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# Radiative recombination in inhomogeneous semiconductors

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Photoluminescence efficiencies and decay rates in inhomogeneous semiconductors depend on the ratio of thermal carrier energy to the energy of internal potential barriers caused by the inhomogeneities. At low temperatures, the barriers separate carrier pairs spatially and thus cause prolonged lifetimes and slowly decaying luminescence of reduced intensity. A criterion for inhomogeneity is found by time- and temperature-dependent luminescence experiments.

Radiative recombination of excess electron-hole pairs is a sensitive indicator for purity and perfection of solid-state materials. Photoluminescence techniques have therefore become widely used tools for the characterization of semiconductors.[1,2] Fine details of doping and defect structures can be extracted from luminescence spectra, especially for highly perfected materials such as silicon, gallium arsenide, or gallium phosphide.

The less-developed semiconductors of inferior perfection present difficulties for photoluminescence analyses. Inhomogeneities constitute particular problems. Composition and doping levels often vary considerably from sample to sample and even within one specimen. Ternary as well as quaternary alloys of $A^{\mathrm{III}}$-$B^{\mathrm{V}}$ compounds,[3] the $A^{\mathrm{II}}$-$B^{\mathrm{VI}}$ materials,[4] and typically the selenides and sulfides of arsenic[5] are important materials which often suffer from such inhomogeneities.

This paper addresses the general question of luminescence emerging from a semiconductor with potential fluctuations. The rate of decay of radiative recombination of photogenerated excess carrier pairs is investigated with the lattice temperature as a parameter. The compositional and dopant fluctuations cause potential barriers which spatially separate the pairs, thus reducing the probability of recombination, and therefore diminishing luminescence output and lengthening the carrier lifetimes. These effects disappear when the temperature is sufficiently elevated to cause thermal carrier energies to exceed the average potential barrier. The resulting characteristic luminescence decay as a function of temperature is the subject of this Rapid Communication.

The semiconductor material here is approximated by a uniform gap $E_g$ and a sinusoidal variation of doping. Thus, I treat the sample like a $n$-$i$-$p$-$i$ structure, featuring carrier-separating $n$-$p$ junctions.[6] Such inhomogeneities can arise from nonuniform dopant incorporation during growth; "striations" are a frequent indication of such nonuniformity.[7] I neglect variations of $E_g$, which cause even more severe effects, such as a possibly misleading predominance of recombination radiation out of regions of the lowest gap energy, where carriers of either sign might accumulate.

A further assumption is a constant ratio of radiative-to-nonradiative transitions throughout the sample. The atomistic mechanism of recombination is here not specified; such intricacies as excitons or donor-acceptor–pair transitions[1] are ignored. These details can, however, be included; the experiments on the less perfected inhomogeneous specimens, however, do not often clearly distinguish between the variety of recombination channels; broad spectral emission is often observed.

The material is consequently characterized by two numbers (i) a recombination lifetime $\tau_0$ of excess carriers which would apply in case of uniformity, and (ii) a single barrier height $V_b$ describing the modulation of the potential. The barriers separate the carriers and strongly prolong the lifetime. Ploog and Döhler[6] have summarized the currently available treatments of these extremely long lifetimes in semiconductor superlattices with deliberately incorporated barriers. Harmonic oscillator ground wave functions are a good approximation

$$\zeta_{i,0}(z)=\pi^{-1/4}\alpha_i^{-1/2}\exp(-z^2/2\alpha_i^2) \ , \tag{1}$$

where

$$\alpha_i=h^{1/2}(m_i\omega_i)^{-1/2} \ . \tag{2}$$

The index $i$ applies to valence and conduction bands with the respective masses $m$ and the bulk plasma frequencies $\omega$. The coordinate $z$ describes the direction of $n$-$i$-$p$-$i$ superlattice modulation. The recombination rate can then be calculated by finding the square of the overlap integral; a comparison to the unmodulated bulk case yields a ratio

$$\tau^{\mathrm{bulk}}/\tau^{\mathrm{nipi}}=[2\alpha_1\alpha_2/(\alpha_1^2+\alpha_2^2)]\exp[-(d^2/4)/(\alpha_1^2+\alpha_2^2)] \ , \tag{3}$$

where $d$ is the period of the superlattice.

The most remarkable feature is the extreme lifetime enhancement, of factors $10^{13}$ or even above, for typical superlattice parameters.[6] This enhancement can also be much more simply approximated in terms of the separating barrier voltage $V_b$ (Ref. 6)

$$\tau/\tau_0\sim\exp(+qV_b/kT) \ , \tag{4}$$

where $q$ is the electron charge and $kT$ the thermal energy at temperature $T$. We shall use this simple model to demonstrate the influence of the barriers. Thus, the model merely uses the fundamental ideas of junction theory.[8] The proportionality factor in Eq. (4) contains a characteristic length by which the carriers are separated;[6] this length is here assumed to be uniform and independent of temperature.

