

## ON THE THEORETICAL DESCRIPTION OF PHOTOLUMINESCENCE IN DISORDERED QUANTUM STRUCTURES

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A theory is suggested for the description of luminescence in semiconductor structures, with the essential role of localized states caused by disorder. The theory is based on the set of rate equations. In contrast to most previous theoretical studies, electrons and holes are treated not in the form of excitons but rather as independent species. Theoretical results are compared with new experimental data for the time-resolved photoluminescence in GaInNAs/GaAs quantum wells.

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### 1. Introduction

Semiconductor quantum-well (QW) structures have been intensively studied experimentally and theoretically in the last decade, because of their potential for applications in optoelectronic devices. Most of the theoretical work in this field is based on idealized systems where the effects of disorder are disregarded. However, all semiconductor heterostructures possess a certain degree of disorder due to their alloy structure and imperfect interfaces. The disorder gives rise to localized states which can essentially influence the dynamics of photoexcited charge carriers and affect the optical properties of the system. While quite a number of experimental papers on the dynamics of optical excitations in disordered environment exist, the theoretical literature on this subject is comparatively scarce. Furthermore, in the existing theoretical studies of such effects, it has usually been assumed that electrons and holes are strongly spatially correlated in the form of excitons [1-3]. This assumption, however, is not always valid. For example, if the amplitude of the disorder potential is higher than the binding energy of excitons, the assumption of a strong spatial correlation between electrons and holes cannot be justified. Therefore, in this study we suggest a theoretical picture for luminescence provided by uncorrelated electrons and holes.

While the excitonic model of recombination with a constant lifetime can be easily treated by a kinetic computer simulation [1-3], the system with uncorrelated electrons and holes can hardly be treated in a straightforward simulation because of the extremely broad distribution of the recombination times which depend exponentially on the distances between recombining partners. This exponentially broad distribution of recombination times along with the necessity to treat simultaneously the independent dynamics of electrons and holes makes the computer simulation procedure extremely time-consuming. Therefore, we choose for our theoretical study here an analytical method based on a set of rate equations.

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The structure of the paper is the following. In section 2 we present our theoretical model and give the set of rate equations. In section 3 we present new experimental data on the time dependent photoluminescence in GaInNAs/GaAs quantum wells, and compare these with the theoretical results.

## 2. Theoretical model

We assume that disorder in QWs caused by their alloy composition and imperfect interfaces creates a set of localized states that can trap photogenerated charge carriers. We will consider two-dimensional uncorrelated sets of randomly distributed localized states for electrons and holes with concentration  $N_0$  and localization length  $\alpha$ . For simplicity we consider a symmetrical case with equal concentrations of localized states and localization lengths for electrons and holes. Let the corresponding densities of states (DOS) be  $g_e(\mathcal{E})$  and  $g_h(\mathcal{E})$ , respectively. In a system with strong enough disorder, charge carriers are captured into localized states after their photogeneration. From these states the carriers can either recombine or perform a phonon-assisted hopping transition to other localized states. Since both these processes occur in localized states, their probabilities depend exponentially on the distances involved. The rate for a localized electron to recombine with a localized hole at a distance  $R$  is

$$\Gamma_r(R) = \tau_0^{-1} \exp(-2R/\alpha), \quad (1)$$

where  $\tau_0$  depends on the particular recombination mechanism. In the case of radiative recombination,  $\tau_0$  is of the order of the exciton radiative lifetime. A rate for a charge carrier to perform a non-radiative hopping transition from an occupied state  $i$  to an empty localized state  $j$  over a distance  $r_{ij}$  is determined by the Miller-Abrahams expression [4]

$$\Gamma_{ij} = \nu_0 \exp\left(-\frac{2r_{ij}}{\alpha} - \frac{\mathcal{E}_j - \mathcal{E}_i + |\mathcal{E}_j - \mathcal{E}_i|}{2kT}\right), \quad (2)$$

where  $\mathcal{E}_j$  and  $\mathcal{E}_i$  are the energies of states  $j$  and  $i$ , respectively, and  $\nu_0$  is the attempt-to-escape frequency. The latter is of the order of a phonon frequency  $10^{12} \text{ s}^{-1}$ .

