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Time-resolved photoluminescence of heavily nitrogen-doped ZnSe: role of fluctuations

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Abstract

Results of time-resolved photoluminescence of several heavily nitrogen-doped ZnSe samples ([N] > 10^{18} cm^{-3}) are presented, with emphasis on the decay at relatively long times and at a particular wavelength of decay. Both these aspects are well explained by the presence of potential fluctuations in such materials, but not by earlier theories which neglected fluctuations. The observed decay as a function of N concentration is also well explained by our model. We obtain quantitative agreement, and obtain good values for the decay constant W_0 and for the net acceptor concentrations.

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It is well-known that ZnSe and related alloys are of high interest for application to light emitting devices in the blue–green range (see, e.g., Refs. [1,2]). For improved device performance, better p-type conductivity is desirable. To date, nitrogen appears to be the best p-type dopant; at present, net acceptor concentrations range up to only 10^{18} cm^{-3}, although greater than 10^{19} cm^{-3} of nitrogen can be incorporated (e.g., Ref. [3]).

It has been established that at "intermediate" total nitrogen concentrations (around $10^{18}cm^{-3}$), there is formation of deeper donors (at about 45–50 meV) which are evidenced by donor–acceptor pair (DAP) photoluminescence (PL) with

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a zero-phonon peak at about 2.685 eV [4], versus the peak with "standard" shallow donors, at about 2.697 eV (e.g., Refs. [3,4]). With even higher concentrations, the spectrum changes to a very broad red-shifted band with a peak in the 2.550–2.650 eV region [3,5–8].

The present paper focuses on this deep band, and a brief review of its properties appears to be useful. With increasing intensity of excitation, the peak shifts towards the blue, and at very high intensities, a regular DAP spectrum with phonon replicas has been recovered in at least one instance [5]. With increasing temperature, this deep band shows a relatively strong shift towards the red [6,7]. The appearance of such a band was attributed, in Refs. [5–7], to the presence of fluctuations in internal electric fields due to a random distribution of charged impurities. However, it was also suggested that such a broad band could arise from the presence of additional, deeper levels [8].

In this paper, we present data which prove, unambiguously, that fluctuations *are* present. We would like to emphasize that fluctuations are *expected* to exist in heavily doped semiconductors [9] regardless of what type of impurities are present; thus our approach *does not* prove the absence of deep levels, but merely shows that if there are such levels, there must be fluctuations in addition. Specifically, we prove the presence of fluctuations by a detailed analysis of the time-resolved photoluminescence (TRPL) of DAP recombination.

We note that the "standard" DAP theory, i.e. the theory without fluctuations (e.g., see Ref. [10]), cannot be used to explain the observed decay. It predicts a predominantly [11] exponential decay for luminescence at a particular wavelength, whereas our observed decay is strongly non-exponential (see Ref. [11]), which we fit by including the fluctuations in the theory.

The ZnSe : N samples were grown on GaAs substrates by MBE. Samples A – C were grown at Philips Research with increasing RF power; sample D was grown at West Virginia University [8]. Some sample characteristics are presented in Table 1. [N] was obtained by SIMS, and the hole concentration from Hall measurements.

For samples A – C the TRPL data were obtained at Columbia University using a nitrogen-pulsed laser operating at 337 nm (3.679 eV) and a dye module providing variable excitation wavelengths; the pulse width is about 5 ns. Most of the data were obtained with excitation at a photon energy of 2.908 eV, which is just above the band gap of ZnSe. This choice gave a relatively low excitation intensity, as well as a decrease in possible hot-electron effects. All results were obtained at $T = 11$ K (the sample temperature was monitored by a silicon diode mounted close to the sample). The data on sample D were obtained at West Virginia University using the 355 nm output from a Q-switched Nd : YAG laser operating at a 10 Hz repetition rate as described elsewhere [8].

Table 1
Sample characteristics

Sample	RF power(W)	[N]; [p] at RT (10^{17} cm^{-3})
A	180	
B	280	
C	300	200
D	200	150; 0.2

[a]Sample at West Virginia University grown using RF plasma source Oxford CARS-25.

