

Using the excitation-dependent radiative efficiency to assess asymmetry in the defect-related density of states

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Measurements of steady-state radiative efficiency versus photoexcitation rate probe the carrier-density-dependent competition between nonradiative and radiative mechanisms in semiconductors. Nonradiative recombination through defect levels is proportional to the product of defect level occupation and carrier density in the opposing band. Band-to-band radiative recombination scales with the product of band densities. The excitation rate required for defect level saturation establishes the effective density of participating defects. More subtle features in the changeover from defect-related to radiative-dominated recombination, and its temperature dependence, provide additional insight into the distribution of defect levels. In this letter, the authors consider the effect of asymmetry about the midgap. © 2007 American Institute of Physics.
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Imperfections in a periodic quantum system lead to discrete energy levels in the band structure whose wave functions are localized near the defect site. Photoexcited carriers can be trapped in these states, which often facilitate nonradiative recombination—the dominant energy loss mechanism in most optoelectronic devices. But if the traps are sufficiently shallow, thermally activated escape can alleviate this loss. Defect-related recombination depends strongly on the quality of the structure and the nature of the defects. Minor perturbations, such as substitutional donor and acceptor impurities, yield shallow hydrogenic levels that act primarily as traps rather than recombination centers. Defect-related recombination occurs more readily through deeper levels, where thermally activated escape is less probable. Deep energy levels are usually associated with defects whose atomic structure differs substantially from the underlying lattice.

Determination of the distribution of energy levels at defects, and how the distribution depends on the defect configuration, is an important ongoing theoretical and experimental challenge. Theoretical treatment of this problem is complex and sensitive to specific and often inadequately determined features of the defects. Estimation of the localized energy levels and analysis of recombination at dislocations and other extended defects are particularly difficult.¹ Hence, an experimental approach, followed by phenomenological interpretation, is generally most fruitful for characterization of deep states. We are finding that rich detail in the spectrum and occupation of defect levels, and the resulting impact on recombination, can be extracted from a sophisticated theoretical analysis of excitation- and temperature-dependent radiative efficiency experiments.

When optical excitation generates nonequilibrium electron-hole pairs in a semiconductor, recombination balances photoexcitation to establish steady-state carrier populations. Depending on carrier densities, temperature, and intrinsic and growth-dependent properties of the structure, a

variety of mechanisms contributes to the recombination process. These mechanisms can be separated into two general categories: those that produce photons (radiative) and those that do not (nonradiative). The radiative efficiency, or number of photons emitted relative to photons absorbed, is the ratio of the radiative and total (radiative plus nonradiative) recombination rates.

At moderate temperatures, the dominant radiative mechanism is usually band-to-band (*B-B*) recombination. Neglecting excitonic effects, which are weak when the thermal energy kT exceeds the exciton binding energy (~ 4 meV in GaAs), the *B-B* radiative rate is² proportional to the product of carrier densities in the bands and inversely proportional to $T^{3/2}$. Meanwhile, defect-related recombination scales linearly with occupation in a single band. As the incident laser power is increased, the photoexcited carrier densities and net recombination rate increase together. For undoped semiconductors, it is customary to assume that radiative recombination is dominated by *B-B* events and the photoexcited density of electrons in the conduction band n equals that of holes in the valence band, so the radiative rate is given by $r_{\text{rad}} = B(T)n^2 \text{ cm}^{-3}/\text{s}$, where

$$B(T) = \frac{B_{300}}{N} \left(\frac{300}{T} \right)^{3/2}. \quad (1)$$

$B_{300} \sim 2 \times 10^{-10} \text{ cm}^3/\text{s}$ is the radiative coefficient in GaAs at room temperature and N is the photon recycling factor.³ We estimate that $N \sim 9$ in the structure tested here.

In a radiative efficiency experiment, the integrated photoluminescence intensity I_{PL} is measured at fixed laser power P_{ex} , with the ratio $I_{\text{PL}}/P_{\text{ex}}$ giving a relative measure of the radiative fraction of the net recombination. This relative measurement is scaled by assuming that the internal radiative efficiency approaches one under low-temperature, high-excitation conditions.⁵ The incident laser power (corrected for surface reflection) is converted to the steady-state rate of electron-hole pair generation and recombination r_{net} by dividing by the laser energy ($E_{\text{ex}} = 2.33 \text{ eV}$ in our experiment)

