IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Defects in dilute nitrides

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2004 J. Phys.: Condens. Matter 16 S3027

(http://iopscience.iop.org/0953-8984/16/31/003)

View the table of contents for this issue, or go to the journal homepage for more

Download details:
IP Address: 129.252.86.83
The article was downloaded on 27/05/2010 at 16:20

Please note that terms and conditions apply.

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **16** (2004) S3027–S3035 PII: S0953-8984(04)76861-7

Defects in dilute nitrides

I A Buyanova[1], W M Chen[1] and C W Tu[2]

[1] Department of Physics and Measurement Technology, Linköping University, 58183 Linköping, Sweden

[2] Department of Electrical and Computer Engineering, University of California, La Jolla, CA 92093-0407, USA

Received 1 March 2004
Published 23 July 2004
Online at stacks.iop.org/JPhysCM/16/S3027
doi:10.1088/0953-8984/16/31/003

Abstract

An overview of our present knowledge and understanding of defects in dilute nitrides will be provided and their important roles in determining the success of dilute nitrides for optoelectronic device applications will be underlined. A brief summary of experimental results of defects by various techniques reported so far in the literature will be given. Our recent results from optically detected magnetic resonance studies of grown-in non-radiative defects in Ga(In)NAs and Ga(Al, In)NP will be discussed in some detail, in an effort to provide chemical identification and experimental signatures of defects. Among them, intrinsic defects such as antisites and self-interstitials have been positively identified, and the effects of growth conditions, chemical compositions and post-growth processing on the formation of the defects were studied. The information retrieved from the experimental findings is expected to provide useful guidance for designing strategies to eliminate defects that are harmful to device performance.

1. Introduction

Dilute nitrides have derived from conventional III–V semiconductors such as GaP, or Ga(In)AsP by the insertion of nitrogen into the group V sub-lattice, which has profound effects on the electronic properties of the resulting alloys and allows widely extended band structure engineering [1]. Remarkable fundamental properties of the (Ga, In)(N, As, P) alloys, in combination with the possibility of varying over a wide range the lattice constants of the alloy materials by varying N content, provide a new opportunity to tailor material properties for desired applications in optoelectronic devices. For example, GaInNAs alloys are recognized as a new key material system for long wavelength solid-state lasers emitting within the fibre-optic communication wavelength window (1.3–1.55 μm) with a better high temperature performance [2–4]. The GaInNAs alloys are also predicted to improve the efficiency of multi-junctional solar-cells [5, 6]. In the case of GaNP alloys, the crossover from an indirect to a

 © 2004 IOP Publishing Ltd Printed in the UK

direct bandgap induced by N incorporation [7–10] promises high radiative efficiency, whereas a N-induced reduction in the lattice constant offers a possibility of lattice matching between optically efficient III–V compounds and Si wafers, desirable for the integration of the two technologies [11, 12].

A major problem in the growth of high quality dilute nitrides, however, is a large miscibility gap between GaAs (or GaP) and GaN. Thus the alloys can only be grown under non-equilibrium conditions, e.g. at low temperatures [13–15]. Low temperature growth and large lattice mismatch are known to cause severe non-uniformities in N distribution, and also to facilitate the formation of various defects, which typically act as efficient non-radiative (NR) centres leading to degradation of optical efficiency and carrier lifetime. Understanding formation mechanisms and designing strategies to eliminate defects that are harmful to device performance are therefore crucial to the success of dilute nitrides for optoelectronic device applications.

In this paper we will provide a brief overview of our present knowledge and understanding of point defects in dilute nitrides, and will underline their important roles in determining the success of these materials for optoelectronic device applications. A brief summary of experimental results of defects by various techniques reported so far in the literature will be given. Our recent results from optically detected magnetic resonance (ODMR) studies of grown-in non-radiative defects in Ga(In)NAs and Ga(Al, In)NP will be discussed in some detail, in an effort to provide chemical identification and experimental signatures of defects. Among them, intrinsic defects such as antisites and self-interstitials have been positively identified and the effects of growth conditions, chemical compositions and post-growth processing on the formation of the defects were studied. The information retrieved from the experimental findings is expected to provide useful guidance for designing strategies to eliminate defects that limit the performance of optoelectronic devices based on dilute nitrides, and thus to achieve their intrinsically possible efficiency.

