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# Nonexponential photoluminescence transients in a Ga(NAsP) lattice matched to a (001) silicon substrate

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Ga(NAsP) grown lattice-matched on (001) silicon substrate is a very promising material for future integrated, electrically pumped lasers on silicon. Here, we present experimental and theoretical studies of the time-resolved photoluminescence in Ga(NAsP)/Si quantum well structures. The experimental results obtained at 10 K show a strong nonexponential transient behavior for the photoluminescence signal. A detailed comparison with theoretical calculations based on rate equations and on straightforward Monte Carlo simulations reveals that this effect is controlled by an interplay between the fast capture of carriers on nonradiative centers and the slow radiative recombination via localized states. We demonstrate that the measurement of the time-resolved photoluminescence can serve as a convenient tool for estimating the relative concentrations of nonradiative and radiative centers in compound materials.

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## I. INTRODUCTION

The development of optoelectronic integrated circuits (OEICs) has attracted much interest, because it provides a promising new field of devices with novel functionalities and enhanced performance, e.g., for chip-to-chip and on-chip optical data transmissions. However, the key component of such OEICs, an integrated electrically pumped semiconductor laser, is still missing.

Although there have been several different approaches to develop an appropriate semiconductor laser that can be integrated on silicon substrates,[1–6] a reliable device concept that satisfies the requirements of electrical pumping, long device lifetime, and compatibility to the advanced complementary metal oxide semiconductor (CMOS) technology is still unavailable. One problem is the indirect band gap of Si, which prohibits a sufficient light emission and optical gain directly from bulk or layer structures. Although optical gain has already been demonstrated in Si nanocrystals,[1] an electrically pumped laser diode based on Si is still missing. The monolithic integration of standard III/V laser materials is a significant challenge, too, due to the large lattice mismatch of conventional laser materials like GaAs or InP to the Si lattice.[7] This usually leads to the formation of a large misfit and threading dislocation density. The dislocations act as efficient nonradiative centers and significantly reduce both device performance and device lifetime.[8] The novel dilute nitride material Ga(NAsP) is a very promising candidate to overcome these fundamental limitations, since it can be grown lattice matched on an exactly oriented (001) Si substrate.[9] Its high amount of As of more than 80% in combination with the anticrossing interaction[10–12] between the localized nitrogen states and the extended GaAsP states of the semiconductor matrix guarantees its direct bandgap, whereas the small covalent radius of the incorporated N additionally reduces the lattice constant of the GaAsP host material. This allows to grow Ga(NAsP) defect free and lattice matched on Si substrate using a GaP nucleation layer,[13,14] providing multiple quantum well structures with excellent optical qualities and high room temperature modal gain.[15,16] Electrically pumped lasers operating at room temperature have been reported for Ga(NAsP) structures grown on GaP substrates[17–19] and even first structures grown on exactly oriented (001) Si substrate show laser operation at temperatures up to 165 K.[20] This demonstrates the potential and suitability of this emerging material system as an active material for lasers integrated on Si.

In this paper, we present experimental and theoretical results for the time-resolved photoluminescence of a Ga(NAsP) quantum well sample grown lattice-matched on Si in order to investigate the influence of remaining defects and nitrogen-induced disorder in detail. Localization and disorder effects have been found in Ga(NAsP) samples grown on GaP before.[21] Disorder, originating from alloy fluctuations or interface imperfections between the quantum well and the barrier layers, usually leads to additional localized states inside the band gap. These additional states increase the radiative recombination and hence increase the effective carrier density required to generate sufficient optical gain for laser operation via extended states. Another negative factor affecting the optical gain is the recombination of carriers through nonradiative centers. Both radiative and nonradiative centers reduce the operation efficiency and the device performance. However, radiative localized states typically are energetically much closer to the band edges than nonradiative centers, and their influence on the device performance is less crucial. At sufficiently high temperatures, charge carriers are thermally activated from localized into extended states and thus still can promote the stimulated emission processes. Measurements of the photoluminescence (PL) response along with the theoretical interpretation of experimental results has become an efficient tool for estimating these important material characteristics and thus allow for an optimization of the material system even in an early state of development.

A simple phenomenological model was suggested in Ref. 22, which gives an explanation for PL features of many compound semiconductors. This model can be applied for theoretical interpretations of time-integrated[21–28] as well as time-resolved PL measurements.[29] The results of time-integrated measurements provided evidence that the energy scale of disorder and the relative concentrations of nonradiative and radiative centers can be estimated from the temperature-dependent PL.

In the following, we will demonstrate that an analysis of the time-resolved PL behavior using the theoretical model suggested in Ref. 22 permits one to estimate the relative concentrations of nonradiative and radiative centers in compound semiconductor systems without performing the temperature-dependent PL measurements. According to our experimental results, the decay of the time-integrated PL signal in Ga(NAsP) QW structures exhibits a nonexponential behavior. This effect is more pronounced at higher optical excitation intensities. The nonexponential character of the PL signal is not an unique property of Ga(NAsP) compound materials. A similar behavior was observed in other semiconductor compounds[30,31] as well. This feature was explained by the indirect-direct band gap crossover[30] or by the interplay between the hopping dynamics of optically excited electrons and holes treated as independent particles.[31] However, the arsenic-rich Ga(NAsP) compound studied in the present paper is a direct semiconductor material and, at sufficiently low temperatures, the dynamics of photoexcited electrons and holes can be described in form of correlated electron-hole pairs.[21,27] Using an exciton model in the following, we are able to explain the nonexponential time behavior of the PL in Ga(NAsP) quantum-well (QW) structures by the interplay between radiative and nonradiative recombination processes of photoexcited carriers. A detailed comparison between experimental and theoretical results allows us to estimate the relative concentrations of nonradiative and radiative centers.

