

The role of potential fluctuations in continuous-wave donor–acceptor pair luminescence of heavily doped materials

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It has recently become apparent that “standard” (low-concentration and low-compensation) theory for donor–acceptor pair (DAP) photoluminescence (PL) is totally incapable of explaining results in highly doped and compensated material. It can be noted that such material is often of high technological interest. It has been argued, mainly qualitatively, that the discrepancies result from potential fluctuations due to random ionic charges. We here present a *quantitative* theory for cw DAP PL, using an approximate model. We also present data for the concentration and intensity dependence of DAP PL in heavily doped ZnSe:N, and show that the results are explained very satisfactorily by our fluctuation model. © 1999 American Institute of Physics.

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Wide-band-gap semiconductors are presently of high interest for various device applications, which require good doping in both *n* and *p* material. Historically, it has been difficult to obtain this and, when obtained, such materials have often been highly compensated (see, e.g., Ref. 1).

Photoluminescence (PL) has been extensively used to characterize wide-gap materials, since it is convenient, non-destructive, and can be quite informative. However, although PL is generally quite well understood in low-doped materials,² it is becoming increasingly apparent that heavily doped and compensated materials contain potential fluctuations, which strongly affect the PL.³

We shall here focus on donor–acceptor pair (DAP) PL, where cw spectra have been routinely used to obtain donor and/or acceptor energies in the lightly doped case.² However, for the highly doped materials of current interest, the PL bands are strongly shifted toward the red, as well as being strongly broadened (see, e.g., Refs. 4 and 5 for ZnSe, Refs. 6 and 7 for GaAs, and Ref. 8 for GaN) with these effects increasing with doping.⁹ A simple qualitative explanation for such phenomena is given by the fluctuation model as follows. Here, the redshift is due to the recombination between the electrons localized in the “valleys” and the holes localized in the “hills” (see, e.g., Fig. 3 of Ref. 5). The broadening results from the wide range of photon emission energies which are made possible by the potential fluctuations. Furthermore, higher doping levels and/or compensation give stronger fluctuations. More detailed, but still qualitative, discussions can be found elsewhere.^{4–9}

In the present letter we show that quantitative, analytic, results can be obtained relatively simply by use of an approximate model, in which the Fermi level of the majority dopant remains essentially constant. We note that the only other quantitative analysis of such PL is an attempt via Monte Carlo simulations,¹⁰ where band broadening was

achieved mainly by adding phonon replicas (LO) to the spectrum. However, the estimated magnitude of the fluctuations^{4,9} is usually larger than the energy of the LO phonon, so that phonon replicas should be washed out by fluctuations.

Following our earlier treatment,³ the energy of the emitted photon ($h\nu$) of the DAP PL in the presence of potential fluctuations of energy U^{11} is

$$h\nu = E_G - (E_A + E_D) + e^2/\epsilon R + U[\varphi], \quad (1)$$

where U is the so-called fluctuation term (given in Ref. 3), R is the pair separation, and the remaining notation is standard.³ Following Ref. 3 we also use $E = h\nu - E_G + E_A + E_D$ as an emission energy, instead of $h\nu$. It is very important to realize that while $h\nu$ is always positive, E can be either positive or negative, depending on the magnitude and a sign of the fluctuation energy term in Eq. (1).

In the random fluctuating potential only donors with levels below, and acceptors with levels above, the corresponding quasi-Fermi levels μ_D and μ_A (i.e., neutral impurities N_A^0 and N_D^0) will contribute to the luminescence. Moreover, μ_A and μ_D will depend on the excitation intensity.

The quantitative treatment of this problem becomes relatively simple if the quasi-Fermi level of the majority dopant (which we take as μ_A) is not appreciably changed by the excitation from the Fermi level in the dark. This will be fulfilled for $(N_A^0)_{\text{photogenerated}} \ll (N_A^0)_{\text{dark}}$ [note that $(N_D^0)_{\text{dark}} = 0$], which holds for $N_A \gg N_D$ and for low excitation intensities; N_A and N_D are the concentrations of acceptors and of compensating donors.¹² Now, only μ_D will change under excitation.

