

Spectral and time dependences of the energy transfer of bound optical excitations in GaP(N)

T Niebling¹, O Rubel¹, W Heimbrod¹, W Stolz¹, S D Baranovskii¹,
P J Klar² and J F Geisz³

¹ Department of Physics and Material Sciences Center, Philipps-University Marburg,
Renthof 5, 35032 Marburg, Germany

² Institute of Experimental Physics I, Justus-Liebig University, Heinrich-Buff-Ring 16,
35392 Gießen, Germany

³ National Renewable Energy Laboratory Golden, 1617 Cole boulevard, Golden,
CO 80401, USA

E-mail: tobias.niebling@physik.uni-marburg.de and oleg.rubel@physik.uni-marburg.de

Received 21 September 2007, in final form 12 November 2007

Published 7 December 2007

Online at stacks.iop.org/JPhysCM/20/015217

Abstract

Low-temperature kinetics of the energy transfer of localized optical excitations in a nitrogen-doped GaP bulk sample with a nitrogen content of 2.1% are studied by means of time-resolved spectroscopy. Both the spectral and time dependences of the photoluminescence decay are described quantitatively on a timescale from nanoseconds to a microsecond by a phenomenological theory of hopping and energy relaxation of localized excitons. The microscopic parameters, which characterize the luminescent states, are determined by comparison between experiment and theory.

1. Introduction

Hopping of optical excitations trapped into shallow localized states within the energy gap of semiconductors has attracted considerable attention for decades. Due to the spatial overlap of wavefunctions of adjacent bound states, excitations can tunnel between localized states changing their spatial position and energy in the course of time. By using low-temperature time-resolved photoluminescence (PL) measurements, the existence of the energy transfer of optical excitations between localized states was verified for a variety of compound heterostructures exhibiting the presence of energetic disorder and exciton localization [1–6]. A strong dependence of the PL decay time on the photon energy is inherent for the energy transfer of excitations from shallow to energetically deeper localized states in a pseudogap.

According to the theory [7, 8], the spectral dependence of the PL decay is governed by the interplay between two processes: exciton recombination and its energy-loss hopping. The latter process is assumed to occur via a phonon-assisted tunneling between localized states [1]. Recently we obtained an analytical expression for the spectral dependence of the

PL decay time that takes into account basic properties of disorder and localization as well as the time delay after the pulsed excitation [9]. The form of this expression turns out to be sensitive not only to the hopping mechanism (tunneling in our case), but also to the spatial dimensionality of the system under study. The new theory significantly extends the range of applicability of the former theory of Gourdon and Lavallard [10] and enables the transient evolution of the spectrum of PL decay times to be described.

Here we present an experimental verification of the phenomenological model of hopping and recombination of localized excitons in an attempt to describe *both* the spectral and the time dependences of the PL decay in a GaP(N) bulk crystal in a wide range of delays after the pulsed excitation. We will show that this theory quantitatively describes experimental data in a wide range of delay times, assuming only one time-dependent parameter, namely the exciton lifetime.

2. Experimental details

It is known that the PL in GaP(N) is dominated by the recombination of optical excitations bound to localized states created

by nitrogen and its complexes [11–15]. At an extremely dilute nitrogen content, the PL spectrum is composed of a series of sharp lines associated with different nitrogen complexes [11]. For a nitrogen content above approximately 2%, the PL spectrum becomes featureless [16], which indicates a continuous energy distribution of luminescent states. Furthermore, the long carrier lifetime of about 100–1000 ns provides an opportunity to observe the developed energy relaxation of localized excitations [13, 14, 16, 17] that makes GaP(N) an optimal candidate for our study.

The nitrogen-doped GaP sample with a layer thickness of 1 μm was grown by metal–organic vapor-phase epitaxy on a (100) GaP substrate. X-ray diffraction measurements confirm a nominal nitrogen content of 2.1% and pseudomorphic growth of the GaP(N). A pulsed Nd:YAG laser tripled to a wavelength of 355 nm was used to excite the sample at energies above the direct band gap of GaP. The duration of the laser pulse was about 5 ns. The sample was mounted in a liquid helium cryostat and kept at 10 K. The photoluminescence signal was collected by a lens system and dispersed in a 0.25 m grating monochromator. A gated silicon-based intensified charge-coupled device with a minimum gate switching time of 2 ns was used to detect the signal. The PL decay is examined within the first microsecond after the excitation pulse.