The paper is organized as follows. In Sec. II, we present our experimental results. In Sec. III, we describe the theoretical approaches exploited to characterize the time decay of the integral PL signal in studied Ga(NAsP) QW structures, and compare our calculations with our experimental observations. Concluding remarks are gathered in Sec. IV.

## II. EXPERIMENT

We study the time-resolved photoluminescence (TRPL) behavior of a Ga(NAsP) multi-quantum-well (MQW) structure grown lattice matched on exact silicon (001) substrate at $T = 10$ K temperature at various optical excitation densities. The sample under study is grown by metal-organic vapor-phase epitaxy in a commercial horizontal growth reactor (AIX 200-GRF). A Si buffer layer followed by a 50–100-nm thick GaP nucleation layer in combination with a specific annealing procedure is used in order to achieve an antiphase domain and disorder free nucleation of the III-V material on exactly oriented Si substrate. More details about the defect free nucleation can be found in Refs. 13 and 32. The sample consists of three compressively strained Ga(NAsP) QWs with a thickness of 4.5 nm each. The QWs consist of 6.4% N, 80.4% As, and 13.2% P. The composition of the quaternary Ga(NAsP) was estimated from the in-plane strain measured by high-resolution x-ray diffraction (HR-XRD) in combination with various test structures for investigating the incorporation of the different group V elements during MOVPE growth. The QWs are surrounded by 60-nm thick tensile strained BGaP barriers with a boron concentration of 4.5%. 5-nm thin GaP intermediate layers were embedded between the QWs and the barrier layers in order to prevent the formation of B-N bonds, which otherwise would have a strong negative impact on the optical properties of the sample.[33] Additional in-plane optical confinement is provided by a 500-nm (bottom) and 50-nm (top) thick BGaP separate confinement layer structure containing 3.3% B. The sample was annealed directly in the growth chamber for 30 min at 850 °C in order to improve the optical quality of the structure. More details about the growth process and the used metal-organic precursors have been published elsewhere.[14]

In order to investigate the TRPL of the sample, we used a mode-locked Ti:Sa laser with 200-fs pulse width (Coherent Mira HP) as excitation source. The sample was mounted in helium-flow cold-finger cryostat (Cryovac KONTI Spectro A) in order to allow for low-temperature investigations. The sample was excited quasiresonantly into the QW states with an excitation wavelength of 800 nm. Light transmitted through the QWs will potentially excite carriers in the Si substrate, too. However, we do not expect a significant contribution of such carriers to the carrier density in the Ga(NAsP) QWs, because the GaP nucleation layer should serve as an efficient blocking layer between QWs and substrate. The PL of the samples was detected using a spectrometer (Bruker Spec 25015) followed by a streak camera with 2-ps maximal time resolution (Hamamatsu C5680). The energy integration window was chosen between 1.26 and 1.56 eV. All measurements were performed at 10-K sample temperature.

The experimental TRPL results for a series of excitation densities varying from $1.59 \times 10^{14}$ to $5.58 \times 10^{14}$ photons/cm$^2$ are shown in Fig. 1. The corresponding time-integrated spectra are shown in Fig. 2(a). The results show a strong non-single-exponential relaxation behavior of the carrier density, which is more pronounced for higher excitation densities. This nonexponential transient behavior can not be fitted with a single time constant only, but with a double exponential decay using two independent time constants or a stretched exponential fit using, e.g., a Kohlrausch-Williams-Watts function, as typically used for disordered samples.[34] In the following, we will compare these results with two different theoretical concepts taking localization effects and nonradiative recombination into account in order to investigate the nature of the observed nonexponential decay and the influence of disorder in this novel metastable dilute nitride material system.

## III. THEORETICAL CONCEPTS AND COMPARISON TO EXPERIMENT

All semiconductor heterostructures possess a certain degree of disorder due to their alloy structure and imperfect interfaces. The disorder gives rise to localized states acting as radiative recombination centers that affect the PL response of the system essentially. Nonradiative recombination is another important factor which affects the optical properties of the system, especially the quantum efficiency of the PL. The main

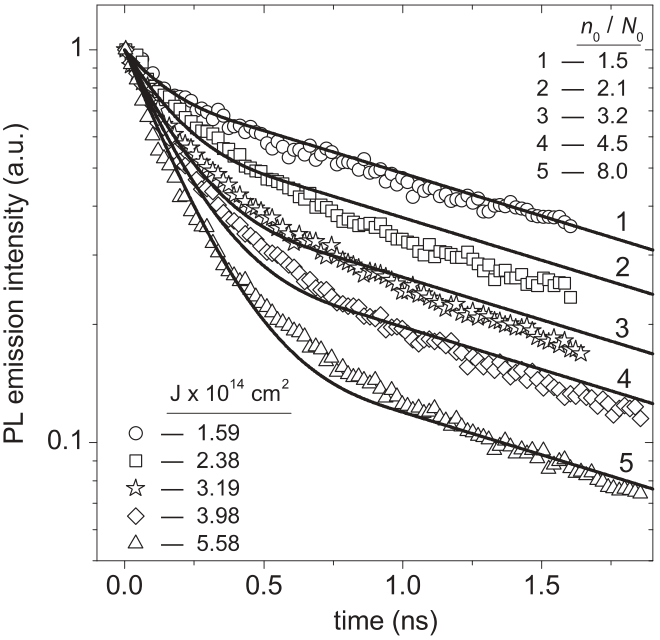

FIG. 1. Time dependence of the integral PL intensity in Ga(NAsP) observed experimentally at various intensities of the optical excitation (symbols), and data from simulations using the theoretical model based on the rate equations (3) and (4) with various initial densities of photoexcited excitons (solid lines).