In general, the experimentally observed PL intensity is determined by the concentrations of neutral impurities, by the probability of radiative transitions, $W(R)$, and by the quasi-Fermi levels (μ_D , in the present approximation). The latter must be obtained self-consistently as a function of the disorder¹³ (the magnitude of the fluctuations) and the excita-

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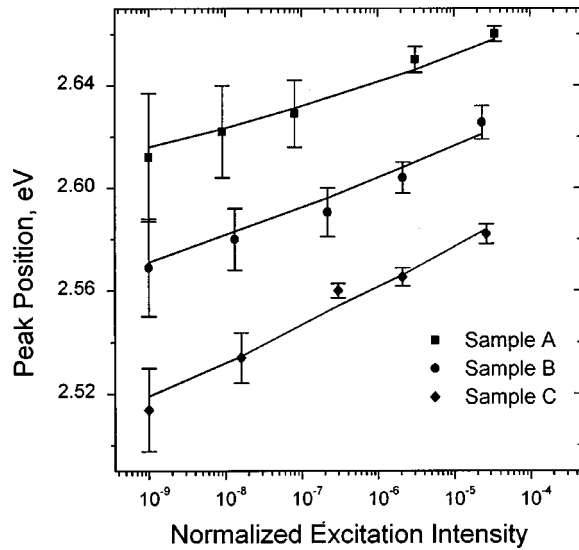


FIG. 1. Peak position dependence on normalized excitation intensity for samples A–C. Symbols are the experimental data and solid lines are the fitting according to Eq. (11). The fitting parameters are: $\xi=4.85$, $\eta=0.066$, $\tilde{n}=0.007$, and $e^2/\epsilon R_s=46$ meV for sample A; $\xi=3.80$, $\eta=0.089$, $\tilde{n}=0.003$, and $e^2/\epsilon R_s=57$ meV for sample B; and $\xi=3.10$, $\eta=0.110$, $\tilde{n}=0.001$, and $e^2/\epsilon R_s=69$ meV for sample C.

tion intensity. Then, the luminescence intensity $I_E(g)$ per unit energy at an energy E as a function of excitation intensity g [$\text{s}^{-1}\text{cm}^{-3}$] can be written

$$I_E(g) = 4\pi N_A N_D \int_0^\infty dR R^2 P(R) W(R) \times \langle \delta(E - (e^2/\epsilon R) + e[\varphi(\mathbf{r} + \mathbf{R}) - \varphi(\mathbf{r})]) \times \Theta(\mu_D - e\varphi(\mathbf{r})) \rangle_{\{\varphi\}}, \quad (2)$$

where $W(R) = W_0 \exp[-2R/R_B]$ (R_B is the Bohr radius of the shallower impurity; see, e.g., Ref. 14), $P(R)$ is a probability distribution function for the interimpurity separation R (e.g., Refs. 15–19), a δ function selects a specific photon energy,³ $\langle \dots \rangle_{\{\varphi\}}$ means the functional average over the fluctuations,^{3,20} and $N_D^0 = N_D \langle \Theta(\mu_0 - e\varphi(r)) \rangle_{\{\varphi\}}$, where Θ is the Θ function.²¹

For $P(R)$ we use the nearest-available-neighbor (NAN) model,^{17–19}

$$P(R) = [1 + (4\pi/3)^1 (N_A - N_D) R^3]^{-1}.$$

If we introduce the quantum efficiency of excitation, $\gamma < 1$, then the number of emitted photons will be equal to γg . Furthermore, the integrated intensity (over all possible emission energies) also gives $\gamma g = \int_{-\infty}^\infty I_E(g) dE$, which allows us to calculate μ_D as a function of g (note that, as has been pointed out above, E can be either positive or negative):

$$\tilde{g} = g \gamma [4\pi N_A N_D \int_0^\infty dR R^2 P(R) W(R)]^{-1} = \langle \Theta(\mu_D - e\varphi(\mathbf{r})) \rangle_{\{\varphi\}}, \quad (3)$$

where \tilde{g} is a normalized excitation intensity. Here, the average of the Θ function represents the fraction of donors which are neutral, i.e., those which are active in recombination processes. Explicit averaging, as described elsewhere,^{3,20} gives

$$\tilde{g} = (1/2) [1 + \text{erf}(\mu_D \sqrt{\epsilon R_s / 2e^2 T_g})], \quad (4)$$