3. Theory

The theory of low-temperature spectral and time dependences of the PL decay of bound excitons is described in detail in [9]. Here we only briefly outline the main concept of this theory in order to facilitate further discussion. According to the model, electrons and holes generated by a pulsed optical excitation form excitons, which are captured into localized states created by the disorder potential. Our focus is the case of low temperatures and low excitation densities, when trapped excitons relax independently from each other via energy-loss hopping between localized states. The PL decay is thus determined by the interplay between the radiative rate, τ_0^{-1} , and the hopping rate $\nu(r)$; the latter has a broad distribution due to the distribution of hopping distances r . Assuming the hopping transition to occur via phonon-assisted tunneling between localized states, the PL decay at some detection energy E and time t after the pulsed excitation can be written as [1, 7]

$$I(E, t) = (\text{const}) e^{-t/\tau_0} \times \int_0^\infty \rho(r, E) \exp(-t\nu_0 e^{-2r/\alpha}) dr, \quad (1)$$

where $\rho(r, E)$ is the distribution of hopping distances, α is the decay length of the localized exciton center-of-mass wavefunction, and ν_0 is the phonon-related attempt-to-escape frequency. It is convenient to put the origin of the energy scale at the exciton mobility edge E_{ME} , such that $E = \hbar\omega - E_{\text{ME}}$, where $\hbar\omega$ is the photon energy.

In the three-dimensional case, the distribution of hopping distances is the nearest-neighbor distribution

$$\rho(r, E) = 4\pi N(E)r^2 \exp[4\pi N(E)r^3/3], \quad (2)$$

where $N(E)$ is the density of states available for the hopping transition. Owing to the inequality $t\nu_0 \gg 1$, which holds for all practical times, one can regard the term $\exp(-t\nu_0 e^{-2r/\alpha})$ in equation (1) as a step function that yields

$$I(E, t) \approx (\text{const}) e^{-t/\tau_0} \int_{R_c(t)}^\infty \rho(r, E) dr = (\text{const}) \exp\left[-\frac{t}{\tau_0} - \frac{4\pi}{3} R_c^3(t) N(E)\right], \quad (3)$$

where $R_c = (\alpha/2) \ln(t\nu_0/\ln 2)$.

By definition, the PL decay time is given by the inverse logarithmic derivative of the PL signal

$$t_0^{-1} = -\frac{d}{dt} \ln I. \quad (4)$$

Corresponding differentiation of equation (3) eventually yields the transient spectral dependence of the PL decay time for the three-dimensional case in the form

$$t_0^{-1}(E, t) \approx \tau_0^{-1}(t) + \frac{\pi N(E)\alpha^3}{2t} \ln^2\left(\frac{t\nu_0}{\ln 2}\right). \quad (5)$$

This result has a rather simple interpretation. There are two competitive processes—the radiative recombination and the hopping downward in energy—which are responsible for PL decay at the selected energy. In this case, the decay rate is determined by the sum of reciprocal times responsible for each individual process, likewise in equation (5). Therefore, the second term in equation (5) represents the typical hopping rate downward in energy. This rate, however, is not a constant; it decreases in the course of time since the greater the time, the more distant pairs of nearest-neighbor sites contribute to the hopping.

When applying equation (5) to experimental data, one should bear in mind that this result is valid for the low-temperature limit and it is a subject of the following assumptions. First, we neglected feeding of the low-energy states due to the energy relaxation of excitons from the localized states with higher energies. Such processes can be ignored, unless the initial rise of the PL at its low-energy tail is considered. Second, we used the greatest rate approximation [7], which implies that the hopping transition occurs between the nearest-neighbor states available. This approximation is justified, provided the transition rates have a broad distribution, which is the case of hopping rates. Third, we assumed the exciton density to be sufficiently low, so that the band tail states can be considered unoccupied. This regime can be achieved at low pump intensities.