kinetic processes determining the dynamics of photoexcited charge carriers in compound semiconductor materials are schematically shown in Fig. 3. After an optical excitation an electron-hole pair can radiatively recombine from the extended states (process-1) or it can be captured either by a nonradiative recombination center (process-2) or by a radiative localized state (process-3). An exciton captured by a localized state can radiatively recombine (process-4) or it can be thermally reactivated into the extended states (process-5). The additional important kinetic process is a hopping transition of the exciton between localized states (process-6). Hopping transitions from localized states to nonradiative centers can be neglected because the concentration of the nonradiative centers is usually much smaller than the concentration of localized states.[23] The interplay between all kinetic processes determines the PL behavior of the compound semiconductor materials.

According to our experimental results presented in Sec. II, the time decay of the integral PL intensity in the Ga(NAsP) quaternary compound has a nonexponential character. This feature is more pronounced for large optical excitation intensities. The simplest explanation of our experimental results would be the interpretation of the initial rapid decay of the integral PL intensity as a photoluminescence of free excitons from the extended states followed by the photoluminescence of localized excitons from the band tail assuming that the lifetime of localized excitons $\tau_0$ is much larger than the lifetime of free excitons $\tau_e$. However, under such an assumption on very different lifetimes for free and localized excitons, the time-integrated PL spectra would be at essential variance to the observed data as evidenced by the comparison between Figs. 2(a) (experiment) and 2(b) (simulation with $\tau_0/\tau_e = 8$). The details are given in Sec. III B. Below we estimate the restrictions on the ratio between the lifetimes of localized and free excitons and argue that the nonexponential PL decay is mainly caused by the nonradiative recombination of excitons. In order to show this, we begin with a simple theoretical approach based on a rate equation model.

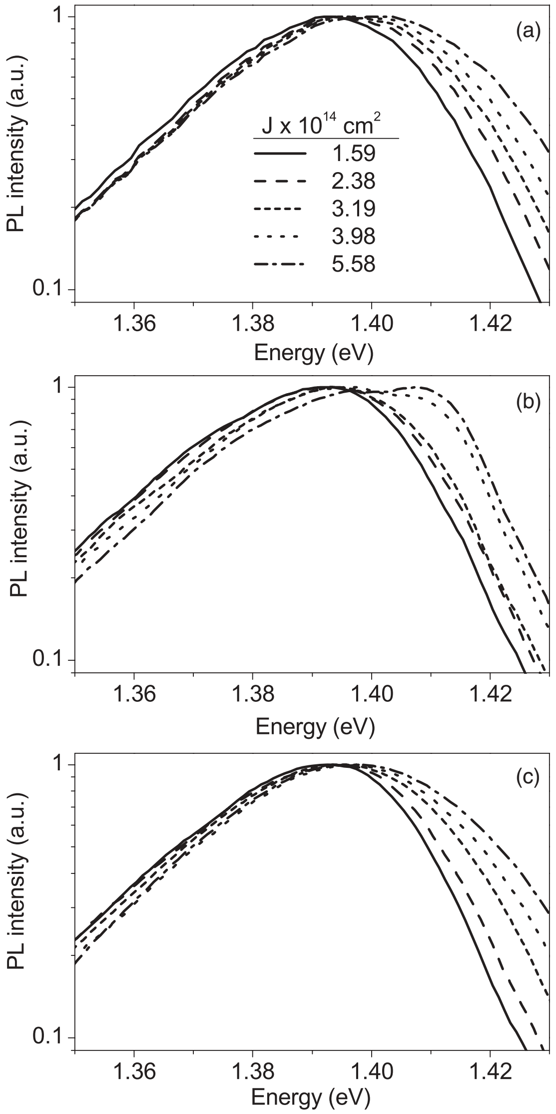

FIG. 2. Time integrated PL spectra in Ga(NAsP) observed experimentally at $T = 10$ K at various excitation intensities (a) and data from Monte Carlo simulations obtained for significantly different (b) and for equal lifetimes (c) for localized and free excitons.

### A. Rate equations

In this approach, we neglect the hopping motion of excitons and their thermal activation. Then, the PL time decay can be described by the following set of rate equations:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = -\frac{n}{\tau_\mathrm{e}} - \frac{n}{\tau_c}\left(\frac{N_\mathrm{nr}}{N_0}\right) - \frac{n}{\tau_c}\left(\frac{N_\mathrm{r} - n_c}{N_0}\right), \tag{1}$$

$$\frac{\mathrm{d}n_c}{\mathrm{d}t} = -\frac{n_c}{\tau_0} + \frac{n}{\tau_c}\left(\frac{N_\mathrm{r} - n_c}{N_0}\right), \tag{2}$$

where $n$ is the density of excitons in the extended states, $n_c$ is the density of excitons captured by the localized states, $N_\mathrm{r}$ and

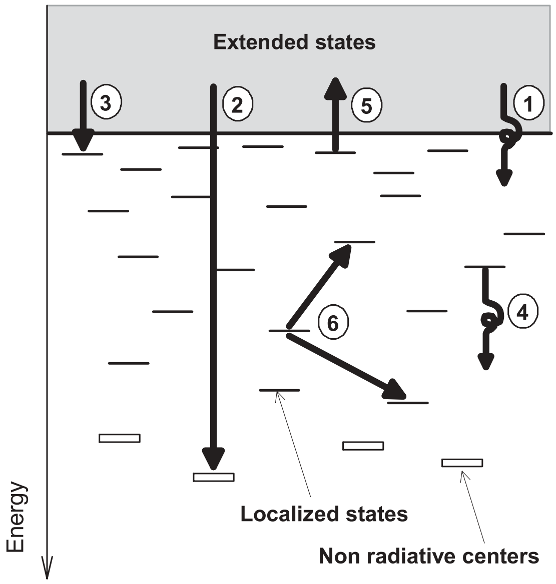

FIG. 3. Schematic representation of the main kinetic processes controlling the PL behavior of compound materials with inherent disorder: (1) radiative recombination of free exciton, (2) exciton capture by nonradiative centers, (3) exciton capture by localized states, (4) radiative recombination of localized exciton, (5) thermal excitation of the exciton from localized into extended states, and (6) hopping transitions of the exciton between localized states.

