

Optical properties of semiconductors with the Coulomb potential fluctuation: case of co-doped ZnSe:(N,Cl)

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We discuss properties of cw and time-resolved photoluminescence (PL) as well as photoluminescence excitation (PLE) from co-doped ZnSe:Cl,N samples. These samples are characterized by the presence of the potential fluctuations due to charged donors and acceptors. We compare intensity dependent cw PL with the theory and find a good agreement. We also find that the material parameters obtained from cw PL and time-resolved PL agree well.

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1 Introduction It is widely accepted that the Coulomb potential fluctuations due to charged impurities play a major role in the photoluminescence (PL) from heavily compensated semiconductors (see, e.g. Refs. [1-4]). One of the most interesting and direct evidence about the presence of the Coulomb potential fluctuations as well as their effects on PL was given by Behringer et al. [3] who studied co-doped ZnSe:Cl:N. Such an intentional simultaneous introduction of donors and acceptors allows one to vary the magnitude of the fluctuating potential in a somewhat controlled manner, which is important for our further discussions.

We present in this paper the experimental data on a series of similar co-doped ZnSe:Cl:N samples, which will clearly exhibit properties associated with the Coulomb potential fluctuations and which we shall describe qualitatively and, where possible, quantitatively, comparing with previously developed theories [2, 4].

2 Samples The samples studied in this work were grown by molecular beam epitaxy (MBE) and their characteristics are shown in Table 1. The net impurity concentrations were measured by electro-chemical CV profiling, and Cl concentrations were estimated from the flux.

Table 1 Co-doped ZnSe:Cl,N samples.

Sample No.	Cl Concentration, cm ⁻³	Net impurity Concentration, cm ⁻³
A	2×10^{16}	3×10^{17}
B	2×10^{17}	3×10^{17}
C	6×10^{17}	3×10^{17}

3 CW photoluminescence In Figs. 1(a)–(c) we show cw PL from the co-doped samples at different excitation intensities. At the highest excitation intensity, sample A (Fig. 1(a)) exhibits a shallow donor-

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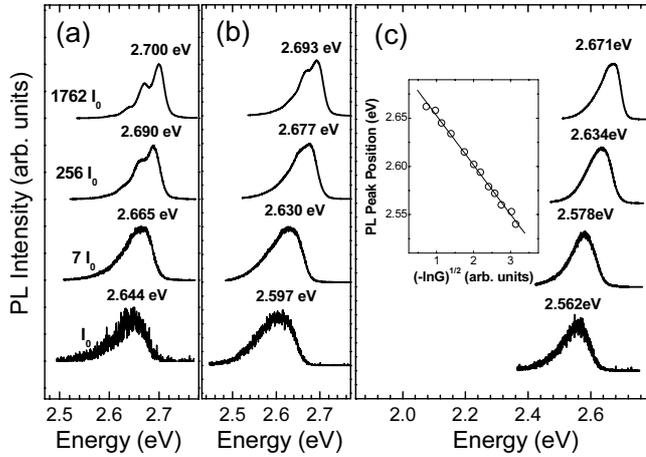


Fig. 1 The intensity dependent photoluminescence of (a) sample A, (b) sample B and (c) sample co-doped ZnSe:(N,Cl) with increasing concentration and compensation (Table 1); C the inset shows the peak position for sample C as a function of excitation intensity.

acceptor pair (D^sAP)-like emission accompanied by phonon replicas; sample C (Fig. 1(c)) shows no such structures and its PL is significantly shifted to the red; sample B (Fig. 1-(b)) exhibits the “intermediate” behavior. All the PL spectra obtained from these samples at low excitation intensities are peaked well below 2.666 eV that corresponds to the lowest DAP emission energy for N acceptor and a “deep” donor associated with nitrogen doping [5]. Furthermore, in the samples with higher degree of compensation the recovery, if any, of phonon replicas occurs at higher excitation intensities, as expected from the theoretical prediction [4]. We note that we did recover phonon replicas in sample C under pulsed laser excitation.

All three co-doped samples show large PL energy shifts as functions of excitation intensity with such a shift larger in samples with higher degree of compensation. The explanation to the observed behavior has been given previously based on the quasi-Fermi levels shifts [4] as well as due to screening effects [1–4]; both occur due to the increase in the concentration of neutral species caused by photogenerated carriers.