Aiming at the description of the charge carrier dynamic behaviour in the disorder potential, we use below the theoretical approach suggested by Marshall [5]. According to this, one divides the energy range where the localized states are distributed into a set of  $m$  energy slices with a given width, and formulates the rate equations for carrier densities in those energy slices. The time evolution of the carrier concentration  $n_k$  in slice number  $k$  is determined by the equation

$$\frac{dn_k}{dt} = \sum_{\substack{j=1 \\ j \neq k}}^m (n_j \Gamma_{j \rightarrow k} - n_k \Gamma_{k \rightarrow j}) - n_k \Gamma_r, \quad (3)$$

where  $\Gamma_{i \rightarrow j}$  denotes the rate of a charge carrier transition from a state in slice  $i$  to a state in slice  $j$ , and  $\Gamma_r$  is the recombination rate.

Let us consider first the transition rate,  $\Gamma_{k \downarrow}$ , from slice  $k$  downward in energy. Since the transition occurs via energy loss hopping, only the tunnelling term remains in Eq. (2). Therefore, one can write the downward transition rate as

$$\Gamma_{k\downarrow} = v_0 \exp\left(-\frac{2R_k}{\alpha}\right). \quad (4)$$

Here  $R_k$  is the typical hopping distance, which is determined by the concentration of unoccupied states with energies below  $E_k$ . In a two-dimensional case it can be estimated as

$$R_k = \left\{ \pi \sum_{i=k}^m [d_i - n_i(t)] \right\}^{-1/2}, \quad (5)$$

where  $d_j$  denotes the concentration of localized states in the energy slice  $j$ . Using Eq. (4), one can derive the downward hopping rate,  $\Gamma_{k\rightarrow j}$ , between two energy slices as a fraction of  $\Gamma_{k\downarrow}$  proportional to the fractional concentration of free states in the target slice [5]. Therefore, the downward-in-energy transition rates between states in two energy slices  $k$  and  $j$  ( $E_k > E_j$ ) can be written in the form

$$\Gamma_{k\rightarrow j} = v_0 \exp\left(-\frac{2R_k}{\alpha}\right) \times \frac{d_j - n_j(t)}{\sum_{i=k}^m [d_i - n_i(t)]}. \quad (6)$$

Transition rates for carriers between two slices  $j$  and  $k$  upward in energy can be derived from an appropriate downward transition rate  $\Gamma_{k\rightarrow j}$  taking into account the detailed balance condition, which is expressed as

$$\Gamma_{j\rightarrow k} = \Gamma_{k\rightarrow j} \frac{d_k - n_k(t)}{d_j - n_j(t)} \exp\left(-\frac{\varepsilon_k - \varepsilon_j}{kT}\right). \quad (7)$$

Hence, for the upward-in-energy transition one obtains the expression

$$\Gamma_{j\rightarrow k} = v_0 \exp\left(-\frac{2R_k}{\alpha} - \frac{\varepsilon_k - \varepsilon_j}{kT}\right) \times \frac{d_k - n_k(t)}{\sum_{i=k}^m [d_i - n_i(t)]}. \quad (8)$$

Let us now discuss the recombination term in Eq. (3). Since electrons and holes recombine via tunnelling transitions, and since no spatial correlation in their positions is assumed, one could suppose that the recombination rate  $\Gamma_r$  is determined by tunnelling transitions over the typical distance between electrons and holes. If the concentration of charge carriers at time  $t$  is  $n$ , the corresponding recombination rate would then be of the order  $\Gamma_r(n^{-1/2})$ . One should however recognize that since the spatial distribution of localized states is random, there are some configurations where a localized state for electrons is located very close to a localized state for holes. Although such configurations are rare, the rate of transitions in such close pairs is exponentially higher than the transition rate over a typical distance  $n^{-1/2}$ . One can show that for recombination, the most efficient ones are the pairs of localized states in which the state for electrons is as close to the state for holes as the localization length  $\alpha$  [6]. The recombination time of such pairs does not contain the exponential factor, and is close to  $\tau_0$ . The concentration of such efficient recombination pairs is of the order of magnitude of the product of the density of filled electron states  $n$  and the probability  $n\alpha^2$  that there is a filled hole state at a distance  $\alpha$  from a filled electron state. Hence the recombination rate in Eq. (3) has the form

$$\Gamma_r \approx \tau_0^{-1} n(t) \alpha^2. \quad (9)$$

The luminescence spectrum is calculated as a convolution of the energy dependent carrier densities:

$$I(\hbar\omega, t) \propto \int_{-\infty}^{\infty} n^{(e)}(\hbar\omega + \varepsilon, t) n^{(h)}(\varepsilon, t) d\varepsilon, \quad (10)$$

where  $n^{(e)}(\varepsilon, t)$  and  $n^{(h)}(\varepsilon, t)$  denote the densities of electrons and holes, respectively, obtained by solving Eqs. (3) – (9).

