Spectral dependence of the photoluminescence decay in disordered semiconductors

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Kinetics of the energy transfer and the corresponding photoluminescence decay at selected photon energies in disordered semiconductors are studied theoretically. The authors show a straightforward way to arrive analytically at the solutions for the spectral and time dependences of the photoluminescence decay within a model based on the interplay between the radiative recombination and hopping energy relaxation of localized excitons. The theory is supported by comparison with experimental data, which yields valuable information on major properties of disorder in the underlying structures. © 2007 American Institute of Physics.
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Time-resolved spectroscopy is a powerful technique that is being extensively used to study the recombination kinetics particularly in disordered semiconductors such as II-VI,[1,2] III-V nitride,[3,4] and III-V dilute nitride heterostructures.[5–7] In these structures, the low-temperature photoluminescence (PL) is primarily dominated by recombination of localized excitations.[8–10] The common feature of time-resolved PL data is a strong dependence of the PL decay on the photon energy, in particular, at initial times after the pulsed excitation: the higher the detection energy, the shorter is the decay time. This gives evidence to the energy transfer of optical excitations from shallow bound states in the pseudogap to the states with greater localization energy. A rough theoretical description of the spectral dependence of the PL decay has been given by Gourdon and Lavallard[11] on the basis of a phenomenological model of hopping end recombination of localized excitons.[8,12] In this letter, we improve the former theory and obtain an analytical expression for the spectral dependence of the PL decay, which takes into account basic properties of disorder and localization as well as the delay time after the pulsed excitation. This significantly extends the range of applicability of the theory and gives an additional opportunity for the experimental verification of the PL mechanism.

The widely accepted model of the PL in semiconductors with an essential amount of disorder can be formulated as follows. The luminescing entity is a correlated electron-hole pair (exciton) trapped in a localized state in the pseudogap of the studied structure.[12] Such excitation can either recombine radiatively producing a PL photon or it can hop into another localized state. The interplay between these two processes in the course of time determines the PL kinetics.[8,12] Following these arguments, Gourdon and Lavallard[11] proposed an expression for the spectral dependence of the PL decay in disordered semiconductors in the form

$$t_0^{\mathrm{GL}}(\hbar\omega) = \tau_0\{1 + \exp[(\hbar\omega - E_m)/E_0]\}^{-1}, \qquad (1)$$

where τ_0 is the exciton radiative lifetime, E_0 is the energy scale of an exponential band tail, and E_m is the energy at which the radiative time equals the transition time to the

states with deeper energies.[13] Equation (1) fits well experimental dependences of the initial PL decay on the photon energy. However, it cannot be considered as complete, since none of the material parameters characterizing hopping processes enter Eq. (1). Theoretical approaches were developed that allow one to calculate the dynamics of the exciton thermalization either numerically[14,15] or by the computer simulation.[16] However, even at zero temperature, detailed calculation of the thermalization processes is a complex task, which precludes a simple analytical solution. Our aim is to find such a description for the spectral dependence of the PL decay time, which is at the same time sufficiently simple and sufficiently accurate.

Now we introduce assumptions that will allow us to obtain both the energy and time dependences of the PL decay in a simple mathematical form. First, we neglect 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 use the greatest rate approximation,[12] 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 assume the exciton density to be sufficiently low, so that the band tail states can be considered as unoccupied. This regime can be achieved at low pump intensities.

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. The initial relaxation processes within a band are viewed as instantaneous, and the origin of time is taken to be the moment of the exciton capture. We focuss on the case of low temperatures, when a trapped exciton loses its energy 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 energy $E = \hbar\omega - E_{\mathrm{ME}}$ relative to the exciton mobility edge (ME) can be written as[12,17]

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

where $\rho(r,E)$ is the distribution of hopping distances, α is the decay length of the localized exciton center-of-mass wave function, and ν_0 is the phonon-related attempt-to-escape frequency.

We assume uncorrelated disorder in the sense that the spatial positions and energies of localized states are random. Then the distribution of hopping distances is a nearest-neighbor distribution, which is $\rho(r,E)=2\pi N(E)r \times\exp[-\pi N(E)r^2]$ in two-dimensional (2D) case or $\rho(r,E) =4\pi N(E)r^2 \exp[-4\pi N(E)r^3/3]$ in three-dimensional (3D) case. Here, $N(E)$ is the density of states available for the hopping transition. Since we limited our theory to low temperatures (excitons can only lose their energy via hopping), the localized states available for the hopping transitions are those below energy E, and their density is given by

$$N(E) = \int_{-\infty}^E g(E')dE', \qquad (3)$$

where $g(E)$ is the energy distribution of localized states in the band tail, which is a steep function of energy.

