Impact of recombination centers on the spontaneous emission of semiconductors under steady-state and transient conditions

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We show that recombination centers may affect the spontaneous emission of semiconductors in a different way depending on whether steady-state or transient conditions are established. This asymmetry is an inherent property of recombination centers. Recent publications concerned with this subject have, deliberately or not, ignored the asymmetry between these conditions, and have treated these physically distinct situations as being equivalent. Such a presumption may result in orders-of-magnitude errors when analyzing experimental data. Furthermore, the threshold of stimulated emission is not a unique property of the material under investigation, but is strongly dependent on the experimental conditions employed. [S0163-1829(96)52632-9]

Recombination of carriers in semiconductors takes place in general via several parallel recombination channels.[1] Besides the radiative decay of carriers at or close to the band edge, additional and often nonradiative channels are created by inevitable defects. Experimentally, this complex interplay of recombination processes is most frequently investigated by exciting the semiconductor via either cw or pulsed optical pumping, and by subsequently studying the changes in emission induced by varying the intensity of the pump.[2] The analysis of the experimental data, which is intended to unravel the individual contributions of the participating recombination channels, is, however, often done on an intuitive basis rather than by a physically motivated formalism. In recent studies, for example, either intrinsic[3] or extrinsic[4] recombination has been neglected altogether. In previous work by Brandt *et al.*,[5] one of the present authors, an attempt has been made to treat intrinsic recombination, including free carriers and excitons, on an equal footing with extrinsic recombination via recombination centers: These centers, however, were assumed to be saturated, allowing them to be described by a linearized rate with a single capture constant. In this work, we refrain from this approximation.

We study theoretically the impact of Shockley-Read-Hall (SRH) recombination centers on the spontaneous emission of semiconductors under both steady-state and transient conditions. The physical asymmetry between these conditions is demonstrated. In contrast to other works, we thus do not treat steady-state and transient conditions as being equivalent, but distinguish them as being inherently different. Neglecting this asymmetry may result in a several-orders-of-magnitude error when analyzing experimental data.

For relating our study to materials of practical importance, consider the large band-gap semiconductors ZnSe and GaN, both of which are currently in the focus of interest as candidates for lasers in the blue and UV spectral range. These semiconductors are plagued by a high density of defects, and are thus excellent examples of materials for which our considerations are relevant. Simultaneously, these semiconductors exhibit an exciton binding energy high enough for excitons being stable up to room temperature. The spontaneous, and even the stimulated, emission from these materials is thought to arise from the excitonic state up to room temperature.[8] In the following, we thus consider not only free-carrier and defect-mediated recombination, but also include excitons, following Ref. 5.

Consider a semiconductor which is characterized by a band-gap energy E_g, an exciton binding energy E_x, coefficients for absorption (α) and radiative recombination (b_r) of light at an energy $\hbar\omega \geqslant E_g$, an exciton radiative decay rate γ_x, a dark electron concentration $n_0 \gg p_0$, and a concentration of recombination centers N_t. These recombination centers are in turn characterized by coefficients b_n and b_p for the capture of electrons and holes, respectively. Exciting this semiconductor by an optical pump with $\hbar\omega \geqslant E_g$, generates an excess electron (Δn) and hole (Δp) density at a rate G. Neglecting carrier diffusion and photon recycling, the temporal evolution of the concentration of electrons, holes, excitons, and recombination centers, is then governed by the following coupled set of differential equations:

$$n' = G - b_r \Delta p (n_0 + \Delta n) - f_x \Delta p (n_0 + \Delta n) + d_x n_x - b_n n_t^+ (n_0 + \Delta n), \tag{1}$$

$$p' = G - b_r \Delta p (n_0 + \Delta n) - f_x \Delta p (n_0 + \Delta n) + d_x n_x - b_p n_0^t \Delta p, \tag{2}$$

$$n_x' = f_x \Delta p (n_0 + \Delta n) - d_x n_x - \gamma_x n_x, \tag{3}$$

$$n_t^{+\prime} = -b_n n_t^+ (n_0 + \Delta n) + b_p n_t^0 \Delta p, \tag{4}$$

where n and p denote the total concentration of electrons and holes with $n = n_0 + \Delta n$ and $p = \Delta p$, respectively, n_x is the concentration of excitons, n_t^+ and n_t^0 are the concentration of empty and filled recombination centers, respectively, where $n_t^+ + n_t^0 = N_t$, and f_x and d_x are the formation and dissociation rates of excitons.