$N_{\mathrm{nr}}$ are the densities of the radiative localized states and of the nonradiative centers, respectively, and $N_0 = N_{\mathrm{r}} + N_{\mathrm{nr}}$ is the total density of recombination centers. $\tau_c$ is the capture time, which we assume equal for radiative and nonradiative centers: $\tau_c \simeq \nu_0^{-1}$, where $\nu_0$ is the attempt-to-escape frequency.

In Eq. (1), $n(t)$ describes the time evolution of the excitons in extended states, controlled by their radiative recombination (first term in the right-hand side of the equation) and by their capture onto the nonradiative centers and onto the radiative localized states (second and third terms, respectively). Similarly, in Eq. (2), $n_c(t)$ describes the time evolution of the localized excitons, controlled by their radiative recombination and by the capture of excitons from extended onto localized states.

The time decay of the integrated PL intensity is determined by the time evolution of the densities of excitons in localized and extended states. In this end, we should solve the set of rate equations (1) and (2) with initial conditions $n_c(0) = 0$ and $n(0) = n_0$, where $n_0$ is the initial density of photoexcited excitons.

Unfortunately, Eqs. (1) and (2) cannot be solved analytically, and numerical iteration methods (for example a step-adaptive Runge-Kutta algorithm) must be applied. Nevertheless, the nonexponential decay of the PL intensity observed in our experimental studies can already be predicted without performing numerical calculations. Furthermore, it can be shown that the nonradiative centers are responsible for the nonexponential PL decay.

In order to see this, we consider the relative probabilities of possible kinetic processes for optically excited excitons. Immediately after the excitation pulse all excitons are in the extended states and all localized states are unoccupied: $n_c \cong 0$ and $N_{\mathrm{u}} \cong N_{\mathrm{r}}$. In an extremely short time period determined by the capture time $\tau_{\mathrm{c}} = \nu_0^{-1}$, some fraction of photoexcited excitons will be captured by the radiative localized states. (At this beginning stage, the capture on nonradiative centers can be neglected since the ratio $N_{\mathrm{nr}}/N_{\mathrm{r}}$ of the nonradiative centers and the radiative localized states is usually small).[23] Afterwards, with increasing occupation of the localized states $n_c$ and hence with decreasing density of the unoccupied states $N_{\mathrm{u}}$, the remaining excitons cannot be captured efficiently by the radiative localized states. They will recombine radiatively from the extended states or will be captured by the nonradiative centers resulting in a PL decay with characteristic time $\tau_1 = (\tau_{\mathrm{e}}^{-1} + \nu_0 N_{\mathrm{nr}}/N_0)^{-1}$. According to our suggestions given in the introduction part of this section, the radiative recombination from the extended states cannot be the dominant decay process in studied Ga(NPAs) compound, though it can be important for the estimation of the material characteristics (see below). For qualitative considerations, we first neglect this process. Beginning from the moment when $N_{\mathrm{nr}} \geqslant N_{\mathrm{u}}$, the nonradiative recombination becomes the dominant kinetic process. As a result, according to Eqs. (1) and (2), the PL intensity decreases exponentially with characteristic time $\tau_1 = \nu_0^{-1} N_0/N_{\mathrm{nr}}$. Evidently, the radiative recombination also occurs in parallel, and some localized states become unoccupied but only for a very short time period. They immediately capture new excitons from the extended states. This situation persists until the "reservoir" of the excitons in the extended states becomes empty ($n \to 0$). After this time, the radiative recombination from the localized states is the dominant kinetic process, and an exponential decay of PL intensity with characteristic time $\tau_0$ takes place.

In summary, we can distinguish three different time domains with different PL behavior: (i) a rapid capture of photoexcited excitons from the extended into the radiative localized states; (ii) an intensive nonradiative recombination of photoexcited excitons resulting in the exponential decay of the PL intensity with characteristic time $\tau_1$; and (iii) a radiative recombination from the localized states resulting in the exponential decay of the PL intensity with characteristic time $\tau_0$. The interplay between these different characteristic times $\tau_1$ and $\tau_0$ determines the nonexponential character of the decay in the integral PL intensity. Furthermore, the relative durations of the different time domains distinguished above depend on the initial concentration of photoexcited excitons $n_0$. The nonexponential character of the decay PL is more pronounced for larger values of $n_0$. This trend is in line with our experimental observations. They show that the deviation from the exponential time dependence of the integral PL emission becomes more pronounced with increasing intensity of the optical excitation.