### 3. Comparison with experimental data, and discussion

The theoretical model described above was stimulated by our experimental study of the photoluminescence (PL) in GaInNAs/GaAs quantum wells. In this work, we performed time-resolved (TR) photoluminescence measurements on a  $\text{Ga}_{0.7}\text{In}_{0.3}\text{N}_{0.005}\text{As}_{0.995}$  multi quantum well (MQW) structure. The sample was grown by metal-organic vapour-phase epitaxy (MOVPE) on a (100)-oriented semi-insulating GaAs substrate at 525°C. The sample consists of a 250 nm thick GaAs buffer layer, five  $\text{Ga}_{0.7}\text{In}_{0.3}\text{N}_{0.005}\text{As}_{0.995}$  quantum wells of 8 nm width separated by 60 nm thick GaAs barriers, and a 30 nm GaAs cap layer. The nitrogen concentration was determined by theoretical dynamic simulations of high resolution x-ray diffraction measurements. The sample was thermally annealed at 725 °C for 1 h stabilized under a constant flow of tertiarybutyl arsine.

For the TR PL measurements, the structure was optically excited by a mode-locked Ti:sapphire laser, providing 100 fs pulses with a repetition rate of 80 MHz. The laser was tuned to a wavelength of 900 nm to exclude absorption in the barriers, thus ensuring direct excitation of the quantum wells. The excitation density was set to 118 W/cm<sup>2</sup>. The sample was examined at different temperatures ranging from 10 K to 300 K by using a cold-finger cryostat. The PL signal was collected by a 78 mm lens and dispersed by a 32 cm spectrometer (grating: 150/mm, 1.2 μm blaze, spectral resolution ~ 2 nm). The signal was detected using a Hamamatsu S1 streak camera with an overall time resolution of about 10 ps.

In Fig. 1 we show by the solid line the data for the time decay of the integral PL intensity after a short excitation pulse with power density 118 W/cm<sup>2</sup> at  $T = 10$  K. A remarkable feature of this decay is its non-exponential character. Such behaviour indicates a rather broad distribution of recombination times, which is difficult to bring into agreement with an exciton picture of the PL since in the case of excitons the time decay would be exponential with a decay rate given by the lifetime of excitons. It is the non-exponential time decay that suggests a model of uncorrelated electrons and holes described in Section 2.

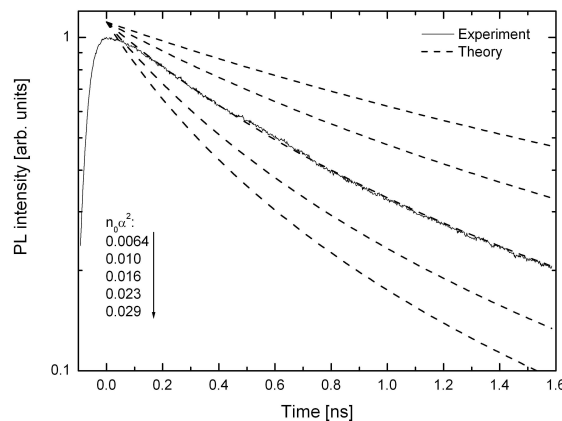


Fig. 1. Time decay of the integral PL intensity. Solid line: experimental data. Five dashed lines: theoretical results for different  $n_0 \alpha^2$  values, where  $n_0$  is the initial concentration of electron-hole pairs just after the generation pulse.

