alloys. Our time-resolved DEPL studies revealed that the hole trapping and NIR-induced de-trapping processes occur on the time scale of $\sim$ tens of milliseconds. The observed traps were shown to be common in both gas-source and solid-source MBE-grown Ga(In)NP alloys, insensitive to growth temperatures ranging from 460 °C to 590 °C, N and In compositions and strain. Based on many similarities between the studied hole traps and the Cu impurity in GaP, we suggest Cu as a possible origin of the observed traps that originate from contamination by the nitrogen plasma source employed in the MBE growth.

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