where $\text{erf}[x]$ is the error function; we also introduced the screening radius R_s and the freezing temperature T_g .³ It is important to note that the screening radius itself must be calculated self-consistently. We are not aware of any unique way to calculate this, but by use of the Debye–Hückell approach one can show that it is a reasonable approximation to relate R_s to T_g as (see, e.g., Ref. 20 and references therein) $R_s^2 = \epsilon T_g / 8\pi e^2 (N_D - N_D^0)$.²¹ Then one can obtain

$$R_s^2 = \epsilon T_g [4\pi e^2 N_D [1 - \text{erf}(\mu_D \sqrt{\epsilon R_s / 2e^2 T_g})]]^{-1}. \quad (5)$$

This equation together with Eq. (6) allows one to obtain μ_D , self-consistently, as a function of the normalized intensity, by solving the following transcendental equation:

$$\tilde{g} = (1/2) \{1 + \text{erf}[\mu_D (\epsilon^3 [32N_D e^6 T_g (1 - \tilde{g})]^1)^{1/4}]\}. \quad (6)$$

We now specialize to the case of low excitations, $\tilde{g} \ll 1$. First, this means that \tilde{g} in the denominator of Eq. (6) can be neglected. Second, as previously stated, we require g small enough so that $(N_A^0)_{\text{photogenerated}} \ll (N_A^0)_{\text{dark}}$. As a third requirement, $N_D^0 \ll N_D$; this also means (see above) that, as long as \tilde{g} remains small, changes in R_s with excitation are negligible. Thus, all changes in the spectral position can be predominantly attributed to the movement of μ_D toward the conduction band. Simplifying further, by using the first term in the asymptotic series for a function $1 + \text{erf}[z]$ with $z < 1$ [since $\tilde{g} \ll 1$, it follows from Eq. (6), that $\mu_D \sqrt{\epsilon R_s / 2e^2 T_g}$ is a relatively large negative number], we get

$$\tilde{g} = -\exp(-\tilde{\mu}^2) / (2\sqrt{\pi}\tilde{\mu}), \quad (7)$$

where $\tilde{\mu} = \mu_D \sqrt{\epsilon R_s / 2e^2 T_g}$. Further, $\tilde{\mu}$ in the denominator of Eq. (9) can be replaced, over a fairly wide range of the quasi-Fermi level, by some average value $\tilde{\mu}_{\text{ave}}$, since the exponent in the numerator is changing much faster than $\tilde{\mu}^{-1}$. Then, we obtain the *central equation* of our theory:

$$\mu_D = -\sqrt{-2e^2 T_g \ln \hat{g} / \epsilon R_s}, \quad (8)$$

where we introduced a renormalized excitation intensity $\hat{g} = -2\sqrt{\pi}\tilde{g}\tilde{\mu}_{\text{ave}}$.

Now we can obtain an expression for the PL intensity by performing explicit averaging in Eq. (3):

$$I_E(\hat{g}) = 4N_A N_D W_0 R_s^3 / \sqrt{\pi} \times \sqrt{\frac{\epsilon R_s}{e^2 T_g}} \int_0^\infty du \frac{u^{5/2}}{\sqrt{u-1} + \exp[-u]} P(u) \times \exp\left[-\xi u - \eta \frac{(\tilde{E}u - 1)^2}{u(u-1 + \exp[-u])}\right] \times \left\{1 - \text{erf}\left[\frac{\sqrt{-2 \ln \hat{g} u + \sqrt{\eta}(\tilde{E}u - 1)}}{\sqrt{u(u+1 - \exp[-u])}}\right]\right\}, \quad (9)$$

with $P(u) = 1/[1 + \tilde{n}\xi^3 u^3/6]^{-1}$. We have introduced³ a dimensionless energy $\tilde{E} = \epsilon R_s E / e^2$, as well as the parameters $\xi = 2R_s/R_B$, $\eta = e^2/(4T_g \epsilon R_s)$, and $\tilde{n} = \pi(N_A - N_D)R_B^3$. Equation (9) gives the spectrum of the zero-phonon line of DAP PL in the presence of fluctuations as a function of excitation intensity for the case of relatively low intensities and $N_A > N_D$.