2. Ga(In)NAs alloys

Electrical properties of various defects as well as their role in carrier trapping and recombination have primarily been evaluated from deep level transient spectroscopy (DLTS) measurements. Whereas a number of electron and hole traps have been detected, only some of them were suggested to act as important recombination centres that control carrier lifetimes [16–21]. Unfortunately, with a few exceptions, the chemical identity and microscopic structure of defects responsible for the revealed recombination centres remain largely unknown, as the DLTS technique is insensitive to the chemical nature of the defects.

Chemical identification of point defects in Ga(In)NAs alloys was obtained by nuclear reaction analysis (NRA) combined with the Rutherford backscattering (RBS) channelling technique [22–24], positron annihilation spectroscopy [23, 25] and optically detected magnetic resonance measurements (ODMR) [26–28]. Several point defects related to N interstitials, Ga vacancies and As_{Ga} antisites were positively identified. However, with the exception of a complex defect involving As_{Ga} antisites, shown to be an important NR centre from the ODMR studies, the participation of other point defects in recombination processes is not yet well established.

2.1. N interstitials

The combined studies by NRA and RBS channelling have provided strong evidence that a large amount of N atoms in MBE grown GaNAs layers reside at non-substitutional

positions [22–24]. The ratio between the on-site and off-site N atoms seems to critically depend on growth conditions. For example, a very high (2.3×10^{19} cm^{-3}) concentration of N interstitials in GaNAs alloys with only 0.7% of N, which remains constant with a further increase of N content up to 3%, was detected in the epilayers grown by gas-source molecular beam epitaxy (MBE) [23, 24]. By contrast, the formation of N interstitials was apparent only for relatively high N compositions exceeding 2.9% in the GaNAs epilayers grown by solid source MBE [22]. The concentration of N interstitials N_i can be substantially suppressed upon annealing [23, 24] by up to one order of magnitude, accompanied by a narrowing of the high resolution x-ray diffraction peak and improved luminescence efficiency. Therefore nitrogen interstitials could be among important NR centres responsible for the low PL efficiency of as-grown Ga(In)NAs.

Recent theoretical studies [29] fully support this view and predict that N–N split interstitials have a low formation energy and, thus, are likely abundant in GaNAs alloys. According to the calculations, the defect has a midgap energy level and is an efficient NR recombination centre. Further experimental studies are required to determine the exact microscopic configuration and energy level positions of N interstitials in GaInNAs alloys.

2.2. Ga vacancies

The formation of Ga vacancies (V_{Ga}) in Ga(In)NAs alloys has been established by using positron annihilation spectroscopy [23, 25]. Since isolated Ga vacancies in GaAs are known to have low thermal stability, a complex involving V_{Ga} has been suggested. The defect concentration increases with increasing N content in the alloy reaching a value of 10^{18} cm^{-3} for $x = 5\%$, but can be suppressed after annealing. It anti-correlates with integrated PL intensity, possibly indicating the importance of the detected Ga vacancies in the NR recombination.

Defect creation during MBE growth was attributed to damage induced by energetic N ions from the rf plasma and also to a low adatom mobility at the low growth temperature of 450 °C [23]. On the other hand, recent first principle calculations [30] suggest that formation of Ga vacancies is promoted by the presence of N and is further facilitated by hydrogen, resulting in a low formation energy for the (N–H–V_{Ga}) complex. This might explain the high concentration of the V_{Ga}-related complexes in GaNAs layers grown by metalorganic vapour phase epitaxy (MOVPE) [25], as H is highly abundant during MOVPE growth.

2.3. As antisites

Firm microscopic evidence for the existence of As antisites in Ga(In)NAs alloys grown by gas source MBE has been provided by the ODMR measurements [26–28]. The participation of an As atom in the defect was concluded from the experimentally resolved hyperfine (hf) structure, i.e. a group of four ODMR lines, characteristic for the interaction between an unpaired electron spin $S = 1/2$ and the nuclear spin $I = 3/2$ of the ^{75}As atom (100% natural abundance)—figure 1. The hf splitting parameter, $A = 2.21$ GHz, and the g-value of the unpaired electron localized at the defect, $g = 2$, were determined by fitting experimental data with the effective spin Hamiltonian

$$H = \mu_B \mathbf{BgS} + \mathbf{SAI}. \tag{1}$$

The first and second terms in equation (1) are the electron Zeeman and hyperfine interaction terms, respectively; μ_B denotes a Bohr magneton. The obtained A value is about 15% smaller than that known for the isolated As_{Ga} in GaAs [31], suggesting that the revealed defect is a complex involving As_{Ga}. The microscopic structure of the complex does not depend on the N