For steady-state conditions, Eqs. (1)–(4) are, by definition, equal to zero. It follows that the terms describing electron and hole capture in Eqs. (1) and (2), respectively, are equal, resulting in identical equations for electrons and holes. Assuming now that both exciton formation and dissociation are rapid enough to satisfy $f_x \Delta p (n_0 + \Delta n) \gtrsim d_x n_x \gg \gamma_x n_x$, i.e., the radiative decay rate of excitons is supposed to be

very much smaller than the rates associated to these processes,[4] we can summarize Eqs. (1)–(4) into one equation:

$$G - B\Delta p(n_0+\Delta n) + \frac{b_n b_p N_t (n_0+\Delta n)}{b_n(n_0+\Delta n)+b_p\Delta p}\Delta p = 0. \quad (5)$$

The third term of this equation is the classical SRH expression for the recombination rate of carriers at recombination centers. The effective radiative recombination coefficient $B=b_r+\sigma_x\gamma_x$, where $\sigma_x=f_s/d_x$ is the scattering volume for free carriers into the exciton state, contains both free-carrier and exciton recombination.[5] If the exciton state is spectrally not distinct from free-carrier transitions, as assumed in this work, excitons do only increase the net radiative recombination rate, and are thus indistinguishable from free-carrier recombination since the individual contributions are not known *a priori*. Note that this approximation breaks down as soon as the rate of radiative decay of the exciton becomes comparable to its formation and dissociation rates, i.e., at low temperatures.[6]

Equation (5) contains both Δp and Δn and is thus underdetermined. Previous investigators have *ad hoc* assumed that $\Delta n=\Delta p$, which, however, is valid for purely radiative recombination only for which the neutrality condition guarantees equal electron and hole concentrations.[7] In the case of nonvanishing SRH recombination the neutrality condition reads

$$\Delta n + n_0 = \Delta p + n_D^+ + n_t^+, \quad (6)$$

where n_D^+ is the concentration of ionized donors which is equal to n_0. It is seen that, in general, $\Delta n \neq \Delta p$, and the assumption of equal electron and hole concentrations is only justified in the limit of a vanishing concentration of recombination centers.

Equations (5) and (6) form a coupled system of equations of effectively fifth order in Δn (Δp) and may thus not be solved in closed analytical form. Here, we solve this equation system numerically in order to simulate the radiative intensity I_r of spontaneous emission as a function of the generation rate (or, equivalently, the intensity of the incident light $I_{\mathrm{in}}=(\hbar\omega G/\alpha)$ which follows from the solution of Eqs. (5) and (6) as

$$I_r = (E_g/\alpha)B\Delta p(n_0+\Delta n). \quad (7)$$

Figure 1 shows selected examples of these simulations, assuming values for the relevant parameters as given in Table I. The most important feature which all of these plots have in common is the superlinear increase of the radiative rate with excitation density at a certain value. This value is to be identified with the saturation of the SRH centers. As it is evident from the plots displayed in Fig. 1, the saturation depends sensitively on the specific parameters of the participating recombination channels. In any case, the carrier density required for saturating the SRH centers is well below their actual concentration (note that the right axis of Fig. 1 is valid for curve *I* only). This finding results from the dynamic equilibrium between the fast hole and the slow electron capture enforced by steady-state conditions, predicting, to first order, a carrier density of $(b_n/b_p)N_t$ for achieving saturation.[9] Particularly interesting in this respect are the curves labeled *IIa* and *IIb*. Saturation is evidently delayed with increasing background doping density, i.e., with decreasing monomolecular radiative lifetime. This finding may be understood by considering that the superlinear region is not related to the characteristics of the SRH centers alone, but involves the competition of bimolecular recombination with the combined monomolecular radiative and SRH terms. Finally, curves *IIIa* and *IIIb* show that the rate of electron capture determines the intensity for which saturation occurs, while curves *IVa* and *IVb* evidence that the rate of hole capture defines the small-signal quantum efficiency and thus the abruptness of saturation.

