



## On the nature of radiative recombination in GaAsN

B. Q. Sun, M. Gal, Q. Gao, H. H. Tan, and C. Jagadish

Citation: [Applied Physics Letters](#) **81**, 4368 (2002); doi: 10.1063/1.1526913

View online: <http://dx.doi.org/10.1063/1.1526913>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/81/23?ver=pdfcov>

Published by the [AIP Publishing](#)

---

### Articles you may be interested in

[Origin of radiative recombination and manifestations of localization effects in GaAs/GaNAs core/shell nanowires](#)  
Appl. Phys. Lett. **105**, 253106 (2014); 10.1063/1.4905090

[Exciton recombination dynamics in a  \$\pi\$ -plane \(Al,Ga\)N/GaN quantum wells probed by picosecond photo and cathodoluminescence](#)

J. Appl. Phys. **107**, 043524 (2010); 10.1063/1.3305336

[Dynamics of carrier recombination and localization in AlGaIn quantum wells studied by time-resolved transmission spectroscopy](#)

Appl. Phys. Lett. **95**, 091910 (2009); 10.1063/1.3222972

[Radiative and nonradiative processes in strain-free Al<sub>x</sub>Ga<sub>1-x</sub>N films studied by time-resolved photoluminescence and positron annihilation techniques](#)

J. Appl. Phys. **95**, 2495 (2004); 10.1063/1.1644041

[Inherent nature of localized states in highly planar monolayer InAs/GaAsN pseudo-alloys](#)

Appl. Phys. Lett. **83**, 3728 (2003); 10.1063/1.1623320

---

**MULTIPHYSICS SIMULATION**  
Modeling and App Design Stories

UNIVERSITY • INTEL • ABB SEMICONDUCTORS • ROCH  
RS • WITRICITY • MEDTRONIC • PURDUE UNIVERSITY • IN  
M DIMATIX • CYPRESS SEMICONDUCTORS • WITRICITY  
CTORS • ROCHE DIAGNOSTICS • FUJIFILM DIMATI  
RDUE UNIVERSITY • INTEL • ABB SEMICONDUCTO  
NDUCTORS • WITRICITY • MEDTRONIC • PURDUE U

COMSOL

READ LATEST ISSUE »

The advertisement features a dark background with a car's front end on the right. On the left, there is a green shield with a white lightning bolt. Two small inset images show simulation results: one with a color gradient and another with a blue and yellow flow pattern. The text 'MULTIPHYSICS SIMULATION' is in large white letters, followed by 'Modeling and App Design Stories' in smaller white letters. A list of company names is partially visible in the background. The COMSOL logo is at the bottom left, and a blue button with white text 'READ LATEST ISSUE »' is at the bottom right.

## On the nature of radiative recombination in GaAsN

B. Q. Sun and M. Gal<sup>a)</sup>

*School of Physics, University of New South Wales, Sydney, Australia 2052*

Q. Gao, H. H. Tan, and C. Jagadish

*Department of Electronic Materials Engineering, Research School of Physical Sciences and Engineering, Institute of Advanced Studies, Australian National University, Canberra, 0200 Australia*

(Received 8 July 2002; accepted 9 October 2002)

Radiative recombination at low temperatures in GaAsN is often associated with localized excitons. In this short note, we report results from high-resolution time-resolved photoluminescence spectroscopy that indicate that excitons, localized or otherwise, cannot be involved in the recombination process of this alloy system. The risetime of the photoluminescence signal is more than two orders of magnitude shorter than that expected, and found from excitonic recombination in other III-V materials, such as GaAs. We suggest that the radiative recombination in GaAsN takes place between localized electrons and delocalized holes. © 2002 American Institute of Physics. [DOI: 10.1063/1.1526913]

Low-nitrogen-content Ga(In)NAs alloys have recently attracted much attention due to their unusual physical properties and their possible use in GaAs-based optoelectronic devices.<sup>1-4</sup> The remarkable physical properties include a very large bowing of the band gap energy as a function of nitrogen content, and the relatively efficient radiative efficiency in spite of the imperfect crystal structure. The luminescence properties of GaAsN, which are also atypical, have been the topic of several publications.<sup>5-8</sup> The spectral distribution of the photoluminescence (PL), its temperature, and excitation intensity dependence are quite unlike that of GaAs, which is a close “relative” of this alloy system. Most authors describe the low-temperature radiative emission in this system in terms of recombination by localized excitons, while at high temperatures, luminescence emission is thought to be the result of recombination between delocalized electrons and holes.<sup>6,8</sup>