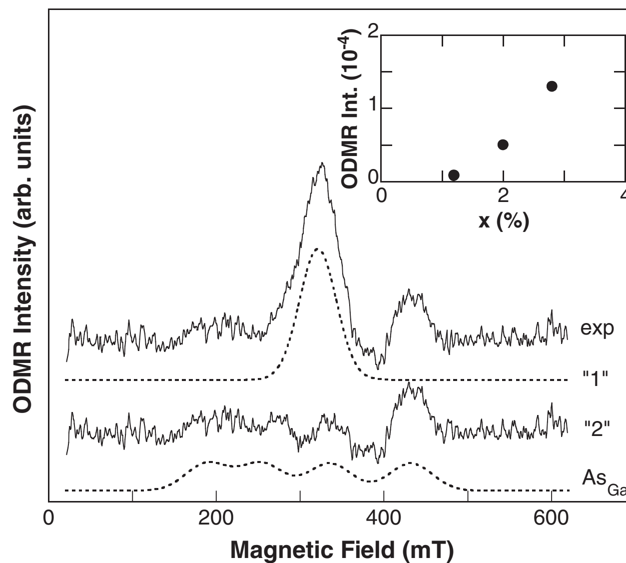

Figure 1. Typical ODMR spectrum measured by monitoring the PL emission from the GaInNAs and GaNAs alloys, obtained at the microwave frequency of 9.28 GHz (the top curve). Two ODMR signals can be deconvoluted. The ODMR signal '1' arises from a deep-level defect with $S = 1/2$ and a g-factor of 2.03. The signal '2' exhibits a four-line hyperfine structure, characteristic for a defect with an electronic spin $S = 1/2$ and a nuclear spin $I = 3/2$. The lowest curve is a simulated ODMR spectrum assuming the involvement of an As_{Ga} antisite complex. The inset shows the compositional dependence of the ODMR signal intensity related to the As_{Ga} antisite complex.

composition in the GaN_xAs_{1-x} layers for $x = 1$–3%, as the defect parameters do not change with x.

The defect formation was largely facilitated by the presence of N—see the inset in figure 1. Such behaviour is not surprising given that N incorporated into GaAs via the N–As exchange mechanism [32, 33] that led to the presence of excess As atoms during growth. On the other hand, only a marginal effect of In incorporation was observed for the studied range of In compositions below 3%. An increase in growth temperatures caused a strong reduction in the intensity of the ODMR signal, suggesting that the studied defect was primarily introduced during the growth at low temperatures [27]. The observed increasing presence of the As_{Ga}-antisites under low temperature growth is likely related to a low adatom mobility during such growth conditions and is also in agreement with the earlier findings of As-rich conditions during the low temperature growth of GaAs. Low formation energy of defects involving As_{Ga} has also been suggested by the first principle calculations [29]. Moreover, according to the theory As_{Ga} is likely attracted by N_{As} forming a N_{As}–As_{Ga} complex, which minimizes the total strain energy associated with the defect. This assumption, however, still awaits experimental verification, as the lack of resolved ligand hf structure of the ODMR signal prevented the identification of the other partner of the studied As_{Ga} complex.

The ODMR studies have also established that the revealed As_{Ga} complex is an efficient centre for non-radiative recombination, based on the fact that a decrease in PL intensity over the entire spectral range was observed upon spin resonance independent of the origin of the PL emissions. (NR defects can be monitored using the ODMR technique since a magnetic resonance induced increase in efficiency of dominant NR channels can lead to a corresponding decrease in free carrier concentration available for radiative recombination and, thus, the PL