Further simplification of Eq. (2) can be achieved approximating the term $\exp(-t\nu_0 e^{-2r/\alpha})$ by a step function, since $t\nu_0 \gg 1$ holds for all practical times. This yields in 2D

$$I(E,t) \approx (\text{const})e^{-t/\tau_0}\int_{R_c(t)}^\infty \rho(r,E)dr = (\text{const})\exp\left[-\frac{t}{\tau_0}\right.$$
$$\left. - \pi R_c^2(t)N(E)\right], \qquad (4)$$

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

In general, the PL time evolution at arbitrary t can be considered as an exponential decay $I(t)=I_0 \exp[-t/t_0(t)]$ with a variable decay time t_0. Thus, the PL decay time is given by the inverse logarithmic derivative of the PL signal,

$$t_0^{-1}(E,t) = -\frac{d}{dt}[\ln I(E,t)]. \qquad (5)$$

The corresponding differentiation of Eq. (4) yields our main result—expression for the PL decay time in terms of the parameters of disorder, localization, interaction with phonons, and delay time

$$t_0^{-1}(E,t) \approx \tau_0^{-1} + \frac{\pi N(E)\alpha^2}{2t} \ln\left(\frac{t\nu_0}{\ln 2}\right). \qquad (6)$$

The inverse decay time given by Eq. (6) is composed of two terms: the radiative decay rate and the effective hopping escape rate. The latter is a decreasing function of time, since in the course of time more and more distant pairs of localized states contribute to the hopping rate. Comparison of Eqs. (1) and (6) shows that both expressions have the same energy dependence governed by $N(E)$, though the rest of the hopping-related term is completely different.

Next, we justify Eq. (6) by comparison to results of the full kinetic Monte Carlo (KMC) simulation performed using the algorithm suggested by Baranovskii et al.[16] The advantage of the computer simulation is that its algorithm takes into account all stochastic processes, which are natural for dynamics of recombining excitons. For this purpose, we cal-
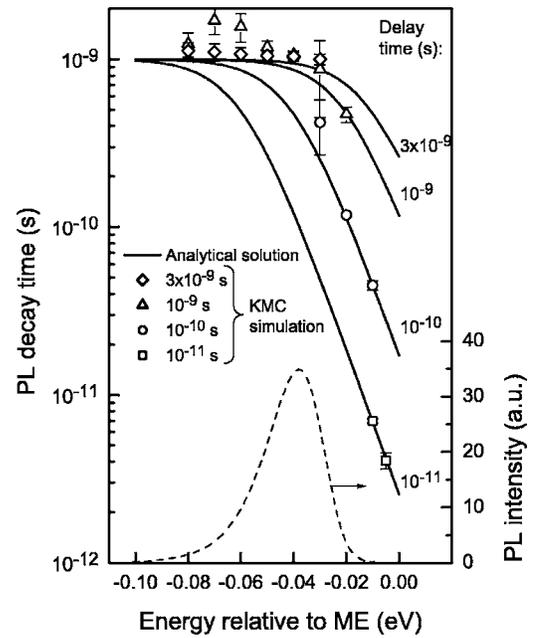
FIG. 1. Zero-temperature time-integrated PL spectrum and spectral dependence of the PL decay time at various delays after the pulsed excitation. PL decay times are calculated according to Eq. (6) and by performing full KMC computer simulation.

culate the energy spectrum of the PL decay time at various delays after the pulsed excitation taking the material parameters appropriate for III-V dilute nitride heterostructures. In the calculation, we assume an exponential energy distribution of localized states,

$$g(E) = (N_t/E_0)\exp(E/E_0), \qquad (7)$$

where N_t is the areal density of localized states, and E_0 is the characteristic energy scale, which is about 10 meV.[18,19] For the other parameters, we take the values $\nu_0=10^{13}$ s^{-1}, $\tau_0 =10^{-9}$ s, and $N_t\alpha^2=0.5$.[18–20]

Spectral dependences of the PL decay times calculated using the two alternative approaches are shown in Fig. 1 along with the time-integrated PL spectrum obtained from the KMC simulation. The primary feature of Eq. (6) is that it enables to calculate kinetics of the PL decay time, instead of focusing on some initial times as in the earlier theory.[11] Therefore, we show in Fig. 1 the results obtained at various time slices. The analytical results match well the simulation data, that confirm the confidence of Eq. (6). The results show both the strong energy and time dependences of the PL decay. The decay times spread over the range from picoseconds to nanoseconds for the states contributing to the high-energy part of the PL spectrum. The distribution of decay times gets narrower for the lower photon energies or longer delays, until the PL decay time finally approaches the radiative lifetime $\tau_0=10^{-9}$ s. In the simulation, however, the decay times longer than the radiative lifetime are observed (see Fig. 1, $t =10^{-9}$ s). This is due to the feeding disregarded in the analytical model.