Recently, a detailed theory for TRPL in the presence of fluctuations has been developed [12]. The basis of the theory is that in the presence of fluctuations, characterized by a random potential $\varphi(\boldsymbol{r})$, the energy of emitted photons ($h\nu$) for DAP recombination should contain an additional term – the fluctuation energy $U[\varphi]$ (see also Ref. [13]):

$$h\nu = E_G - (E_A + E_D) + \frac{e^2}{\varepsilon R} + U[\varphi], \tag{1}$$

where E_G is the band-gap energy, E_A and E_D are the ionization energies of an acceptor and a donor, respectively, in the absence of fluctuations, R is the distance between a donor and an acceptor, ε is the dielectric constant, e is the electron charge, and

$$U[\varphi] = e[\varphi(\boldsymbol{r}_D) - \varphi(\boldsymbol{r}_D + \boldsymbol{R})]. \tag{2}$$

This term arises due to the potential difference of the electron at the donor coordinate $\boldsymbol{r}_D$ and the acceptor coordinate $(\boldsymbol{r}_D + \boldsymbol{R})$, where $|\boldsymbol{R}| \equiv R$.

It is important to note that while in the case $U[\varphi] = 0$ (no fluctuations) $h\nu$ and R have a unique correspondence [10], an essential change in this

theory is that the presence of $U[\varphi]$ breaks this unique relation. *In other words, DAPs with all possible separations and appropriate fluctuation energies can, in principle, contribute to the emission at hv.*

The transient intensity, thus, is an average over all possible realizations of the fluctuation potential, and with use of Eq. (1) and (2) it is possible to show that the decay is non-exponential, relatively close to stretched-exponential, or even slower, particularly at very low temperatures. A critical difference from previous analyses (e.g. Ref. [10]) is that these predicted essentially an exponential decay at a *particular* wavelength [11] whereas in the presence of fluctuations the decay becomes non-exponential. It has been shown [12] that the decay $I_E(t)$ at a particular wavelength, in the limit $T = 0$, at longer times, is given by:

$$I_E(t) \propto \sqrt{\xi}\exp(-\eta\tilde{E}^2)\frac{[\ln(W_0t)]^2}{W_0t} \times \exp[-0.483(N_A - N_D)R_B^3[\ln(W_0t)]^3], \quad (W_0t) \to \infty . \tag{3}$$

Note: the decay is now the same for all wavelengths (except for a scale factor). Here W_0 is the maximum probability of radiative DAP recombination; N_A and N_D are the acceptor and donor concentrations, respectively; R_B is the Borh radius of the shallower impurity (donor in ZnSe : N); $\tilde{E}$ is the normalized emission energy; ξ is the normalized donor Borh radius, and η is a parameter representing the effect of the fluctuations. The normalization factor is $e^2/\varepsilon R_s$, where R_s is the screening radius.

We would like to note, before presenting experimental results, that Eq. (3) provides a means for the estimation of W_0 and of the net acceptor concentration.

Figs. 1–3 show experimental data of TRPL on samples A – D as well as the results of the theoretical analysis using Eq. (3). Fig. 1 shows the time decay for sample D up to 8 μs for luminescence at 2.530 eV. The solid curve is the theoretical fit according to Eq. (3). Fig. 2 shows the time decay at three different emission energies, and the theoretical curves, for sample C (see also Ref. [13]). Fig. 3