Equation (4) indicates that the spatial segregation of holes into valence-band maxima and electrons into conduction-band minima (see inset of Fig. 1) reduces their initial recombination rate by a factor $\exp(-qV_b/kT)$. The luminescence $I$ is thus suppressed relative to the homogene-

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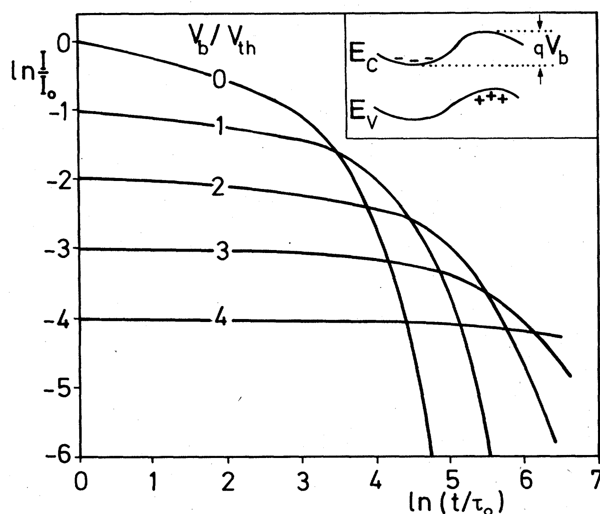


FIG. 1. Decay of a photoluminescence intensity $I$ with time $t$, plotted double logarithmically (in arbitrary units of $I_0$ and $\tau_0$) for various ratios of barrier height $V_b$ to thermal voltage $V_{th}=kT/q$. The ratio $V_b/V_{th}$ is indicated at the curves. The inset shows schematically the model used: potential barriers of height $V_b$ spatially separate electrons ( $-$ ) and holes ( $+$ ); $E_c$ and $E_v$ are edges of conduction and valence bands.

ous case, $I_0$, by

$$I/I_0=\exp(-qV_b/kT) \quad . \tag{5}$$

The carriers do not all recombine but remain in their respective extrema with extended lifetimes $\tau$. In actual experimental fact, these long lifetimes truly prevail since even nonradiative recombinations are excluded by the separation of the pairs.[6]

I now compare the luminescence decay for various temperatures $T$ under the assumption that a total number $P$ of electron-hole pairs has been generated by the photoexcitation, which terminated at time $t=0$. The area under a linear plot of intensity versus time is therefore given by $\eta P$, where $\eta$ is the fraction of radiative transitions. Figure 1 shows a family of curves with temperature as a parameter, as measured in units of a thermal voltage $V_{th}=kT/q$. The plot is doubly logarithmic, since experiments are often presented in this form.[9]

At high temperatures, $V_b/V_{th}\rightarrow 0$, we observe the usual rapid exponential decay, which may be evaluated for homogeneous specimens in a standard technique to obtain a true bulk lifetime $\tau_0$. Lowering of the temperature, however, reveals the effect of the separating barriers. The luminescence becomes appreciably depressed initially [Eq. (5)], but also shows a much longer duration [Eq. (4)]. For very large ratios of $V_b/V_{th}$, the output may fall below practical detection limits; yet these excessively long carrier lifetimes may now become accessible by electrical conductance measurements and a "persistent photoconductivity" can be observed.[10,11]

Notice that the initial intensity $I(t=0)$ multiplied by the lifetime $\tau$ is a constant, $\eta P$, under our assumption of neglected nonradiative bypass channels, which are, however, often unavoidable, for example, when electrical contacts must be applied. The observation that "the product of the intensity and decay time is approximately independent of temperature" has been reported in the literature[12] for crystalline $As_2Se_3$.

The powerful consequence of these considerations is a simple criterion to test a semiconductor for uniformity by measuring total light output versus time for different temperatures. Such measurements should complement spatially resolved luminescence characterization.[13] Often, at least an estimate for an average barrier height should be possible. It would, on the other hand, usually be fallacious to interpret the rise of $I$ with increasing temperature $T$ as an increase of radiative efficiency of some microscopic recombination mechanism or to conclude a thermal quenching of competing nonradiative channels. Figure 1 also indicates the importance of covering as wide a range in time $t$ of observing luminescence decay as possible. Limitation to brief time spans could, for example, mislead one to assume totally incorrect temperature coefficients of recombination rates, depending on measurement times prior or after the characteristic crossings of the curves of Fig. 1.

Experimental results on $As_2Se_3$ similar to those of Fig. 1 have, for example, been published by Kastner and coworkers.[9,12] An interpretation different from the one suggested here is claimed to be supported by other experimental observations.[14]

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