Finally, we verify our theory by comparison to the experimental data for spectral dependence of the initial PL decay time measured by Vinattieri et al.[6] on Ga(NAs)/GaAs quantum wells. Since the energy position of the exciton mobility edge was experimentally not determined, for the fitting procedure we locate it at[16]
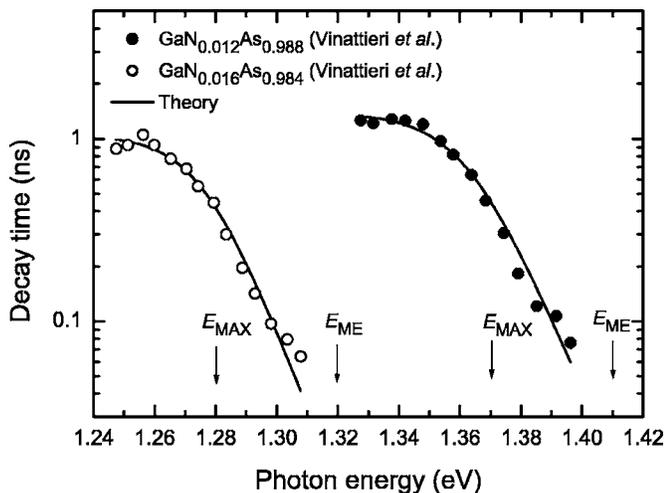
FIG. 2. Spectral dependence of the initial PL decay time measured by Vinattieri *et al.* (Ref. 6) on Ga(NAs)/GaAs quantum wells at $T=10$ K and the theoretical results calculated according to Eq. (6) assuming the exponential density of localized states [Eq. (7)]. Arrows indicate the position of the measured PL peak energy, E_{max}, and of the exciton mobility edge, E_{ME}, calculated according to Eq. (8).

$$E_{ME} \approx E_{max} + E_0 \ln[(\pi N_t \alpha^2/4)\ln^2(\tau_0 \nu_0)], \qquad (8)$$

where E_{max} is the peak energy of the time-integrated PL spectrum. Due to the uncertainty in the exact position of the exciton mobility edge, it is not possible to determine the product $N_t\alpha^2$ unambiguously, and, thus, we assume as above $N_t\alpha^2=0.5$. Experimental data and the corresponding theoretical fits are shown in Fig. 2. Quantitative agreement with the experiment is achieved for the physically reasonable parameters: $\tau_0=1.4$ ns, $E_0=11$ meV, and $t=40$ ps for the sample with the nitrogen content of 0.012, and $\tau_0=1.1$ ns, $E_0=10$ meV, and $t=120$ ps for the sample with the nitrogen content of 0.016. The attempt-to-escape frequency $\nu_0=10^{13}$ s^{-1} is assumed to be the same for both samples. It is worth mentioning, that the disorder energy scale E_0 extracted from the fit appears in the typical range (5–15 meV) for III-V dilute nitride heterostructures.[19,21]

The real challenge for the model will be to explain quantitatively both the spectral and time dependences of the PL decay using the same set of parameters. In order to adjust the model to a particular experimental situation, Eq. (6) can be easily modified for the 3D case and/or for another transfer mechanism, e.g., for Föster (dipole-dipole) hopping. In the case of tunneling, the proportionality $t_0 \propto t$ can be anticipated [see Eq. (6)] independently of the space dimensionality for detection energies in the high-energy part of the PL spectra and relatively short times ($t \ll \tau_0$). In the case of Föster hopping, weaker time dependences of the PL decay are achieved: $t_0 \propto t^{2/3}$ and $t_0 \propto t^{1/3}$ in 2D and 3D cases, respectively. It would be interesting to check this experimentally.