In this letter, we shall revisit the question of the mechanism of radiative recombination in GaAs<sub>1-x</sub>N<sub>x</sub>. We shall show that in this alloy system at low temperatures, the time evolution of the PL is not compatible with the excitonic recombination model (localized or otherwise), but can be explained in terms of recombination between localized electrons and delocalized holes. We have drawn our conclusions from high-resolution time-resolved PL (TRPL) measurements, which indicate that the risetime of the PL is close to two orders of magnitude shorter than the risetime required for recombination involving excitons. Our time-resolved measurements are based on the PL upconversion technique, which provides a temporal resolution of 100 fs.

The samples used in this study were grown on semi-insulating GaAs (100) substrate by low-pressure metalorganic chemical vapor deposition. Trimethylgallium and trimethylindium were used as group-III sources, arsine, phosphine, and 1,1-dimethylhydrazine were used as group-V sources. GaAsN epilayers between 300–800 nm thick were grown at 76 Torr on a 200 nm undoped GaAs buffer. The

nitrogen composition was estimated from double-crystal x-ray rocking curves using (004) reflection. Rapid thermal annealing was performed on all the GaAsN samples at 750 °C for 30 s using GaAs proximity capping in an N<sub>2</sub> ambient.

The continuous wave (cw) PL was excited by the 514 nm line of an Ar-ion laser, dispersed with a 0.33m monochromator and detected by cooled Ge detector. The PL upconversion experiments<sup>9</sup> were performed using an Ar-ion laser pumped femtosecond self-mode locked Ti:Sapphire laser. Upconversion spectroscopy is based on measuring the upconverted PL emitted from the sample using a nonlinear crystal and the pump beam that first passes through a variable delay line. This system acts as an optical gate that enables the luminescence to be resolved temporally with high resolution, which in our case was approximately 100 fs. The Ti:Sapphire laser was tunable between 750 and 900 nm, the pulse width was 80 fs, the repetition rate 85 MHz and the output power was 180 mW at  $\lambda=780$  nm. The optically excited carrier concentration was approximately  $3 \times 10^{10}$  carriers/cm<sup>2</sup>. The samples were mounted in a variable temperature, closed-cycle, He cryostat, the temperature of which could be varied between 10 K and room temperature.

The characteristic features of PL in GaAsN-related emission reported by most authors (see for example, Ref. 4 and references therein), and confirmed by our experiments, include an asymmetric PL lineshape with a sharp high-energy cutoff and an exponential low-energy tail. The PL peak energy exhibits a strong shift to lower energies (redshift) with increasing nitrogen content, which has been shown to correspond to the decrease in the band gap energy of this alloy due to the bowing effect. The temperature and excitation intensity dependence of the PL spectrum of this alloy are also unusual. The energy of the PL peak intensity exhibits an unexpectedly large redshift with increasing temperature between approximately 10 and 70 K, followed by a shift to higher energies (blueshift) for temperatures between 80 and 140 K. Above 140 K, the energy of the PL peak follows the anticipated temperature dependence of the band gap to lower

<sup>a)</sup>Electronic mail: m.gal@unsw.edu.au

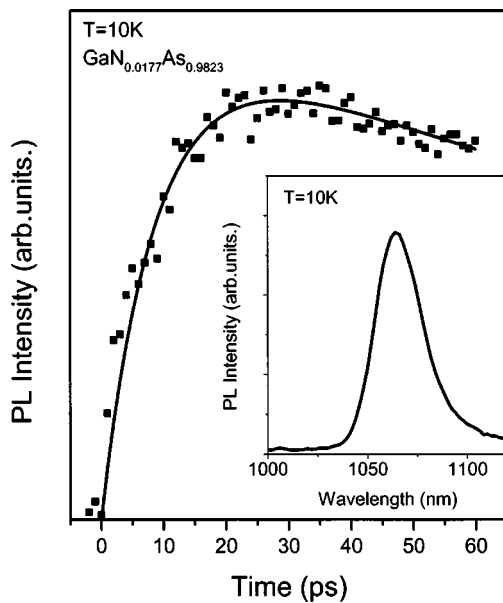


FIG. 1. Time evolution of the PL of a  $\text{GaAs}_{0.9823}\text{N}_{0.0177}$  sample in the first 60 ps after excitation. The inset shows the PL spectrum of the sample. In the time-resolved spectrum, the square dots represent the measurement; the line is a guide for the eyes.