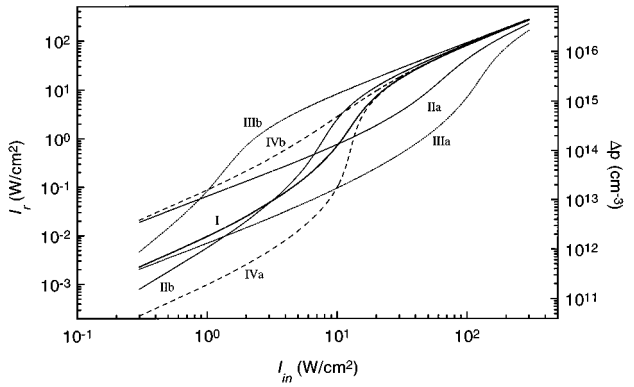

FIG. 1. Steady-state radiative intensity as a function of incident intensity for various different values of the recombination parameters. Note that the excess carrier concentration given on the right axis is valid for curve *I* only.

For transient conditions, previous investigators have once again assumed validity of Eq. (5) derived above for steady-state conditions together with the presumption that $\Delta n=\Delta p$.[3,9,10] This simplification, while being a reasonable approximation for steady-state conditions in the limit of a small concentration of recombination centers, may lead to grossly erroneous results for transient conditions even in this limit. The physical origin of this asymmetry lies in the fact that the detailed balance between electron and hole capture is never, in principle, strictly fulfilled under transient conditions, but is at most approximately fulfilled for special cases

TABLE I. Parameters used for the simulations. The rows are numbered with roman numerals corresponding to the simulations shown in Fig. 1. The values printed in italic are those which are varied with respect to the values given in row I. For the simulations shown in Fig. 2, the parameters given in row I have been used. In all cases, we have assumed $\alpha=10^5$ cm^{-1}, $B=3\times10^{-10}$ cm^3/s, $\hbar\omega=3.5$ eV, $E_G=3.4$ eV, and $N_t=2\times10^{18}$ cm^{-3}.

	n_0 (cm^{-3})	b_n (cm^3/s)	b_p (cm^3/s)
I	1.5×10^{18}	3×10^{-13}	3×10^{-8}
IIa	$\mathit{1.5\times10^{19}}$	3×10^{-13}	3×10^{-8}
IIb	$\mathit{1.5\times10^{17}}$	3×10^{-13}	3×10^{-8}
IIIa	1.5×10^{18}	$\mathit{3\times10^{-12}}$	3×10^{-8}
IIIb	1.5×10^{18}	3×10^{-14}	3×10^{-8}
IVa	1.5×10^{18}	3×10^{-13}	$\mathit{3\times10^{-7}}$
IVb	1.5×10^{18}	3×10^{-13}	$\mathit{3\times10^{-9}}$

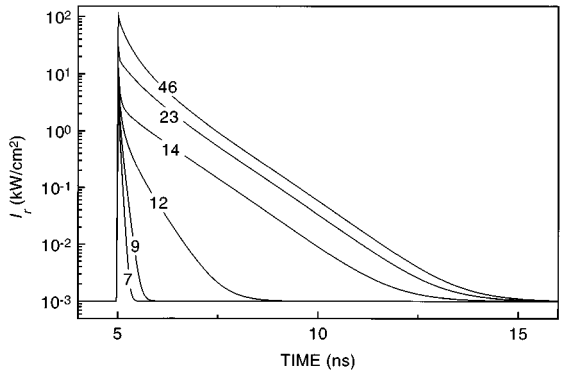

FIG. 2. Transient radiative intensity after excitation with a ps pulse having a fluence between 7 and 46 μJ/cm^2, as indicated by the numbers labeling the transients. Note the sudden increase of the decay time between 9 and 14 μJ/cm^2, and the nonexponential slope of the initial decay at the highest fluence.