4. Results and discussion

PL spectra taken at different times after the pulsed excitation are shown in figure 1 along with the time-integrated PL spectrum. The broad linewidth of the PL spectra suggests that the PL emission originates from a tail of localized states associated with nitrogen (see inset in figure 1). It is evident that the PL maximum shifts gradually to lower energies in the course of time. This is attributed to the

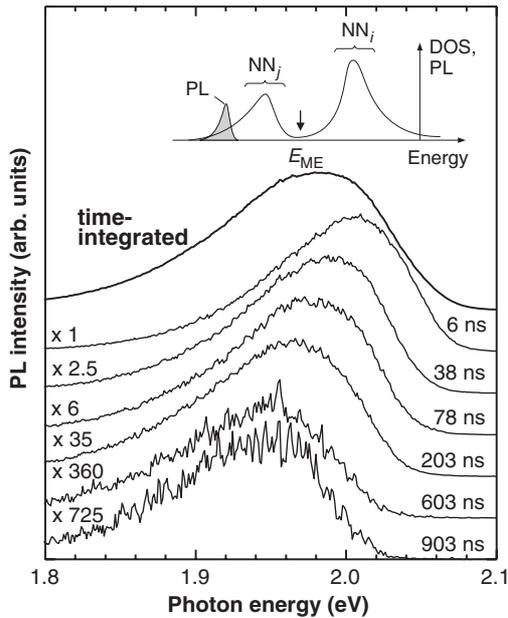


Figure 1. Photoluminescence spectra of a GaP_{0.979}N_{0.021} sample taken at different times after the excitation pulse and a time-integrated spectrum (integrated over the first 10 ms after the laser pulse). The inset illustrates schematically the density of states (DOS) due to nitrogen clusters, the position of the mobility edge E_{ME} , and the PL signal.

energy relaxation of localized excitations extensively studied in previous works [1, 13, 16, 18, 19].

To gain further insight into the energy transfer and recombination processes involved, we analyze the PL decay at different detection energies. The results are shown in figure 2. Obviously, the PL decay at higher detection energies is faster than that for lower energies, and it has a strongly non-exponential character for all detection energies. Remarkably, the time evolution of the energy-integrated PL (figure 2, solid line) is also strongly non-exponential, indicating a wide distribution of recombination times τ_0 shown in the inset to figure 2.

When studying the energy transfer processes, the spectrum of PL decay times is usually analyzed only at initial times after the excitation pulse [10]. Here we extend the analysis beyond this state and consider the transient change of the spectrum of PL decay times. Experimental decay times t_0 can be determined from the PL decay data in figure 2, approximating them by exponential functions $I(t) = I_0 \exp(-t/t_0)$ in a narrow range of times near t . The spectral dependence of t_0 is shown in figure 3 for a wide range of delays. The decay time remains almost constant for emission from localized states contributing to the low-energy tail of PL and progressively decreases with increasing energy in the high-energy tail of PL. The spectral variation of the PL decay time is more developed for shorter delays. Qualitatively these observations are consistent with the energy relaxation of localized excitons [8–10]. Our goal is to describe the transient change of the PL decay spectra quantitatively in the framework of the hopping model by using equation (5).

The energy dependence of the density of available states $N(E)$ in equation (5) is governed by the energy spectrum of

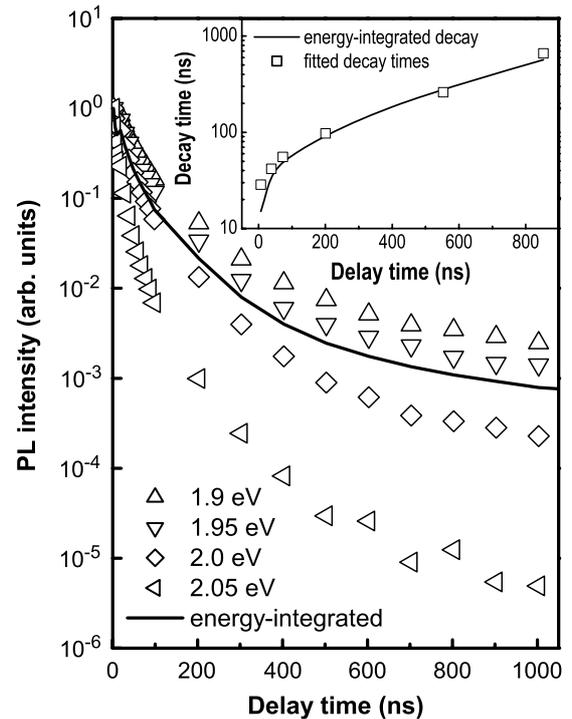


Figure 2. Decay of the PL intensity of selected photon energies (symbols). The solid line shows the decay of the energy-integrated PL intensity. The inset illustrates a transient evolution of the PL decay time determined from the energy-integrated PL intensity (solid lines) and that determined from the theoretical fit to the experimental data in figure 3 (open symbols).