To check our predictions, we perform numerical calculations. For this purpose, we rewrite the set of Eqs. (1) and (2) in a more convenient form:

$$\frac{\mathrm{d}x}{\mathrm{d}\bar{t}} = -\left[\beta + \nu_0\tau_0\,(1-y)\right]x, \tag{3}$$

$$\frac{\mathrm{d}y}{\mathrm{d}\bar{t}} = -y + \nu_0\tau_0\,(1-\gamma-y)\,x, \tag{4}$$

using the dimensionless variables $x \equiv n/N_0$, $y \equiv n_{\mathrm{c}}/N_0$, $\bar{t} \equiv t/\tau_0$, and the dimensionless parameters $\gamma \equiv N_{\mathrm{nr}}/N_0$, $\beta \equiv \tau_0/\tau_{\mathrm{e}}$. We solve Eqs. (3) and (4) with initial conditions

$x(0) = n_0/N_0$ and $y(0) = 0$ using the step-adaptive Runge-Kutta iteration method.

Let us estimate essential model parameters from the experimental data in Fig. 1. In the case of equal lifetimes of free and localized excitons $\beta = 1$ and zero concentration of nonradiative centers $\gamma = 0$, Eqs. (3) and (4) give the exponential decay of integral PL intensity with characteristic time $\tau_0$. In the case of $\beta = 1$ and $\gamma \neq 0$, according to the considerations above, the beginning of the PL decay is controlled by the nonradiative recombination of free excitons with characteristic time $\tau_1 = \nu_0^{-1}\gamma^{-1}$. After some time period, in which majority of excitons are captured by the localized states, the PL decay is controlled by the radiative recombination from the extended and localized states with characteristic time $\tau_0$. In the general case of $\beta \neq 1$ and $\gamma \neq 0$, the characteristic time of the initial PL decay is given by the expression

$$\tau_1 = \frac{\tau_0}{\beta + \nu_0\tau_0\gamma}. \tag{5}$$

We estimate the value of the radiative lifetime of localized excitons as $\tau_0 = 2$ ns from the logarithmic slope of the experimentally observed PL decay (see Fig. 1) in its long-time domain, and estimate the value of the combined characteristic time $\tau_1 = 0.25$ ns from the logarithmic slope of the experimentally observed PL decay in its short-time domain. So far, we used the PL decay observed at the largest optical excitation intensity (triangles in Fig. 1) where the initial decrease in the PL intensity is most pronounced. For $\tau_0 = 2$ ns and $\tau_1 = 0.25$ ns, Eq. (5) gives the possibility to estimate the typical values of the ratio of localized and free exciton lifetimes $\beta = \tau_0/\tau_e$ and the relative concentrations of nonradiative centers $\gamma = N_{\mathrm{nr}}/N_0$ necessary to explain the experimentally observed decays of PL integral intensity in Ga(NAsP) compound. Indeed, we have already shown that the radiative recombination cannot be the dominant kinetic process for excitons in the extended states. Therefore according to Eq. (5), the upper limit for the values of $\beta$ can be estimated as $\beta < \nu_0\tau_0\gamma$. We assume the radiative lifetime of free excitons equal to the radiative lifetime of localized exciton as a lower limit $\beta = 1$. Furthermore, taking into account that according to Eq. (5), $\nu_0\gamma = \tau_1^{-1} - \beta\tau_0^{-1}$, the final range of the possible values of the parameter $\beta$ can be estimated as $1 \leqslant \beta < 4$. The corresponding values of the relative concentration of nonradiative centers $\gamma$ depend on the value of the attempt-to-escape frequency $\nu_0$ and are determined as $2 \times 10^9\nu_0^{-1} < \gamma < 4 \times 10^9\nu_0^{-1}$. The typical values of the attempt-to-escape frequency are usually taken in the range of $\nu_0 = (10^{12} - 10^{13})$ s$^{-1}$. Therefore the values of the relative concentration of nonradiative centers can be estimated as $2 \times 10^{-4} < \gamma < 4 \times 10^{-3}$. The question arises on whether this estimate for the relative concentration of nonradiative centers is reasonable or not. So far, such estimations were carried out on the basis of the temperature dependence of the integrated PL intensity.[21,23] The relative concentration of the nonradiative centers $\gamma = 1.4 \times 10^{-3}$ estimated in Ref. 23 for Ga(NAsP) compound agrees with our estimations. It is, however, smaller than the relative concentration of the nonradiative centers given in Ref. 21. The difference between these estimations is evidence of the different temperature dependencies of the integrated PL intensity experimentally observed in Refs. 23 and 21. It might be caused by different preparation conditions of the samples.

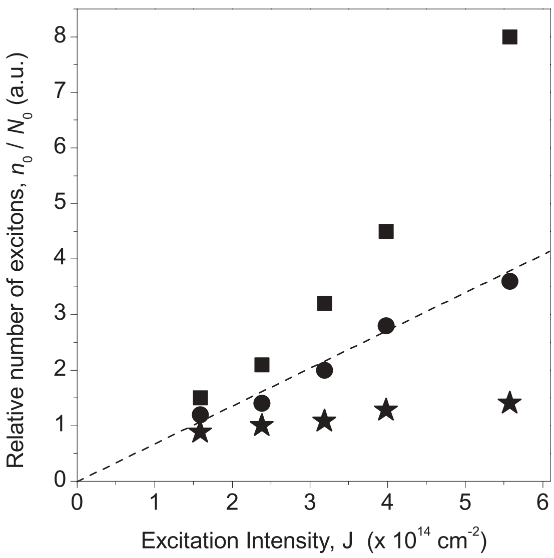

FIG. 4. Dependence of the relative number of photoexcited excitons on the optical excitation intensity. The estimates are made by the comparison between the experimental PL decays at various excitation intensities and our calculations using the simple rate equation model (3), (4) with $\tau_0 = \tau_e$ (squares) and using the Monte Carlo simulation for $\tau_0/\tau_e = 1$ (circles) and for $\tau_0/\tau_e = 8$ (stars). The dashed line is a guide to the eye showing a linear dependence ($n_0 \propto J$).