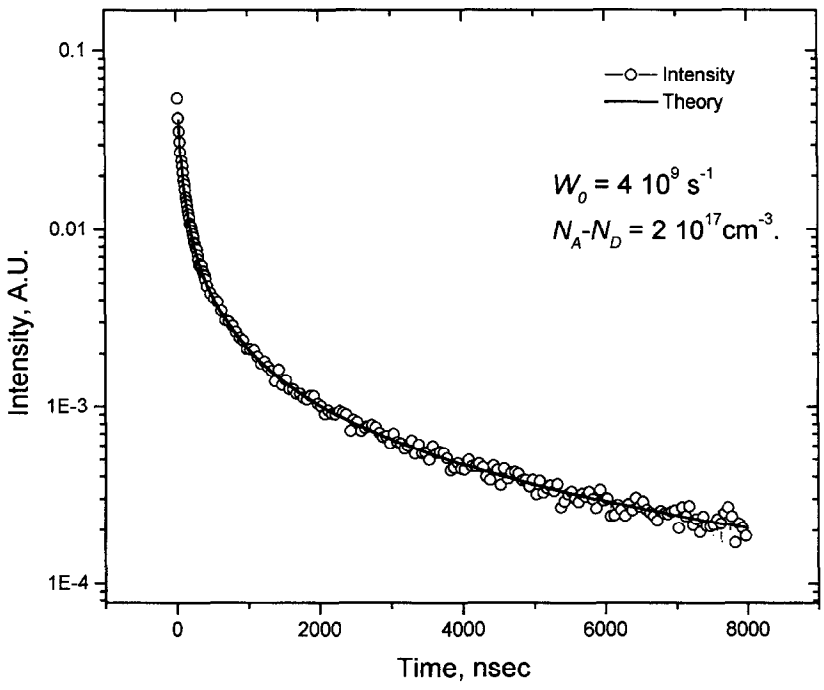

Fig. 1. Time-resolved photoluminescence of Sample D at an emission energy of 2.53 eV. The solid curve is the theoretical fit according to Eq. (3).

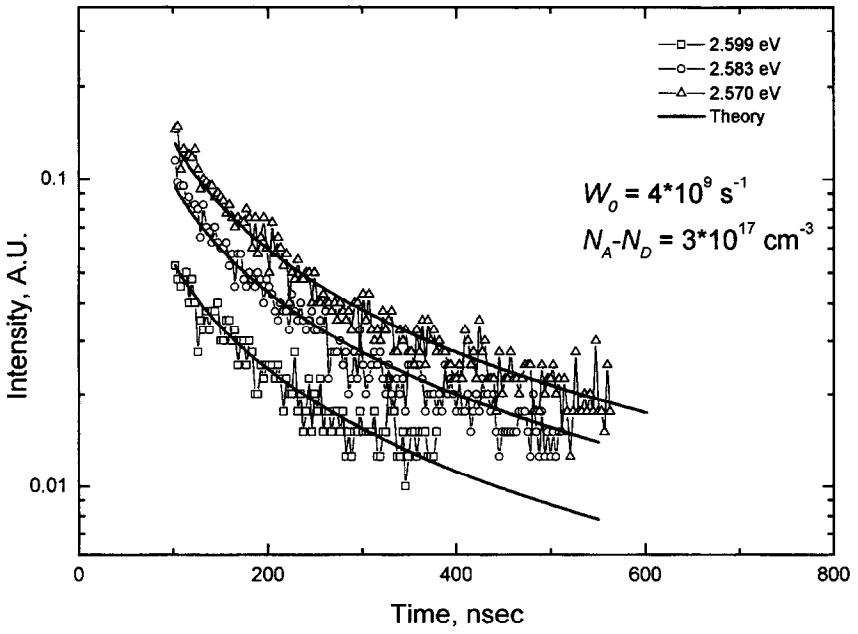

Fig. 2. Time-resolved photoluminescence of Sample C at three different emission energies. Solid curves are the theoretical fit according to Eq. (3).