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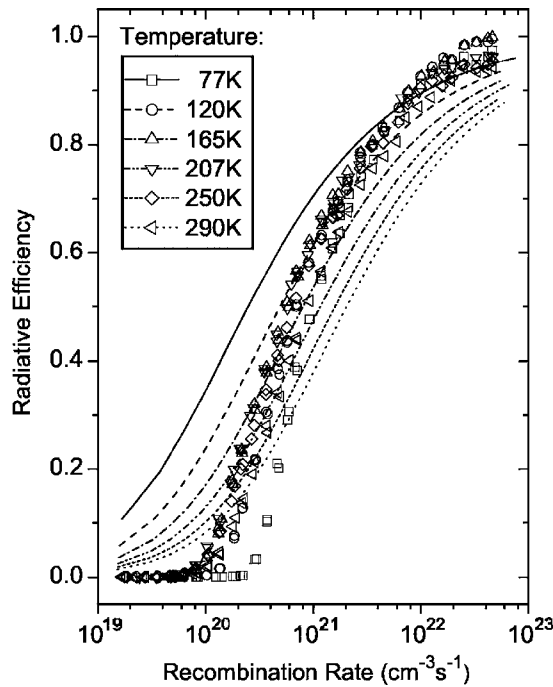


FIG. 1. Radiative efficiency of a lattice-matched GaAs/GaInP heterostructure vs the rate of electron-hole pair generation and recombination in steady state. The curves are theoretical fits assuming defect levels are clustered near the center of the band gap.

and photoexcitation volume (0.014 cm² laser spot size by 1.5 μm active layer thickness). Scattered laser light is removed by a 2.17-eV low-pass filter, so the I_{PL} detection band extends from the silicon photodiode cut-on at 1.16 eV to the filter cutoff at 2.17 eV. In this letter, we present results for a nominally lattice-matched GaAs/GaInP double heterostructure grown by metalorganic vapor-phase epitaxy, with a temperature-dependent photoluminescence peak position between 1.43 and 1.51 eV. Since the room-temperature band gap of our GaInP is 1.85 eV, the target thickness of the top window is 0.05 μm to provide sufficient carrier confinement while minimizing absorption in this layer.

Figure 1 shows how the radiative efficiency of our test structure varies with recombination rate and temperature. The curves are simple theoretical fits, assuming that the radiative mechanism behaves as described above and the defect-related rate $r_{def}=An$, where the fitting parameter $A \sim 1.5 \times 10^5 \text{ s}^{-1}$ is independent of temperature. This simple estimate for the defect-related rate is valid only when all defect levels are concentrated near the center of the band gap making thermal activation to the bands negligible.⁴ Nevertheless, the low value for the effective A coefficient confirms the excellent overall quality of the structure under investigation.

Considering the limitation noted above, it is not surprising that the simple theory produces a poor fit. While the simple theory is effective in some systems, we have discovered similar discrepancies in previous studies, which are rectified by allowing for more shallow states.⁵ However, the addition of shallow defect-related states cannot fix the predicament posed here. Shallow states retard defect level saturation by allowing for thermal activation into the bands, which slows the transition between the predominantly non-radiative and radiative regimes.⁶ In contrast, the measured

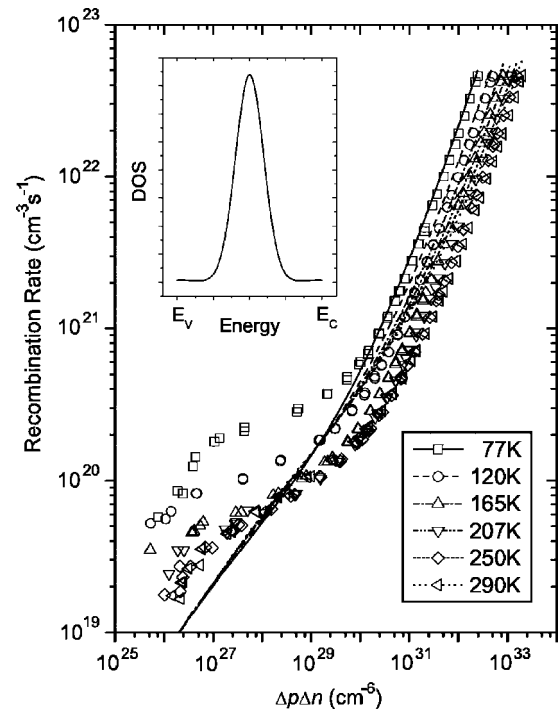


FIG. 2. Revised presentation of Fig. 1 showing the net recombination rate vs the product of band carrier densities. The curves are theoretical fits using the symmetric defect-related DOS function shown in the inset (with valence and conduction band edges E_v and E_c).

transitions shown in Fig. 1 are more abrupt than the simple theory predicts.