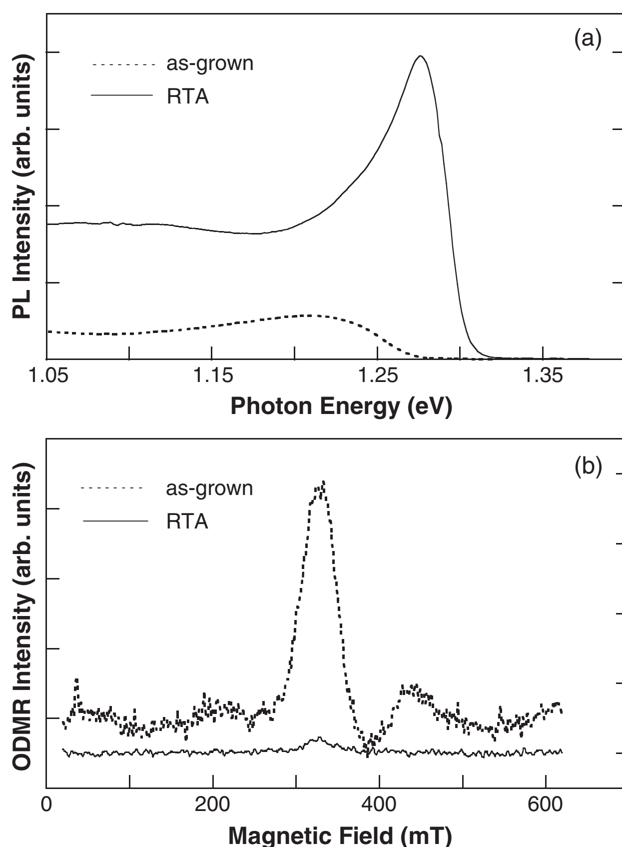

Figure 2. (a) PL and (b) ODMR spectra of the $Ga_{0.97}In_{0.03}N_{0.008}As_{0.992}$ epilayer before and after RTA, respectively. The annealing out of the NR defects, obvious from the strong decrease of the ODMR signal, is accompanied by a pronounced increase in the PL intensity.

intensity.) This conclusion was further supported by a strong anti-correlation observed between the PL and ODMR intensities. Moreover, a dramatic suppression of the ODMR intensity was found after rapid thermal annealing (RTA) treatments of the Ga(In)NAs alloys, accompanied by a significant improvement in the radiative efficiency of the alloys—figure 2.

3. Ga(Al)NP alloys

Similar to Ga(In)NAs alloys, the optical properties of GaNP layers can be severely deteriorated when N compositions exceed a few per cent. This is largely caused by formation of misfit dislocations/cracks, generated to relieve large internal stress in GaNP epilayers due to large lattice mismatch with GaP substrates. In addition, N incorporation likely promotes the formation of various point defects participating in the NR recombination. However, to the best of our knowledge, practically nothing is known so far about their electronic structure and chemical identity. Below we will discuss our recent results from ODMR measurements, which have identified complexes involving Ga interstitials as common NR defects in Ga(Al)NP alloys grown by MBE, and thus provided the first insight into the origin of point defects in this material system.

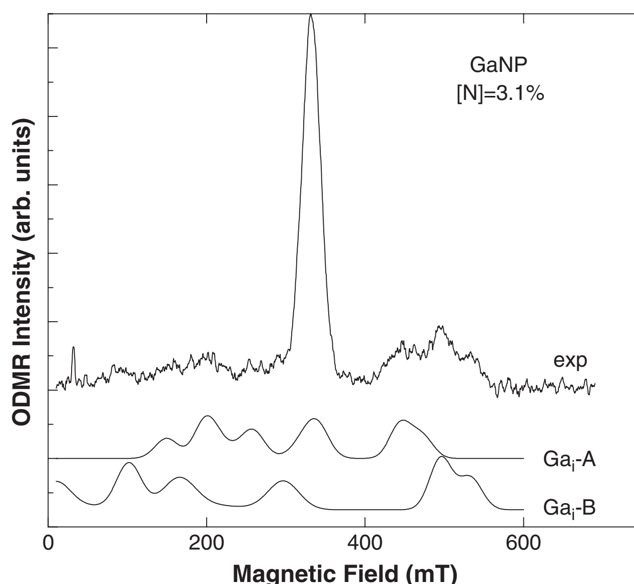

Figure 3. A typical ODMR spectrum measured by monitoring the PL emission from the $GaN_{0.031}P_{0.969}$ epilayer, obtained at the microwave frequency of 9.28 GHz (top curve). In addition to the central ODMR signal of un-known origin, the spectrum contains two sets of the ODMR lines that are attributed to two complex defects (i.e. Ga_i-A and Ga_i-B) involving Ga_i, as shown by the two simulated ODMR spectra. The fitting parameters are given in table 1.