For further considerations we assume the attempt-to-escape frequency $\nu_0 = 10^{12}$ s$^{-1}$ and the relative density of nonradiative centers $\gamma = 0.004$ that corresponds to the equal lifetimes of free and localized excitons ($\beta = 1$). The best agreement between the solutions of Eqs. (3) and (4) and the experimental decays of the PL signal at various excitation intensities was obtained for the initial conditions $x(0) = n_0/N_0$ given in Fig. 1.

The corresponding dependence of the relative number of excitons $n_0/N_0$ on the excitation intensity $J$ is shown in Fig. 4 by squares. This dependence is strongly nonlinear though one would expect that the number of excited carriers is proportional to the radiation intensity. We argue that the reason for this seemingly nonlinear behavior of $n_0(J)$ is the simplicity and incompleteness of the rate-equation model (3) and (4). Indeed, this model neglects the thermal activation of excitons from localized into extended states like in case of zero temperature, whereas our experiments were carried out at finite temperature, $T = 10$ K. Furthermore, hopping transitions between localized states are also neglected in this model.

A more accurate interpretation of our experimental results requires a more appropriate theoretical approach that takes into account the effects of finite temperatures as well as hopping transitions between the localized states. This cannot be done using the rate equations (3) and (4). Instead, we must discretize the DOS of localized states into many energy slices and introduce rate equations for each energy slice. The corresponding theoretical model taking into account hopping transitions between the localized states was suggested by Marshall.[35] An alternative approach is the use of Monte Carlo simulations based on the theoretical model suggested in Ref. 22 and adopted for many-particle systems. We prefer the later approach because Marshall's model gives only an approximate solutions due to the non-Markovian character of the involved kinetic processes. The details of the theoretical model used in our Monte Carlo simulations and the corresponding simulation algorithm are discussed in the next section.

### B. Monte Carlo simulations

We perform Monte Carlo simulations of the time-resolved PL behavior of Ga(NAsP) QW structures using the model suggested in Ref. 22, though with essential modifications. In Ref. 22, the hopping and recombination of mutually independent excitons was considered. This corresponds to the experimental situation where the exciton creation rate is sufficiently low. According to our experimental results presented in Sec. II, the time-resolved PL-behavior of the studied Ga(NAsP) material is significantly affected by the variations in the optical excitation intensity. Therefore the assumption of an independent relaxation of excitons cannot be applied for a correct theoretical interpretation of our experimental results. We adopt the theoretical model suggested in Ref. 22 for many-particle systems following the reasonings given in Refs. 28 and 29 albeit with the following essential difference. In Refs. 28 and 29, it was assumed that the same localized state can act radiatively (at low temperatures when the thermal energy is smaller than the exciton binding energy) or nonradiatively (in the opposite case). Such a consideration requires the assumption of an extremely small value of the exciton binding energy in the studied (GaIn)(NAs)/GaAs QW structures. Here, we use a different approach assuming that comparatively shallow localized states caused by the disorder always act as radiative centers whereas the nonradiative centers correspond to energetically deeper defect states. Our assumptions are based on the following arguments: (i) there is no experimental evidence that the exciton binding energy in Ga(NAsP) QW structure is extraordinary small; (ii) we consider very low temperatures ($T = 10$ K); and (iii) the theoretical model with independent radiative and nonradiative centers was successfully applied to explain the time-integrated PL behavior of Ga(NAsP) QW structures.[21]

The basics of the model used in our Monte Carlo simulations and the corresponding simulation algorithm look as follows. We consider a given number $n_0$ of free excitons at time $t = 0$. Each exciton can participate in the following kinetic processes. (i) The exciton can recombine radiatively (process-1 in Fig. 3). The rate of the radiative recombination is calculated as an inverse of the lifetime $\tau_0$,

$$\nu_{\mathrm{r}} = \tau_0^{-1}. \tag{6}$$

(ii) The exciton can be captured either by localized states that act as radiative centers or by nonradiative centers (process-3 and process-2 in Fig. 3, respectively). We create a set of $N_{\mathrm{r}}$ localized states with random positions in configuration space with exponentially distributed random energies.[21,27] No correlations between the energies of the states and their spatial positions are assumed. We also create a set of $N_{\mathrm{nr}}$ nonradiative centers so that $N_{\mathrm{nr}} \ll N_{\mathrm{r}}$. This strong inequality allows us to neglect hopping transitions between radiative and nonradiative centers. Hence the energy and the spatial distribution of the nonradiative centers are not relevant for our calculations.

The capture rates are determined by the following expressions:

$$\nu_{\mathrm{cr}} = \nu_0 \frac{N_{\mathrm{u}}}{N_0} \tag{7}$$

for a capture of excitons by the radiative centers, and

$$\nu_{\mathrm{cnr}} = \nu_0 \frac{N_{\mathrm{nr}}}{N_0} \tag{8}$$

for a capture of excitons by the nonradiative centers. Here, $N_{\mathrm{u}} = N_{\mathrm{r}} - n_{\mathrm{c}}$ is the number of unoccupied localized states determined as the difference between the total number of localized states $N_{\mathrm{r}}$ and the number of excitons $n_{\mathrm{c}}$ captured by the localized states, and $N_0 = N_{\mathrm{r}} + N_{\mathrm{nr}}$ is the total number of recombination centers.

After an exciton is captured by a localized state, the localized exciton can participate in the following processes.

(iii) The exciton can recombine radiatively (process-4 in Fig. 3). We assume the same lifetime $\tau_0$ for free and localized excitons. Therefore the rate of the radiative recombination of localized excitons is given by Eq. (6).