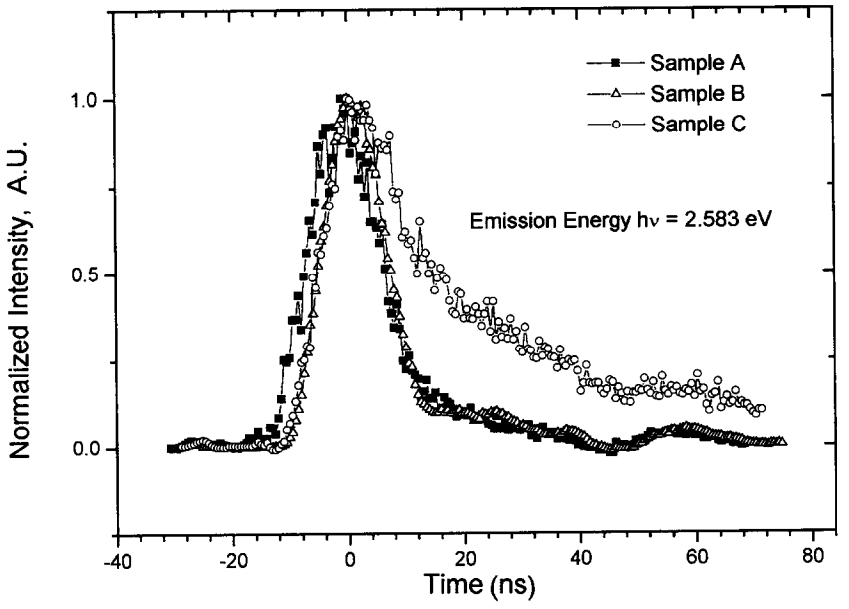

Fig. 3. Comparison of the time-decay of the photoluminescence for three different samples (A – C), at an emission energy of 2.583 eV.

shows the time decay (emission at 2.583 eV) for samples A–C.

Figs. 1 and 2 show similar decays for two differently grown samples (namely D and C); the decay for sample D was taken over several orders of magnitude in both time and intensity scales. As seen from the figures, the fluctuation theory results in excellent fits for both samples. Moreover, the parameters used to fit the decays at all three emission energies for sample C are the same.

It is noteworthy that the value of $W_0 = 4 \times 10^9\ s^{-1}$ has been obtained for both samples C and D, although they were grown in different MBE machines; this result is however expected since W_0 is the same for the same acceptors and donors. The value of W_0 is also consistent with one obtained previously for ZnSe : Na [14]. It was shown that for ZnSe : Na with shallow donors ($E_D = 25$ meV, $R_B = 37$ Å) the value of W_0 is $6 \times 10^8\ s^{-1}$ [14]. In the present samples, the donor is at 45–50 meV [4,6,7,15], so R_B should be smaller. Application of scaled effective-mass theory [14] gives a value between 24–27 Å. Assuming the acceptor Bohr radius to also be scaled [14] and taking $R_B = 24$ Å, we obtain, taking the ususal value of 110 meV for the N acceptor, $W_0 = 2.7 \times 10^9\ s^{-1}$, and for a possible 170 meV deep [8] acceptor, $W_0 = 1.3 \times 10^9\ s^{-1}$. This is in excellent agreement with the value used in the fitting. Corresponding values of the net acceptor concentrations, obtained for $R_B = 24$ Å, are shown in the figures.

Given the low hole concentration obtained for sample D, the estimated value of the net acceptor concentration ($2 \times 10^{17}\ cm^{-3}$) is reasonable since due to high compensation a low value for the free carrier concentration is expected.

It can be seen from Fig. 3 that the decay for sample C (which is grown at the higher RF power (see Table 1)) is slower than that for samples A and B. Note that the higher source power, under otherwise comparable conditions, tends to give both higher total N and higher compensation [3], which in turn increases the magnitude of fluctuations [9]. Since the decay becomes slower with increasing fluctuations, the data shown in Fig. 3 are consistent with our fluctuation model.

In conclusion, we regard our results as proving that potential fluctuations should always be taken into account in the analysis of time-resolved photoluminescence, even though deeper levels [8] might be present, in addition, in heavily doped ZnSe : N. We have shown experimentally that DAP TRPL at a particular emission energy is strongly non-exponential, in contrast to the prediction of "standard" theories [10]. Furthermore, we have confirmed the theoretical predictions for TRPL based on the fluctuation model [12] and have extracted W_0 and net acceptor concentrations by fitting to the TRPL data.

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excitation [6,7]) would lead, based on "standard" theory, to a *negative* (unphysical) Coulomb shift if one uses $E_D \leqslant 50$ meV (the usually reported value, e.g. Refs. [4,6,7]) and $E_A \leqslant 170$ meV (the largest reported value, e.g. Ref. [8]). Such an unphysical Coulomb shift precludes even attempting a fit of the decay, at a given wavelength, with standard DAP TRPL theory [10], since this requires specific value of R; this value, in turn, would have to be obtained from the Coulomb shift.

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