3.1. Ga interstitials

Figure 3 shows a typical ODMR spectrum recorded from GaNP epilayers grown by gas source MBE. The strongest ODMR line at around 330 mT is related to a defect with a g-factor of 2.0079. Due to a lack of hyperfine structure, no chemical identification of this defect can be established, unfortunately. Detailed temperature-dependent measurements have shown that the remaining ODMR spectrum is a result of superposition of two sets of signals from paramagnetic defect centres with an effective electron spin $S = 1/2$, denoted as Ga_i-A and Ga_i-B. An analysis of the ODMR spectra further reveals that each set contains two groups of four ODMR lines characteristic of hyperfine interaction between an unpaired electron spin and a nuclear spin $I = 3/2$. The ratios of the ODMR intensity and hyperfine splitting between the two groups of the four-line ODMR were found to be identical for both defects, which is characteristic for a defect atom with two dominant isotopes of $I = 3/2$. The only nuclei in the GaNP lattice, which satisfies these requirements, is gallium which has two natural isotopes with $I = 3/2$, i.e. ^{69}Ga and ^{71}Ga with the natural abundance of approximately 60% and 40%, respectively. Moreover, two Ga isotopes have different nuclear magnetic moments, responsible for the observed different hyperfine splitting. Therefore, we can conclude that the cores of both Ga_i-A and Ga_i-B defects involve a Ga atom, justifying the proposed defect notations. Spin Hamiltonian parameters for both defects are summarized in table 1. As a much higher strength of the hf interaction is predicted for isolated Ga interstitials in GaP [34], the observed defects are likely complexes involving a Ga_i atom. Formation of both defects is promoted by N incorporation. However, the defect structure, judging from the deduced hf constants, remains the same within the range of the studied N compositions $x = 1$–3.1%.

Addition of Al to GaNP causes a profound effect on the ODMR spectra leading to a strong increase of the ODMR signals related to the Ga interstitials and substantial changes of

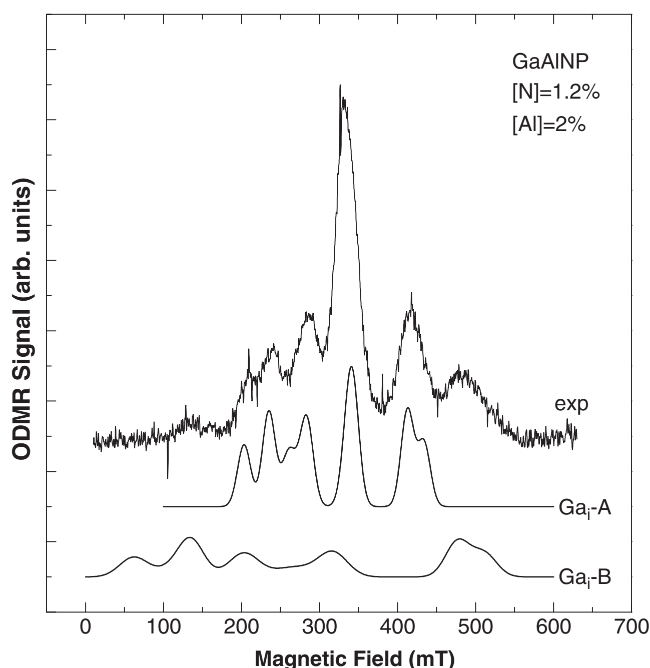

Figure 4. An ODMR spectrum observed at 5 K from the GaAlNP sample with [N] = 1.2% and [Al] = 2% (the top curve). The simulated ODMR spectra for the Ga$_i$-A and Ga$_i$-B defects are also shown with the fitting parameters derived from the spin Hamiltonian analysis (table 1).

Table 1. Spin Hamiltonian parameters determined by fitting the spin Hamiltonian $H = \mu_B \mathbf{BgS} + \mathbf{SAI}$ to the experimental data for the Ga$_i$-A and Ga$_i$-B defects in GaAlNP.

[Al] (%)	0		2		30	
[N] (%)	1.2–3.1		1.2		1.2	
Defect	Ga$_i$-A	Ga$_i$-B	Ga$_i$-A	Ga$_i$-B	Ga$_i$-A	Ga$_i$-B
S	1/2	1/2	1/2	1/2	1/2	1/2
I	3/2	3/2	3/2	3/2	3/2	3/2
g	2.001	2.003	2.005	1.99	2.005	1.99
A (^{69}Ga) (10^{-4} cm^{-1})	770	1200	490	1030	450	980
A (^{71}Ga) (10^{-4} cm^{-1})	995	1550	630	1320	580	1260

the corresponding hf constants—figure 4 and table 1. The latter implies that the microscopic structure of the corresponding defects is modified in the GaAlNP alloys, e.g. due to involvement of neighbouring Al atoms. A higher concentration of the Ga$_i$-related defects in the GaAlNP alloys is probably not surprising, based on the previous results in the AlGaAs material system [35]. Indeed, because of low adatom mobility during growth, Al atoms will likely reside initially at an interstitial site. However, the higher strength of the Al–N(p) bond as compared with the Ga–N(p) bond may favour the subsequent site exchange resulting in the formation of Ga$_i$ and Al$_{Ga}$.