(iv) The exciton can be thermally activated into an extended state (process-5 in Fig. 3). The probability of such a transition is given by

$$\nu_{a,i} = \nu_0 \exp\left(\frac{E_i}{k_{\mathrm{B}} T}\right), \tag{9}$$

where $\nu_0$ is the attempt-to-escape frequency, $E_i$ is the energy of the localized state from which the thermal activation occurs, $k_{\mathrm{B}}$ is the Boltzmann constant, and $T$ is the temperature.

(v) The exciton can perform a transition between localized states (process-6 in Fig. 3). These phonon-assisted transitions are described by Miller-Abrahams tunneling rates,[36]

$$\nu_{ij} = \nu_0 \exp\left(-\frac{2R_{ij}}{\alpha} - \frac{E_j - E_i + |E_j - E_i|}{2k_{\mathrm{B}} T}\right), \tag{10}$$

where $E_i$ and $E_j$ are the energies of the initial and the target localized states, $i$ and $j$, respectively, $R_{ij}$ is the distance between the states, and $\alpha$ is the localization length equal to the decay length of the localized exciton center-of-mass wave function.[37]

For each exciton, we calculate the total rate $\nu$ of all possible actions. The number and type of possible actions depend on the starting state. Thus, for an exciton being in an extended state, we have

$$\nu = \nu_r + \nu_{\mathrm{cr}} + \nu_{\mathrm{cnr}}, \tag{11}$$

and for an exciton in a localized state $i$, we have

$$\nu = \nu_r + \nu_{a,i} + \sum_{j \neq i} \nu_{ij}, \tag{12}$$

where the sum runs over all unoccupied states $j$. Because the hopping rates $\nu_{ij}$ given by Eq. (10) depend exponentially on the distance and energy difference between localized states, only few of them determine the sum on the right-hand side of Eq. (12). Therefore, aiming to reduce the simulation time, we restrict the number of $\nu_{ij}$ terms in the sum by the $M$ largest terms. Typically, $M = 10$ is taken. We checked that the increase of $M$ up to 25 does not change the simulation results.

Using the total rates and a random number $\xi_1$, we determine the particular exciton that will move. The type of the movement is determined taking into account the rates of different kinetic processes calculated for the chosen exciton, using another random number $\xi_2$. Finally, we generate a third random number $\xi_3$ and calculate the real time $\Delta t$ of a given process as

$$\Delta t = \nu^{-1} \ln \xi_3, \tag{13}$$

and advance the current simulation time by $\Delta t$,

$$t \mapsto t + \Delta t\ . \tag{14}$$

If the performed process is a recombination (radiative or nonradiative), we exclude the chosen exciton from the list of considered excitons and reduce the number of excitons by one. In case of a radiative recombination, we additionally store the energy position of the recombined exciton along with the current simulation time.

We repeat this procedure until all excitons have recombined. The results of the simulation are the spectrum of the recombination energies and the distribution of the recombination times. Our data provide the time-integrated PL spectra as well as the decays of the energy-integrated PL intensity. The dependence of the PL behavior on the intensity of the optical excitation can be simulated by varying the initial concentration of excitons $n_0$. The additional simulation parameters involved in the kinetic model are the energy scale of the DOS of localized states $E_0$ and the localization length $\alpha$. According to Refs. 22 and 25, the energy scale of the DOS $E_0$ can be estimated from the temperature dependence of the PL emission peak energy. Following the reasonings given in Refs. 22 and 25, we find $E_0 \cong 10$ meV. Furthermore, according to Ref. 22, the localization length $\alpha$ enters in combination with the density of localized states $N_0$, resulting in a single simulation parameter $N_0\alpha^2$. We can consider the value $N_0\alpha^2 = 1$ as the upper limit that allows us to treat the shallow states of the band tail as localized. It is appropriate to take $N_0\alpha^2 = 0.1$ as the lower limit for a dilute system in which the hopping dynamics is almost suppressed due to the weak coupling between the localized states. Therefore, in our simulations we use $N_0\alpha^2 = 0.5$ which is between the upper and the lower limits. Note that the values of other simulation parameters, including the relative concentration of nonradiative centers $\gamma = N_{\mathrm{nr}}/N_0$, are the same as those used in our rate-equation model (3) and (4). To simulate the time-integrated PL spectra at various excitation intensities, we additionally need the energy distribution of excitons in extended states of QW with step-like DOS. For a given value of the excitation intensity simulated in our model by the initial concentration of excitons $n_0$, we estimate the initial energy spread of free excitons $\Delta E$ by the condition of equal densities of localized and extended states at the mobility edge. With good approximation, the time evolution of $\Delta E$ follows the time evolution of the density of free excitons $n$, since the intraband relaxation time is much less than the characteristic times of all other considered kinetic processes. The final time-integrated PL spectra are obtained taking into account the double-scaled disorder potential inherent for Ga(NAsP) compound materials.[21,27]