TABLE I. Samples characteristics.

Sample	rf Power, W	$[N]$, 10^{19} cm^{-3}	DAP Peak Position, eV
A	180	...	2.660
B	280	...	2.626
C	300	2	2.528

For comparison to the theory, we have taken data on three different nitrogen-doped ZnSe samples, all grown under conditions giving heavy doping—samples A–C (see Table I), grown with increasing rf power of the nitrogen source, which leads to higher compensation^{23–25} and thus stronger fluctuations. We note that the values of $N_A - N_D$ for these samples could not be detected via $C-V$ profiling,²² i.e., they were all highly resistive due to high compensation (note that the values of $N_A - N_D$ still can be relatively large while the concentration of free carriers is too low to give observable currents¹²). The cw DAP spectra of these samples are shown in Ref. 25. This also discusses the results in terms of Eq. (8), which gives very satisfactory qualitative agreement.

Here we checked quantitative²⁶ agreement of the peak shift versus excitation intensity. Figure 1 shows the peak positions as a function of normalized excitation intensity. The observed shifts are 48, 53, and 75 meV for samples A, B, and C, respectively. These large shifts, as well as their increase for samples with larger fluctuations, can be explained by our model, as follows. With increasing pumping, the quasi-Fermi level would move closer to the band edges, according to Eq. (8), giving a blueshifted PL. Furthermore, the change in the position of the quasi-Fermi level is [see Eq. (8)] $\Delta\mu_D \propto \sqrt{2e^2 T_g / \epsilon R_s}$ and would be larger for samples with larger fluctuations, since R_s is now smaller. Thus, one expects that relative changes in the peak position are larger for samples with larger fluctuations.²⁶

We also present in Fig. 1 the fit obtained with the use of Eq. (9)—solid lines. In all cases, we used 2.667 eV for $(E_G - E_A - E_D)$, which corresponds to $E_G = 2.822$ eV, $E_A = 0.110$ eV,²⁷ and $E_D = 0.045$ eV.²⁸ We note that all parameter values used in the fit, as well as their progression from sample A to sample C, are reasonable. In particular, note that $e^2 / \epsilon R_s$, which can be regarded as a measure of the strength of the fluctuations, increases steadily from A to C, in line with the rf power used for growth (see Fig. 1 caption). Furthermore, the values of $e^2 / \epsilon R_s$ are in excellent agreement with photoluminescence excitation data.⁹

In conclusion, we presented a theoretical study of cw DAP PL in heavily doped semiconductors, together with data on the concentration and intensity dependence of this PL for several such ZnSe:N samples. The theory, based on the fluctuation model, gives an excellent agreement with the experimental data, and in particular, explains quantitatively the blueshift with increasing excitation, as well as the increase in this blueshift with increasing compensation.

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¹¹This equation is easily obtained by application of the energy conservation law, given that in the case of impurity disorder the intrinsic band gap is independent of the coordinate; in other words, the profiles of the conduction and valence bands are the same [see, e.g., J. S. Blakemore, *Semiconductor Statistics* (Dover, New York, 1987), as well as Ref. 6].

¹²Experimentally, dark values of N_A and N_D can be determined, at least approximately, by temperature-dependent Hall measurements. Alternatively, $N_A - N_D$ can often be determined by $C-V$ profiling; however, if an impedance analyzer is used, this method breaks down unless there is an adequate free-carrier concentration.

¹³The magnitude of the fluctuations depends on the concentration of ionized species, which depends on doping and compensation. An appropriate measure is given by $e^2 / \epsilon R_s$; R_s is the screening radius (see Ref. 3).

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²⁶In the case of relatively large pumping intensities (when our approximate theory is no longer satisfied), in addition to the μ_D effect, there will be a lower concentration of charged impurities, and thus, a decrease in the magnitude of the fluctuations. This reduces the fluctuation energy term in Eq. (1), and results in an additional blueshift of the spectra. It is important to realize that the onset of the shift due to such increased neutralization, which can be related to a change in R_s , would take place earlier for samples with smaller fluctuations than for those with large fluctuations. Moreover, this effect makes quantitative comparison of the peak shifts per decade of excitation intensity (especially in a limited range at high intensities) very ambiguous.

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