The identification of the nearest neighbours of the Ga$_i$ within the Ga$_i$-A and Ga$_i$-B complexes cannot be determined from the present ODMR measurements, as the ligand hf

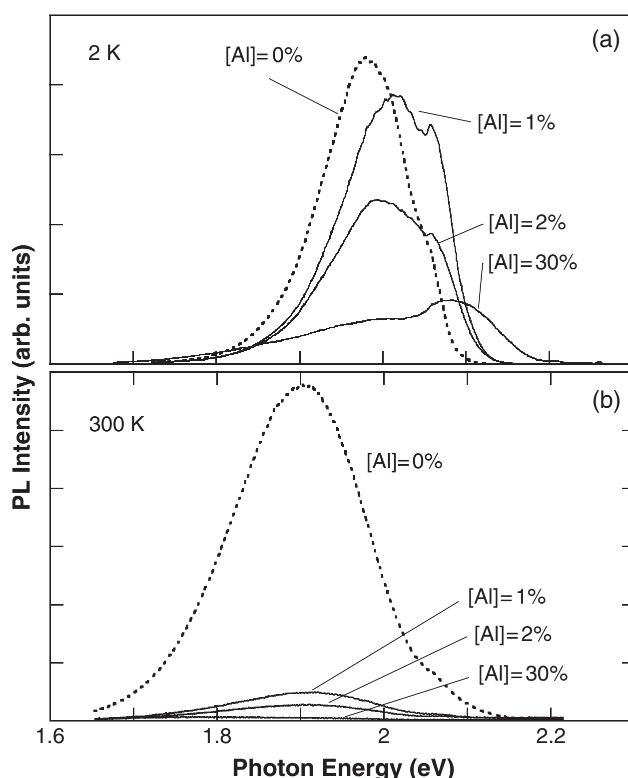

Figure 5. PL spectra of GaAlNP alloys measured as a function of Al composition at 2 K (a) and room temperature (b), respectively.

structure was not resolved. However, the hyperfine parameter of Ga_i-A in GaAlNP is similar to that of the Ga_i centre reported in AlGaAs [35] and seems to decrease with increasing Al composition. One might thus speculate that the Ga_i atom for both defects in the two materials has similar surroundings, e.g. resides on the T_d interstitial site surrounded by group III atoms. On the other hand, the hyperfine parameter of Ga_i-B is similar to that for Ga_i in GaP [36] and also changes slightly with the presence of Al. This might indicate that both group-III and V atoms are located close to the Ga interstitial. Further studies using, e.g. electron nuclear double resonance, are required to resolve this issue.

In all investigated Ga(Al)NP epilayers the ODMR signals related to the Ga_i-A and Ga_i-B defects have a negative sign and can be detected via all emissions within the visible and infra-red spectral regions, i.e. they act as efficient NR centres. The observed anti-correlation between the intensity of the ODMR signals and the efficiency of the visible PL emissions strongly supports this conclusion. The revealed defects seem to also degrade thermal behaviour of the PL emission leading to a severe quenching of the PL intensity at elevated temperatures—figure 5.

Acknowledgments

The financial support by the Swedish Research Council and the Wenner-Gren Foundations is greatly appreciated. We are grateful to H P Xin and Y C Hong for the growth of the structures studied in the ODMR measurements, as well as to N Q Thinh, M Izadifard and I Vorona for their contributions to some of the experimental data included in this paper.