In order to check our model quantitatively, we compare its results with the experimental data in Fig. 1. The time resolved PL intensity was obtained from Eq. (10) as

$$I(t) = \int_{-\infty}^{\infty} I(\varepsilon, t) d\varepsilon . \quad (11)$$

The PL spectrum  $I(\varepsilon, t)$  is calculated from Eq. (10) on the basis of the calculated carrier distribution. The spectrum depends on the DOS shape and temperature. However, the energy integrated PL intensity  $I(t)$  is not sensitive to the DOS and temperature since the recombination rate  $\Gamma_r$  in Eq. (9) depends on the total carrier concentration though not on its particular energy distribution. In the calculations, the magnitude of the parameter  $\tau_0$  was taken as  $\sim 20$  ps, close to the typical lifetime of excitons in III-V semiconductors. Perfect agreement between the theoretical results and experimental data was obtained for the magnitude of the parameter  $n_0\alpha^2 \approx 0.016$ , where  $n_0$  is the initial concentration of electron-hole pairs just after the generation pulse. If one assumes that all photons are absorbed in the quantum well, one should estimate  $n_0$  as about  $4 \cdot 10^{12} \text{ cm}^{-2}$ , which would lead to an estimate for the localization length for charge carriers of  $\alpha \approx 6.5 \text{ \AA}$ . If one, however, takes into account an absorption coefficient of about  $50000 \text{ cm}^{-1}$ , one would estimate the localization length as  $\alpha \approx 28 \text{ \AA}$ .

The localization length is one of the most important parameters characterising the disorder potential. The ability to estimate its magnitude via comparison between theoretical results and experimental data should thus be considered as an advantage of the developed theoretical description.

One of the interesting questions in the interpretation of the PL spectra in quantum structures is whether or not photoexcited carriers achieve thermal equilibrium before they start to recombine efficiently. In order to check the thermalization effect, we have traced the time evolution of the electron density for different energy slices. For this study we have chosen an exponential DOS [2,7]

$$g(\varepsilon) = \frac{N_0}{\varepsilon_0} \exp\left(-\frac{\varepsilon}{\varepsilon_0}\right). \quad (12)$$

with a total concentration of localized states  $N_0$  and an energy scale  $\varepsilon_0$ . The energy in Eq. (12) is counted downward from the mobility edge.

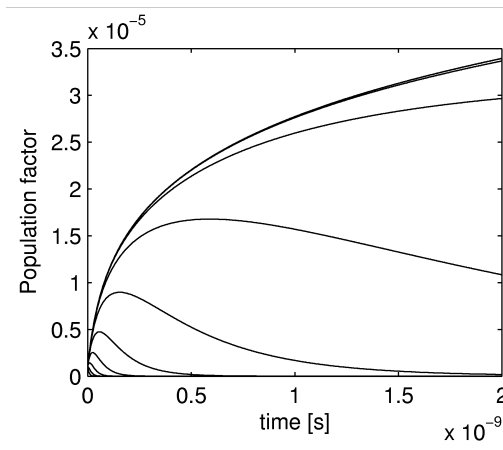


Fig. 2. Time-dependent filling factors for several different energy slices in the exponential DOS.

In Fig. 2, the corresponding time dependent population factors  $n_i(t)/d_i$  are given for several energy slices  $i$  of width  $0.1\varepsilon_0$  in the time interval from the end of the excitation pulse till 2 ns later, for the parameters  $N_0\alpha^2 = 0.45$ ,  $\nu_0 = 10^{12} \text{ s}^{-1}$ ,  $kT = 0.001 \text{ eV}$ ,  $\varepsilon_0 = 8 \text{ meV}$ , and an initial filling factor for all slices of  $\eta = 10^{-6}$ , without taking recombination into account. The time interval of 2 ns was chosen since most photoexcited charge carriers recombine at times smaller than this, as clearly seen in Fig. 1. It is evident from Fig. 2 that the filling factors of all the energy slices considered are essentially time-dependent and are hence non-equilibrium values. One should conclude from this result that the distribution of recombining carriers is essentially non-equilibrium, at least at the low temperatures and low excitation power densities used to obtain the data in Fig. 2. Therefore, the frequently imposed assumption of thermal equilibrium of the recombining photoexcited electrons and holes should be treated with caution.

As a conclusion, one can claim that the suggested theoretical model provides a reasonable description of experimental data on the time decay of PL at low temperatures, as obtained in GaInNAs/GaAs multi quantum wells. In particular, it can reveal an essential material parameter - the localization length of the trapping centres.

We would also like to mention that in systems with less pronounced disorder, the light emission can be computed by a microscopic theory based on the semiconductor luminescence equations [8]. Recently this theory has been successfully applied to a set of  $\text{Ga}_{0.77}\text{In}_{0.23}\text{N}_x\text{As}_{1-x}$  heterostructures [9]. Since nitrogen atoms in these systems are present only in the barrier material, the disorder is expected to play a less important role than in our systems with nitrogen atoms in the well material.

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