In conclusion, we proposed an analytical expression, which describes the spectral dependence of the PL decay time at low temperatures, assuming that the photoluminescence is determined by the interplay between hopping and radiative recombination of localized excitons. In contrast to the previous theoretical studies, our approach includes the details of the transition mechanism between localized states and allows one to calculate the PL decay time at various delays after the pulsed excitation. Decay times of PL calculated analytically are in good agreement with experimental results on Ga(NAs)/GaAs quantum wells and with the results of the numerical simulation. The disorder energy scale $E_0 \approx 10$ meV and the exciton radiative lifetime $\tau_0 \approx 1$ ns are determined from the fit to the experimental data.

[1]C. Gourdon, P. Lavallard, S. Permogorov, A. Reznitsky, Y. Aaviksoo, and Y. Lippmaa, J. Lumin. **39**, 111 (1987).

[2]K. Suzuki, G. Bley, U. Neukirch, J. Gutowski, N. Takojima, T. Sawada, and K. Imai, Solid State Commun. **105**, 571 (1998).

[3]C. K. Choi, Y. H. Kwon, B. D. Little, G. H. Gainer, J. J. Song, Y. C. Chang, S. Keller, U. K. Mishra, and S. P. DenBaars, Phys. Rev. B **64**, 245339 (2001).

[4]Y. Narukawa, Y. Kawakami, S. Fujita, S. Fujita, and S. Nakamura, Phys. Rev. B **55**, R1938 (1997).

[5]R. A. Mair, J. Y. Lin, H. X. Jiang, E. D. Jones, A. A. Allerman, and S. R. Kurtz, Appl. Phys. Lett. **76**, 188 (2000).

[6]A. Vinattieri, D. Alderighi, M. Zamfirescu, M. Colocci, A. Polimeni, M. Capizzi, D. Gollub, M. Fischer, and A. Forchel, Appl. Phys. Lett. **82**, 2805 (2003).

[7]T. Ishizuka, H. Doi, T. Katsuyama, J. Hashimoto, and M. Nakayama, J. Cryst. Growth **298**, 116 (2007).

[8]E. Cohen and M. D. Sturge, Phys. Rev. B **25**, 3828 (1982).

[9]M. Smith, G. D. Chen, J. Y. Lin, H. X. Jiang, M. Asif Khan, and Q. Chen, Appl. Phys. Lett. **69**, 2837 (1996).

[10]L. Grenouillet, C. Bru-Chevallier, G. Guillot, P. Gilet, P. Duvaut, C. Vannuffel, A. Million, and A. Chenevas-Paule, Appl. Phys. Lett. **76**, 2241 (2000).

[11]C. Gourdon and P. Lavallard, Phys. Status Solidi B **153**, 641 (1989).

[12]S. Kivelson and C. D. Gelatt, Phys. Rev. B **26**, 4646 (1982).

[13]M. Oueslati, C. Benoit à la Guillaume, and M. Zouaghi, Phys. Rev. B **37**, 3037 (1988).

[14]A. A. Kiselev, Semiconductors **32**, 504 (1998).

[15]S. A. Tarasenko, A. A. Kiselev, E. L. Ivchenko, A. Dinger, M. Baldauf, C. Klingshirn, H. Kalt, S. D. Baranovskii, R. Eichmann, and P. Thomas, Semicond. Sci. Technol. **16**, 486 (2001).

[16]S. D. Baranovskii, R. Eichmann, and P. Thomas, Phys. Rev. B **58**, 13081 (1998).

[17]P. J. Wiesner, R. A. Street, and H. D. Wolf, Phys. Rev. Lett. **35**, 1366 (1975).

[18]H. Grüning, K. Kohary, S. D. Baranovskii, O. Rubel, P. J. Klar, A. Ramakrishnan, G. Ebbinghaus, P. Thomas, W. Heimbrodt, W. Stolz, and W. W. Rühle, Phys. Status Solidi C **1**, 109 (2004).

[19]O. Rubel, M. Galluppi, S. D. Baranovskii, K. Volz, L. Geelhaar, H. Riechert, P. Thomas, and W. Stolz, J. Appl. Phys. **98**, 063518 (2005).

[20]O. Rubel, S. D. Baranovskii, K. Hantke, B. Kunert, W. W. Ruhle, P. Thomas, K. Volz, and W. Stolz, Phys. Rev. B **73**, 233201 (2006).

[21]S. Kurtz, J. Webb, L. Gedvilas, D. Friedman, J. Geisz, J. Olson, R. King, D. Joslin, and N. Karam, Appl. Phys. Lett. **78**, 748 (2001).