References

[1] For a review, see Buyanova I A, Chen W M and Monemar B 2001 *Mater. Res. Soc. Internet J. Nitride Semiconduct. Res.* **6** 002
[2] Kondow M, Uomi K, Hosomi K and Mozume T 1994 *Japan. J. Appl. Phys.* **33** L1056
[3] Harris J S 2002 *Semicond. Sci. Technol.* **17** 880
[4] Riechert H, Ramakrishnan A and Steinle G 2002 *Semicond. Sci. Technol.* **17** 892
[5] Firedman D J, Geisz J F, Kurtz S R and Olson J M 1998 *J. Cryst. Growth* **195** 409
[6] Geisz J F and Friedman D J 2002 *Semicond. Sci. Technol.* **17** 769
[7] Bellaiche L, Wei S H and Zunger A 1997 *Phys. Rev.* B **56** 10233
[8] Xin H P, Tu C W, Zhang Y and Mascarenhas A 2000 *Appl. Phys. Lett.* **76** 1267
[9] Shan W, Walukiewicz W, Yu K M, Wu J, Ager J W III, Haller E E, Xin H P and Tu C W 2000 *Appl. Phys. Lett.* **76** 3251
[10] Buyanova I A, Pozina G, Bergman J P, Chen W M, Xin H P and Tu C W 2002 *Appl. Phys. Lett.* **81** 52
[11] Momose K, Yonezu H, Fujimoto Y, Furukawa Y, Motomura Y and Aiki K 2001 *Appl. Phys. Lett.* **79** 4151
[12] Yonezu H 2002 *Semicond. Sci. Technol.* **17** 762
[13] Kondow M and Kitatani T 2002 *Semicond. Sci. Technol.* **17** 746
[14] Suemune I, Uesugi K and Seong T-Y 2002 *Semicond. Sci. Technol.* **17** 755
[15] Onabe K 1997 *Mater. Res. Soc. Symp. Proc.* **449** 23
[16] Krispin P, Gambin V, Harris J S and Ploog K H 2003 *J. Appl. Phys.* **93** 6095
[17] Krispin P, Spruytte S G and Harris K H 2001 *J. Appl. Phys.* **89** 6294
[18] Balcioglu A, Ahrenkiel R K and Friedman D J 2000 *Appl. Phys. Lett.* **74** 2397
[19] Kwon D, Kaplar R J, Ringel S A, Allerman A A, Kurtz S R and Jones E D 1999 *Appl. Phys. Lett.* **74** 2380
[20] Kurtz S R, Allerman A A, Jones E D, Gee J M, Bans J J and Hammons B E 1999 *Appl. Phys. Lett.* **74** 729
[21] Kaplar R J, Arenhart A R, Ringel S A, Allerman A A, Sieg R M and Kurtz S R 2001 *J. Appl. Phys.* **90** 3405
[22] Spruytte S G, Colden C W, Harris J S, Wampler W, Krispin P, Ploog K and Larson M C 2001 *J. Appl. Phys.* **89** 4401
[23] Li W, Pessa M, Ahlgren T and Decker J 2001 *Appl. Phys. Lett.* **79** 1094
[24] Ahlgren T, Vainonen-Ahlgren E, Likonen J, Li W and Pessa M 2002 *Appl. Phys. Lett.* **80** 2314
[25] Toivonen J, Hakkarainen T, Sopanen M, Lipsanen H, Oila J and Saarinen K 2003 *Appl. Phys. Lett.* **82** 40
[26] Thinh N Q, Buyanova I A, Hai P N, Chen W M, Xin H P and Tu C W 2001 *Phys. Rev.* B **63** 033203
[27] Thinh N Q, Buyanova I A, Chen W M, Xin H P and Tu C W 2001 *Appl. Phys. Lett.* **79** 3089
[28] Chen W M, Thinh N Q, Buyanova I A, Xin H P and Tu C W 2001 *Proc. Materials Research Society Fall Mtg (Boston, MA, USA, Nov. 2001)* (Pittsburgh, PA: Materials Research Society) pp 67–72
[29] Zhang S B and Wei S H 2001 *Phys. Rev. Lett.* **86** 1789
[30] Jannoti A, Wei S H, Zhang S B, Kurtz S and Van de Walle C G 2001 *Phys. Rev.* B **67** 161201
[31] Wagner R J, Krebs J J, Stauss G H and White A M 1980 *Solid State Commun.* **36** 15
[32] Hauenstein R J, Collins D A, Cai X P, O'Steen M L and McGill T C 1995 *Appl. Phys. Lett.* **66** 2681
[33] Gwo S, Tokumoto H and Miwa S 1997 *Appl. Phys. Lett.* **71** 362
[34] Zhang S B and Limpijumnong S 2003 private communication
[35] Kennedy T A and Spencer M G 1986 *Phys. Rev. Lett.* **57** 2690
[36] Lee K M 1988 *Mater. Res. Soc. Symp. Proc.* **104** 449