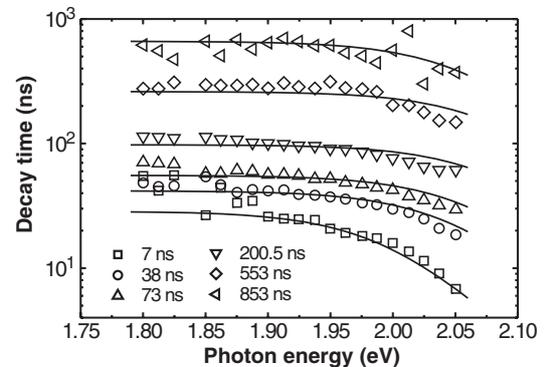


Figure 3. Spectral dependence of the PL decay times at different delays after the excitation pulse (symbols) and fits according to equation (5) (solid lines).

the localized states. Here we assume an exponential energy distribution of localized states, which seems to be a general feature of dilute nitride semiconductors [20, 21]. The integral density of states with energy below E is given by

$$N(E) = N_l \exp(E/E_0), \quad (6)$$

where N_l is the density of localized states and E_0 is the energy scale of the exponential tail. The energy position of the mobility edge, E_{ME} , can be determined from absorption [22] or photocurrent [23] measurements on bulk GaP(N) structures, which yields $E_{ME} \approx 2.1$ eV for a nitrogen content of 2%.

Thus, we have two time-independent fit parameters, $N_t\alpha^3$ and E_0 , and one time-dependent parameter $\tau_0(t)$. This is the minimal set of parameters, which is necessary to describe the main physics of the relaxation processes.

Experimental data for the PL decay times in figure 3 are fitted according to equation (5), assuming an exponential energy distribution of localized states (equation (6)). The theoretical curves are shown in figure 3 by solid lines. In order to describe the experimental data one needs to assume a variation of the exciton lifetime, which turns out to be consistent with the time evolution of the decay time of the energy-integrated PL (see inset in figure 2). From the best fit to the experimental data we determine two model parameters $E_0 = 40$ meV and $N_t\alpha^3 = 0.001$, which will be discussed below. We would like to emphasize that equation (5) describes both the spectral and transient evolutions of the PL decay time in the entire range of delay times, assuming only one time-dependent parameter, namely the exciton lifetime τ_0 .

Finally, we comment on the magnitude of parameters of the energetic disorder obtained from the fit to the data in figure 3. In the case of an exponential energy distribution of localized states, the disorder energy scale E_0 can be independently estimated from the time-integrated PL linewidth simply by dividing the full-width at half-maximum by a factor of 2.5 [21]. In our case the linewidth is 110 meV that yields $E_0 = 44$ meV, which is in agreement with the value of E_0 determined above. The density of localized states can be estimated, provided the exciton localization length is known. We assume the exciton to be localized due to localization of an electron on nitrogen-related states. Then the localization length α will be of the order of the lattice constant of GaP [12, 24]. That yields an estimate for the three-dimensional density of localized states of $N_t \sim 6 \times 10^{18} \text{ cm}^{-3}$. This value of N_t is by two orders of magnitude less than the concentration of nitrogen atoms, which at 2.1% is about $5 \times 10^{20} \text{ cm}^{-3}$. This leads to the conclusion that the PL originates from localized states, which presumably consist of more than two nitrogen atoms due to statistical reasons.

5. Conclusions

The energy relaxation of localized optical excitations in bulk $\text{GaP}_{0.979}\text{N}_{0.021}$ was studied by time-resolved photoluminescence spectroscopy with the goal to examine the recently suggested phenomenological theory, which describes the kinetics of the exciton energy relaxation. Both spectral and time dependences of the photoluminescence decay are quantitatively described by the theory with physically reasonable parameters. This result corroborates the validity of the assumptions made regarding the hopping mechanism of excitons, energy relaxation and the physical processes, which determine the photoluminescence decay time. Fitting experimental data for the spectral and time dependence of the photoluminescence decay time to the theory enables one to identify the energy distribution of the tail of localized states contributing to the photoluminescence as being probably exponential with an energy scale of

40 meV. The density of tail states contributing to the luminescence is estimated to be about $6 \times 10^{18} \text{ cm}^{-3}$, assuming the exciton localization length to be of the order of the lattice constant of GaP. Due to the low density of tail states, the luminescent states are presumably related to complexes, which include more than two nitrogen atoms.