energies. With increased temperature, the high-energy slope of the PL indicates a Boltzmann-factorlike temperature dependence, indicating that free particles are involved in the radiative transitions. The excitation intensity dependence of the PL peak energy indicates a blueshift with excitation power. According to some reports, at very high excitation levels, the PL exhibits an additional high-energy emission band.<sup>8</sup> TRPL data have also been reported.<sup>6,8</sup> According to these reports, at low temperatures, a single exponential can be used to describe the radiative decay, with the PL decay times ranging between 120 ps at the high-energy side of the emission, and up to 8 ns at the low-energy side of the emission. The risetime of the PL emissions has not been discussed in detail, as most experiments did not have the required temporal resolution to correctly measure the risetime.

These uncommon luminescence features have been explained in terms of excitons localized by potential fluctuations at the band edges or LE.<sup>6,8</sup> The localized nature of the carriers assumed in this model is compatible with the observed blueshift in the excitation intensity dependence and the unusual temperature dependence of the PL. The assumption that the recombination is due to excitons, as opposed to localized electron and holes, was based on the observation that the temporal decay of the PL emission can be fitted with a single exponential function.<sup>6,8</sup> Radiative recombination between spatially separated (localized) electrons and holes would result in strongly nonexponential decay. Since the PL decay was found to exhibit an exponential function, it was assumed that the recombination is excitonic in nature.<sup>6</sup> However, recombination between localized electron (holes) and delocalized holes (electrons) would also lead to luminescence decay with a single (effective) time constant. The PL decay measurements alone therefore, cannot distinguish between these two models.

One method capable of differentiating between excitonic and electron-hole recombination is TRPL, and, in particular,

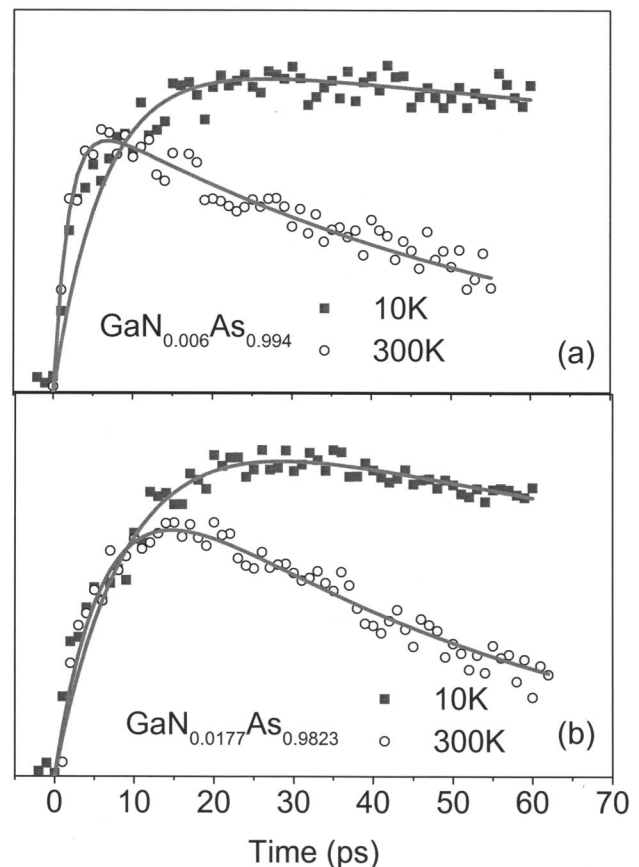


FIG. 2. TRPL of two GaAsN samples with differing amount in nitrogen, measured at two temperatures. The points represent the data; the lines are a guide for the eyes.