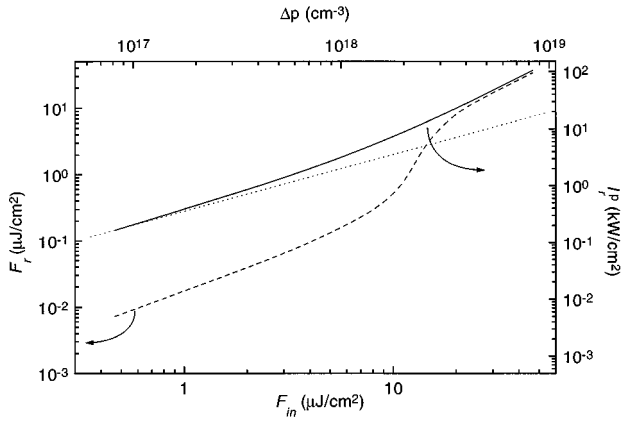

FIG. 3. Radiative fluence (left) and peak radiative intensity (right) as a function of incident fluence. The top axis gives the nominal excess carrier concentration created by the ps pulse.

and certain conditions. For the case of perfect recombination centers (i.e., if $b_n = b_p$), for instance, this approximation holds for high excitation conditions, but fails for low excitation. In general, however, the center is not a perfect recombination center, but tends to preferentially capture one of the two available carrier types, and has thus a more or less pronounced character of a trap.

These considerations lead to the obvious conclusion that, generally, Eqs. (1)–(4) cannot be reduced further for transient conditions. We may, if we like, still hold on to the approximation concerning the participation of excitons in the recombination process,[6] which results in the following set of equations

$$\Delta n' = \{G(t) - B\Delta p(n_0+\Delta n) - b_n n_t^+(n_0+\Delta n) - \sigma_x(n_0+\Delta n)[b_n n_t^+(n_0+\Delta n) - b_p(N_t - n_t^+)\Delta p]\}/[1+\sigma_x(n_0+\Delta n+\Delta p)], \quad (8)$$

$$\Delta p' = \{G(t) - B\Delta p(n_0+\Delta n) - b_p(N_t - n_t^+)\Delta p - \sigma_x\Delta p[b_n n_t^+(n_0+\Delta n) - b_p(N_t - n_t^+)\Delta p]\}/[1+\sigma_x(n_0+\Delta n+\Delta p)], \quad (9)$$

$$\Delta n_t^{+\prime} = -b_n n_t^+(n_0+\Delta n) + b_p(N_t - n_t^+)\Delta p, \quad (10)$$

which is more tractable for physical interpretation when compared to Eqs. (1)–(4), and is more easily integrated numerically. The neutrality condition [Eq. (6)] determines the boundary condition for these differential equations. Note that the participation of excitons is included effectively via the parameters B and σ_x, and thus, unlike the case of steady-state conditions, excitons are now distinguishable from free-carrier recombination as σ_x comes into play explicitly.

In the following, we display the radiative intensity I_r of spontaneous emission [Eq. (7)] obtained from the solution of Eqs. (8)–(10).[11] Figure 2 shows the transient behavior of I_r upon excitation with a ps pulse for values of the incident fluence $F_{\rm in} = \hbar\omega G\Delta t/\alpha$, where Δt is the width of the Gaussian pulse, between $\simeq$7 and $\simeq$46 μJ/cm^2. The parameters assumed for these simulations are given in the first row of Table I. In order not to overly complicate matters, we have set the excitonic contribution to zero. The shape of the transients in Fig. 2 visualizes the evolution of the effective lifetime from small-signal to large-signal excitation. The nonexponential slope of the initial decay at the highest incident fluence stems from the participation of bimolecular recombination.