We show that a more rapid transition is expected when the densities of carriers in the valence and conduction bands increase disproportionately. When the doping concentration is smaller than the defect concentration, this phenomenon points to an asymmetric defect-related density of states (DOS) in the gap. We start by noting that theoretical determination of the underlying recombination rates depends on the general photoexcited band density n , which must be used as a parameter for computing the theoretical rates and efficiencies presented in Fig. 1. Fitting the experimental results in this way is cumbersome and restrictive, but theoretical analysis can be simplified and generalized by eliminating the common parameter n in the following way. We replace n^2 in Eq. (1) with $\Delta p \Delta n$, where Δp and Δn are the hole and electron densities in the valence and conduction bands, respectively. Hence, the radiative efficiency is given by

$$\eta = B(T) \Delta p \Delta n / r_{net}, \quad (2)$$

where r_{net} is the total (radiative+nonradiative) recombination rate. Now, using our theoretical estimate for $B(T)$ and plotting r_{net} against $\Delta p \Delta n$ as determined above, we can compare our experimental results directly with theoretical expectations. When Δp and Δn can differ, the defect rate becomes $r_{def} = \tau^{-1}(\Delta p \Delta n + \Delta n \Delta p)$, where Δn and Δp are the densities of trapped electrons and trapped holes, respectively. To simplify the model, we use a single, temperature-independent time τ to characterize defect state capture.

Preliminary application of this analysis to our nominally undoped, lattice-matched GaAs/GaInP test structure is shown in Fig. 2. The curves are optimized theoretical fits, neglecting unintentional doping, when the defect-related DOS function is assumed to be symmetric about the center

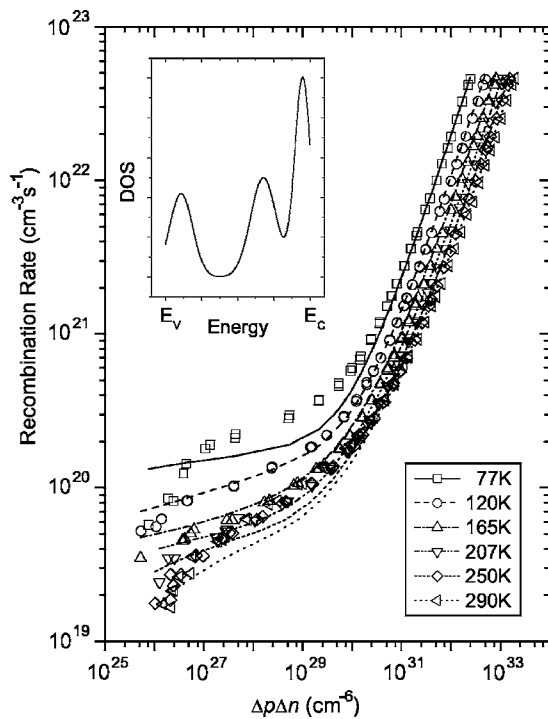


FIG. 3. Results from Fig. 2 with theoretical fits using the asymmetric DOS function shown in the inset.

of the band gap. Our fitting procedure converged on the large central peak shown in the inset. Allowing for an asymmetric DOS produces a much better fit, as shown in Fig. 3. The importance of asymmetry for obtaining a satisfactory fit is striking. In the past, we have always found that simple, symmetric DOS distributions give good fits.^{5,7} In these earlier studies, the primary figure of merit was the ratio of shallow to deep states, which determines the degree of spreading across defect and band levels and the rate of change in occupation with illumination and temperature. Nevertheless, there is no physical basis for this simplification, and Fig. 2 depicts a dramatic example of a system that violates the assumption. We note that asymmetry in the distribution of near-band-edge states is predicted by the theory of disorder induced gap states,⁸ and has been shown to exist in metamorphic heterostructures.⁹ It has also been used to explain transport properties in hydrogenated amorphous silicon.¹⁰

How does asymmetry in the defect-related DOS produce the behavior in Fig. 3? In particular, how can $\Delta p \Delta n$ increase without causing a simultaneous increase in the recombination rate? Consider the incremental filling of levels in the asymmetric DOS distribution shown in the inset of Fig. 3 as the steady-state photoexcitation rate is increased. The quasi-Fermi energies move away from the Fermi energy, and when

the nonequilibrium carrier density is sufficient to saturate the hole traps near the valence band, recombination proceeds primarily via trapped electrons and valence band holes. At a higher excitation level, the electron traps become filled, yielding a rapid increase in conduction band occupation with photoexcitation. Meanwhile, the density of holes in the valence band, which still controls the dominant recombination rate, grows more slowly with photoexcitation because recombination balances generation. Hence, the product $\Delta p \Delta n$ increases without augmenting the recombination rate appreciably.

Our computational framework for modeling this behavior includes (1) the calculation of the Fermi energy for a given temperature, band gap, and defect DOS, (2) the calculation of the electron and hole quasi-Fermi energies for a given nonequilibrium electron-hole pair density (which is chosen to match each experimental value of $\Delta p \Delta n$), (3) the calculation of defect and band level occupations, and (4) the determination of rates and the associated time τ that minimizes the total error. We note that these calculations would be modified by substantial impurity concentrations, which could shift the Fermi energy and produce an analogous asymmetric band filling. Hence, the asymmetric DOS interpretation relies on our low background doping assumption. The curves in Fig. 3 are preliminary results of this analysis, although we note that the deduced DOS function still depends somewhat on the initial DOS parameter choices, and is therefore not unique. We are currently pursuing a more robust algorithm, which we believe may produce a unique solution.

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