the measurement of the luminescence risetime. Excitonic recombination in III-V compounds at low temperatures is known to involve PL with a very slow risetime, while electron-hole recombination is much faster. The risetime of free exciton luminescence in epitaxial (bulk) GaAs was recently measured to be of the order of 1 ns,<sup>10</sup> while that in GaAs quantum wells was found to be somewhat shorter but still of the order of 300–400 ps.<sup>11</sup> It was shown<sup>10</sup> that these very slow risetimes are the result of several gradual processes that include exciton formation (from free electrons and holes), relaxation of the hot excitons via acoustic phonon emission, and the scattering of the luminescing excitons into the  $k \approx 0$  exciton states, the only ones observable by optical techniques.<sup>11</sup> Any exciton-related luminescence in GaAsN therefore, should exhibit a PL signal with a similar slow risetime. In contrast, electron-hole recombination is expected to have short luminescence risetime as none of the aforementioned time-consuming processes are involved. In GaAs, for example, the PL risetime at room temperature is of the order of 10–20 ps.<sup>12</sup>

Therefore, to be able to correctly describe the nature of the recombination process in GaAsN, it is essential to determine the risetime of the PL signal. For this analysis, we define the risetime as the time required for the luminescence to reach the maximum intensity.<sup>11</sup> As mentioned previously, we used the PL upconversion technique to accurately measure the PL risetime in our samples. Figure 1 shows the time evolution of the PL of a GaAsN sample with  $x = 1.77\%$  ni-

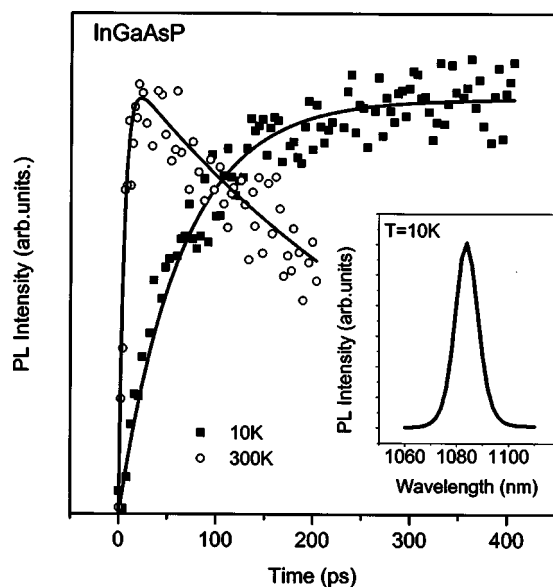


FIG. 3. Time evolution of the PL of an InGaAsP sample at two temperatures. The PL emission spectrum of the same sample at  $T=10$  K is displayed in the inset.

nitrogen content in the first 60 ps after excitation, measured at  $T=10$  K. The inset in Fig. 1 shows the PL spectrum of the same sample, also measured at  $T=10$  K.

As can be seen in Fig. 1, the risetime of the luminescence is of the order of 25 ps. Similar risetimes were measured for all the GaAsN samples investigated, irrespective of their nitrogen content (between 0.6% and 1.77%), the measurement wavelength (within the emission band), and the measurement temperature. In Fig. 2, we show the time evolution of the PL for two samples ( $x=0.6\%$  and  $x=1.77\%$ ) at  $T=10$  K and  $T=300$  K. As can be seen, the risetimes are very similar for the two samples, and change very little with temperature. In all cases, the risetimes were between 10–30 ps. The decay times, however, are markedly different. As has been reported by a number of authors, the decay times depend on the nitrogen content, measurement wavelength, and temperature.<sup>6,8</sup>

To explore whether it is just the alloy nature of the sample that leads to the observed significant reduction in the PL risetime, we have also measured the TRPL signal in a different but related alloy system. We choose a quaternary  $\text{Ga}_{0.2}\text{In}_{0.8}\text{As}_{0.4}\text{P}_{0.6}$  epitaxial layer with similar PL spectrum as that of the GaAsN samples. The TRPL spectra at  $T=10$  K and  $T=300$  K of this quaternary sample is shown in Fig. 3, with the PL spectrum in the insert.