In Fig. 3, we display the peak radiative intensity I_r^p and the radiative fluence F_r (obtained by integrating the transients over time) as a function of $F_{\rm in}$. Whereas the former exhibits a superlinear increase with $F_{\rm in}$, which results from the increasing contribution of bimolecular recombination at these high carrier densities, the latter is characterized by a linear dependence at both small and large values of $F_{\rm in}$, joined by a superlinear increase at $F_{\rm in} \simeq 15$ μJ/cm^2. This behavior resembles that found for steady-state conditions, for which it has been identified as being due to the saturation of SRH centers. However, this saturation occurs at an excess carrier density of 2×10^{14} cm^{-3} (cf. curve I in Fig. 1), while it takes a much (four orders of magnitude) higher carrier density for transient conditions. Indeed, while the mechanisms responsible for this phenomenon are similar, they are not identical. Unlike steady-state conditions, where satura-

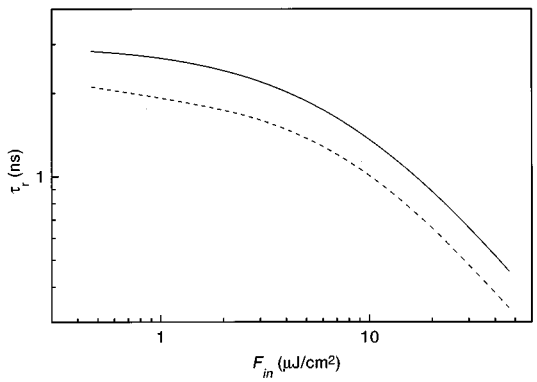

FIG. 4. Apparent and actual radiative lifetime obtained by dividing the incident fluence by the peak radiative intensity with (solid line) and without (dashed line) the participation of SRH centers, respectively.

tion occurs prematurely with respect to the actual concentration or recombination centers thanks to the slow electron capture, the centers have to be actually *filled* with holes for transient conditions. One thus needs a carrier density in excess of N_t for approaching an internal quantum efficiency of unity.

However, the most relevant quantity for defining a quantum efficiency under transient conditions is not F_r, but I_r^p. As I_r^p is determined by the peak carrier density, it is related to the threshold for stimulated emission. In fact, if the pulse would be a δ function, the ratio of $F_{\rm in}$ and I_r^p would directly correspond to the radiative lifetime τ_r. The solid line in Fig. 4 shows this ratio (the apparent τ_r) as a function of $F_{\rm in}$, whereas the dashed line shows the actual values for τ_r which are obtained in the same way without the participation of SRH recombination. The deviation of these curves is caused by the carrier loss to the SRH centers at the onset of carrier decay. This loss is, to first order, described by a constant differential quantum efficiency which may be written as $\eta^d = 1 - \Delta t/(\Delta t + \tau_p)$, where $\tau_p = (b_p N_t)^{-1}$, and is thus determined predominantly by the pulse width if $\Delta t \ll \tau_p$. For the pulse width of 1 ps assumed in this paper, $\eta^d \simeq 0.75$, thus affecting the threshold of stimulated emission only slightly. However, when performing the same analysis with a pulse of 1 ns width, the differential quantum efficiency (which then is strongly depending on Δp) reaches a value of only 0.07 at the highest incident fluence. It is seen that the internal quantum efficiency is a quantity which lacks universal meaning in that it strongly depends on the experimental conditions employed for measuring it. The seemingly different quantum efficiencies discussed here are, however, reconciled when understanding the quantum efficiency as the instantaneous fraction of carriers available for radiative decay.

To conclude, the different mechanisms of the saturation of SRH centers for steady-state and transient conditions have important consequences for the understanding of recombination processes. Acknowledging this asymmetry is necessary for a correct analysis of experimental data. It is, furthermore, clear that experiments concerned with stimulated emission are best made under cw excitation, if possible, and otherwise with short (ps) pulses of high repetition rate for achieving quasi-cw conditions.

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[11] Interestingly, we can obtain simultaneously the rate R_c associated to the recombination centers, be it radiative or nonradiative, as

$$R_c = \frac{b_n b_p n_t^+ (N_t - n_t^+)(n_0 + \Delta n)}{b_n n_t^+ (n_0 + \Delta n) + b_p (N_t - n_t^+)\Delta p}\,\Delta p. \qquad (11)$$

This expression is formally similar to the classical SRH formula valid for steady-state conditions and involves both excess electrons and holes as variables, and in addition the concentration of empty recombination centers.