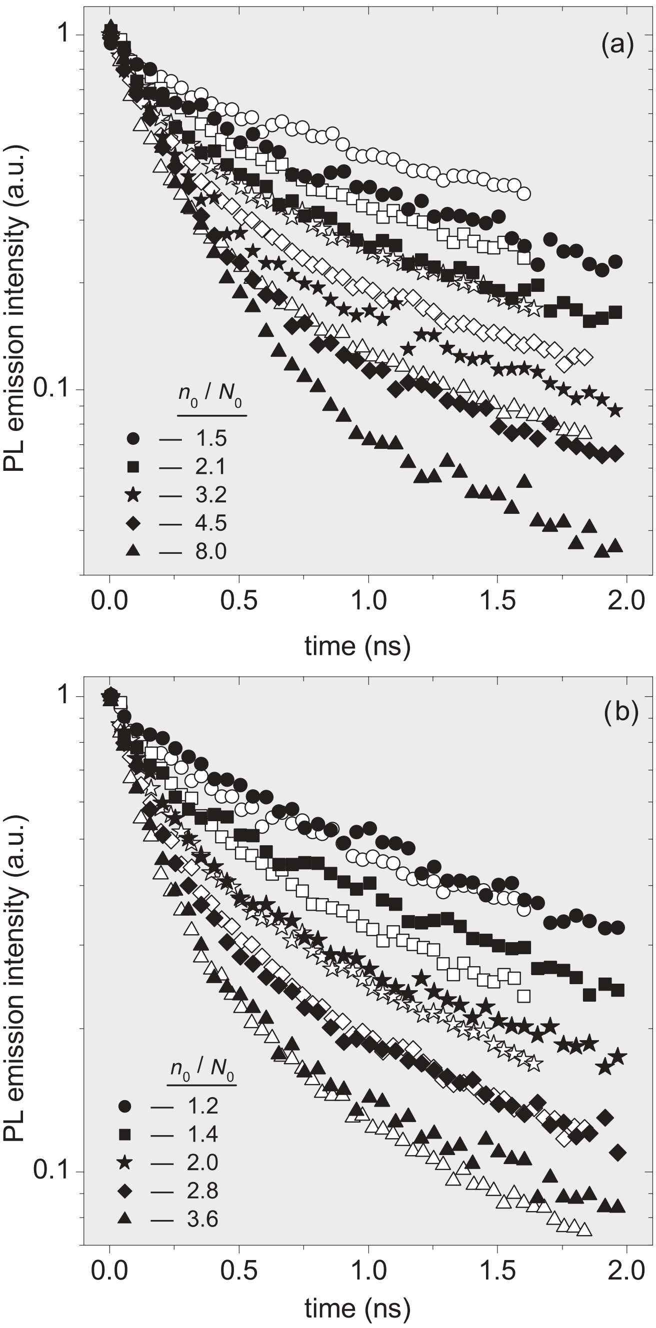

FIG. 5. PL decays obtained by Monte Carlo simulations using the values of the initial number of excitons given in Fig. 4 by squares (a) and by circles (b). The experimental dependencies of Fig. 1 are shown by open symbols, the numerical data are shown by filled symbols.

As an initial test of our kinetic model, we take the same values of $n_0/N_0$ (squares in Fig. 4) that provide a good agreement between the experimentally observed PL decays and the results for the rate-equation description (symbols and lines in Fig. 1, respectively). When the kinetic model reproduces the results of the rate-equation model and therefore gives a good agreement with experimental findings, we can conclude that thermal activation and hopping transport of excitons were not important for the correct description of PL decay in Ga(NAsP) compounds. However, the results of Monte Carlo simulations, given in Fig. 5(a) by filled symbols, show that this is not the case. Hence thermal activation and hopping transport of excitons must be taken into account and the values of $n_0/N_0$ should be redefined in order to provide a good agreement between the experimental and simulation results. The best agreement [see Fig. 5(b)] was obtained for the values of $n_0/N_0$ shown in Fig. 4 by circles evidencing the almost linear increase in the number of excitons with increasing excitation intensity, as intuitively expected. Furthermore, the corresponding time-integrated PL spectra shown in Fig. 2(c), are in good agreement with those experimentally observed at all excitation intensities [see Fig. 2(a)].

Finally, let us check our suggestions about the dominant role of the nonradiative centers in nonexponential PL transients of the studied Ga(NAsP)/Si QW. We perform the Monte Carlo simulation assuming the zero density of nonradiative centers $\gamma = 0$. The ratio of the exciton lifetimes in localized and extended states was taken as $\tau_0/\tau_e = 8$ providing according to Eq. (5) the observed initial decay of PL signal with characteristic time $\tau_1 = 0.25$ ns. The values of $n_0/N_0$ that provide a good agreement between the experimentally observed and simulated time decays of PL signal at various excitation intensities are shown in Fig. 4 by stars. These values are much smaller than those estimated for the equal lifetimes of localized and free excitons (circles in Fig. 4). The initial energy spreads of free excitons $\Delta E$ are accordingly smaller. As a result, the simulated time-integrated PL spectra shown in Fig. 2 b are at essential variance to the observed ones. Therefore we conclude that the lifetime of free excitons cannot be much different from the lifetime of localized excitons and the nonexponential character of transient PL behavior in Ga(NAsP) is mainly determined by the recombination of excitons via the nonradiative centers.

## IV. CONCLUSIONS

The time-resolved photoluminescence behavior of a Ga(NAsP) multi-quantum-well sample grown lattice-matched on (001) Si substrate was studied experimentally and theoretically. The experimental investigations carried out at $T = 10$ K various intensities of the optical excitation reveal a strong nonexponential character of the PL decay. The nonexponential behavior is more pronounced for larger excitation densities. Using a simple theoretical approach based on a rate equation model, which takes filling effects into account, it is shown that the nonexponential character of the PL decay is due to a combination of a fast capture of excitons by nonradiative centers and a slow radiative recombination via localized states. However, by comparing these results with a straightforward many-particle Monte Carlo simulation, we could furthermore demonstrate that a correct description of the transient photoluminescence behavior requires the additional consideration of thermal activation and hopping processes even in the low-temperature regime. A detailed comparison between experimental and theoretical results permits an estimate of the relative concentrations of nonradiative and radiative centers in Ga(NAsP) compound materials.

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