As can be seen in Fig. 3, the risetime of this alloy at  $T=10$  K is more than an order of magnitude longer than that observed in the GaAsN samples and, in fact, the PL intensity still increased 400 ps after excitation. As the temperature is increased, the risetime for this sample is significantly re-

duced, and at  $T=300$  K it is approximately 15 ps. This, again, is similar to that observed for GaAs. We can, therefore, conclude that the alloying process by itself does not lead to the type of PL risetime observed for the GaAsN samples. The short PL risetime and its temperature independent nature are characteristic of this specific alloy structure.

We believe that the short PL risetimes is an indication that the radiative recombination process in the GaAsN system does not involve excitons. Since the temperature and excitation intensity dependence of the cw PL data suggest localized particles, we have to assume that luminescence occurs via electron–hole recombination in which one, or both, of the particles are localized. However, since recombination between localized electron and localized holes would result in nonexponential luminescence decay, which would be contrary to the experimental observations, we, therefore, have to conclude that the recombination process in this alloy system must involve one localized and one delocalized particle. Since the nitrogen is known to mainly affect the conduction band, we can assume that the electrons are localized to the band-edge fluctuations created by the nitrogen, and the holes remain “free”. The photoexcited electrons are known to rapidly relax into band-tail states<sup>13</sup> which, in the InGaN system, is of the order of 0.5 ps. If we assume a similar fast capture process in the GaAsN system, the observed PL risetime is a measure of the radiative recombination rate between the localized electron and delocalized holes.

In summary, the high temporal resolution of our TRPL measurements has provided evidence that the PL risetime in GaAsN is not consistent with the formation and recombination of excitons. All optical evidence points to recombination between LE and delocalized holes.

- <sup>1</sup>S. Sakai, Y. Ueta, and Y. Teuchi, *Jpn. J. Appl. Phys. Lett.* **32**, 4413 (1993).
- <sup>2</sup>W. Shan, W. Walukiewicz, J. W. Ager III, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, *Phys. Rev. Lett.* **82**, 1221 (1999).
- <sup>3</sup>J. D. Perkins, A. Mascarenhas, Y. Zhang, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. K. Kurtz, *Phys. Rev. Lett.* **82**, 3312 (1999).
- <sup>4</sup>I. A. Buyanova, W. M. Chen, and B. Monemar, *MRS Internet J. Nitride Semicond. Res.* **6**, 2 (2001).
- <sup>5</sup>S. Francoeur, G. Sivaraman, Y. Qiu, S. Nikishim, and H. Temkin, *Appl. Phys. Lett.* **72**, 1857 (1998).
- <sup>6</sup>I. A. Buyanova, W. M. Chen, G. Pozina, J. P. Bergman, B. Monemar, H. P. Xin, and C. W. Tu, *Appl. Phys. Lett.* **75**, 501 (1999).
- <sup>7</sup>B. Q. Sun, D. S. Jiang, X. D. Luo, Z. Y. Xu, Z. Pan, L. H. Li, and R. H. Wu, *Appl. Phys. Lett.* **76**, 2862 (2000).
- <sup>8</sup>X. D. Luo, Z. Y. Xu, W. K. Ge, Z. Pan, L. H. Li, and Y. W. Liu, *Appl. Phys. Lett.* **79**, 958 (2001).
- <sup>9</sup>J. Shah, *IEEE J. Quantum Electron.* **24**, 276 (1988).
- <sup>10</sup>M. Gurioli, P. Borri, M. Colocci, M. Gulia, F. Rossi, E. Molinari, P. E. Selbmann, and P. Lugli, *Phys. Rev. B* **58**, R13403 (1998).
- <sup>11</sup>T. C. Damen, J. Shah, D. Y. Oberli, D. S. Chemla, J. E. Cunningham, and J. M. Kuo, *Phys. Rev. B* **42**, 7434 (1990).
- <sup>12</sup>J. Shah, B. Deveaud, T. C. Damen, W. T. Tsang, A. C. Gossard, and P. Lugli, *Phys. Rev. Lett.* **59**, 2222 (1987).
- <sup>13</sup>C. K. Sun, Y. L. Huang, S. Keller, U. K. Mishra, and S. P. DenBaars, *Phys. Rev. B* **59**, 13535 (1999).