Acknowledgments

Various parts of this work were supported by the European Community (IP 'FULLSPECTRUM' (ref. no. SES6-CT-2003-502620)), by the Deutsche Forschungsgemeinschaft in the framework of the Topical Research Group 483 'Metastable Compound Semiconductors and Heterostructures', by the Optodynamics Interdisciplinary Research Center of the Philipps-University, and by the funds of the Chemischen Industrie.

References

- [1] Wiesner P J, Street R A and Wolf H D 1975 *Phys. Rev. Lett.* **35** 1366
- [2] Gourdon C, Lavallard P, Permogorov S, Reznitsky A, Aaviksoo Y and Lippmaa Y 1987 *J. Lumin.* **39** 111
- [3] Golub J E, Baranovskii S D and Thomas P 1997 *Phys. Rev. Lett.* **78** 4261
- [4] Mair R A, Lin J Y, Jiang H X, Jones E D, Allerman A A and Kurtz S R 2000 *Appl. Phys. Lett.* **76** 188
- [5] Choi C K, Kwon Y H, Little B D, Gainer G H, Song J J, Chang Y C, Keller S, Mishra U K and DenBaars S P 2001 *Phys. Rev. B* **64** 245339
- [6] Luo X D, Xu Z Y, Ge W K, Pan Z, Li L H and Lin Y W 2001 *Appl. Phys. Lett.* **79** 958
- [7] Kivelson S and Gelatt C D 1982 *Phys. Rev. B* **26** 4646
- [8] Cohen E and Sturge M D 1982 *Phys. Rev. B* **25** 3828
- [9] Rubel O, Stolz W and Baranovskii S D 2007 *Appl. Phys. Lett.* **91** 021903
- [10] Gourdon C and Lavallard P 1989 *Phys. Status Solidi b* **153** 641
- [11] Thomas D G and Hopfield J J 1966 *Phys. Rev.* **150** 680
- [12] Kent P R C and Zunger A 2001 *Phys. Rev. B* **64** 115208
- [13] Felici M, Polimeni A, Miriametro A, Capizzi M, Xin H P and Tu C W 2005 *Phys. Rev. B* **71** 045209
- [14] Cuthbert J D and Thomas D G 1967 *Phys. Rev.* **154** 763
- [15] Buyanova I A, Rudko G Y, Chen W M, Xin H P and Tu C W 2002 *Appl. Phys. Lett.* **80** 1740
- [16] Yaguchi H, Miyoshi S, Arimoto H, Saito S, Akiyama H, Onabe K, Shiraki Y and Ito R 1997 *Solid-State Electron.* **41** 231
- [17] Hong Q, Dou K and Zhang X 1990 *Phys. Rev. B* **41** 1386
- [18] Buyanova I A, Pozina G, Bergman J P, Chen W M, Xin H P and Tu C W 2002 *Appl. Phys. Lett.* **81** 52
- [19] Izadifard M, Bergman J P, Vorona I, Chen W M, Buyanova I A, Utsumi A, Furukawa Y, Moon S, Wakahara A and Yonezu H 2004 *Appl. Phys. Lett.* **85** 6347
- [20] Grüning H *et al* 2004 *Phys. Status Solidi c* **1** 109
- [21] Rubel O, Galluppi M, Baranovskii S D, Volz K, Geelhaar L, Riechert H, Thomas P and Stolz W 2005 *J. Appl. Phys.* **98** 063518
- [22] Buyanova I A, Izadifard M, Kasic A, Arwin H, Chen W M, Xin H P, Hong Y G and Tu C W 2004 *Phys. Rev. B* **70** 085209
- [23] Güngerich M, Klar P J, Heimbrodt W, Weiser G, Geisz J F, Harris C, Lindsay A and O'Reilly E P 2006 *Phys. Rev. B* **74** 241202
- [24] Harris C, Lindsay A and O'Reilly E P 2007 unpublished