We concentrate here, however, on the fact that the approach outlined in Ref. [4] allows one to quantify such shifts and thus to verify the theory, if concentration of the impurities is known. For this, in the inset in Fig. 1(c) we plot for sample C the PL peak energy vs $\sqrt{-\ln G}$, where G is the normalized excitation intensity in arbitrary units and $G < 1$ [4]. We have chosen this sample because we do not see the recovery of the phonon replicas, and therefore we can neglect the changes in the screening radius. The PL peak energy vs $\sqrt{-\ln G}$ is a linear function, the slope (S) of which is expressed as [4]

$$S = \sqrt{2T_g e^2 / \epsilon R_s}, \tag{1}$$

where T_g is the so-called freezing temperature in energy units [2] and R_s is the screening radius [2,4]. The S value obtained from the inset in Fig. 1(c) is ~ 51 meV. T_g and R_s are interdependent via [2, 4]

$$T_g = \frac{4\pi e^2 R_s^2}{\epsilon} (N_D^+ + N_A^-), \tag{2}$$

where N_D^+ and N_A^- are the concentrations of ionized donors and acceptors respectively. At low temperatures and low excitation intensities (present experimental conditions), one can assume that $N_D^+ \approx N_A^-$ (sample C is n-type). Thus, if one knows S and R_s , independently, the theory can be checked by calculating the concentration of the charged impurities and comparing it to that

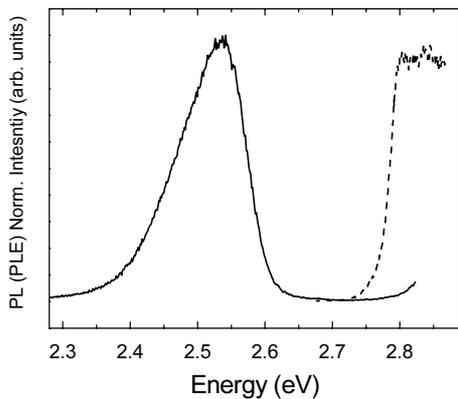


Fig. 2 The PLE spectra (dashed line) for Sample C. PL with above bandgap excitation (solid line) is also shown.

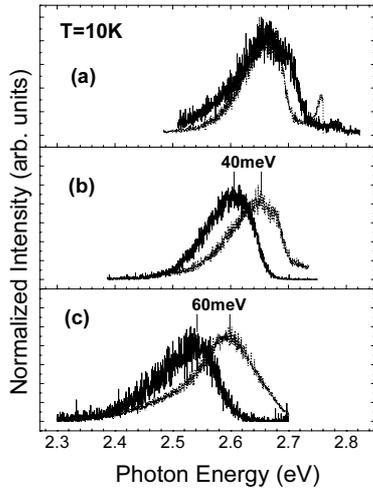


Fig. 3 Comparison of pulsed laser induced PL detected within a cw scheme (solid lines) and the cw PL (dashed lines) for (a) sample A, (b) sample B, and (c) sample C.

given in Table 1. We note that by introducing the screening energy as $E_s = e^2 / \epsilon R_s$, we can obtain R_s independently from S . Indeed, the presence of the potential fluctuation leads to the formation of localized states, which are phenomenologically described by the exponential “tailing parameter”, E_0 , which can be obtained from the absorption experiments (see e.g. Ref. [6]). Thus, one can postulate that E_s can be replaced by E_0 since both parameters increase with increasing fluctuations. We further note that at low temperatures the absorption spectra could be replaced by photoluminescence excitation (PLE) spectra, especially in the band-edge region [7]. Thus, we assume that the localization energy obtained from the PLE corresponds to the screening energy E_s . Using the definition for E_0 [6]:

$$I_{PLE} \propto \exp\left[-\frac{h\nu}{E_0}\right] \quad (3)$$

as well as the PLE spectrum shown in Fig. 2, we estimate $E_0 \approx 16$ meV, which results in $R_s \approx 100$ Å for ZnSe. Thus, combining Eqs. (1), (2), we obtain $N_A^- \approx 2 \times 10^{17}$ cm⁻³, giving the total $N_D^+ \approx 5 \times 10^{17}$ cm⁻³, which is in excellent agreement with the total donor concentration of 6×10^{17} cm⁻³ (Table 1).

4 Time-resolved photoluminescence We have used pulsed laser PL to attain several goals. First, the pulsed laser we used allow us to observe recovery of phonon replicas in sample C (not shown here), which we could not do with the cw laser (Fig. 1-(c)). Second, we have observed that the PL shifts to the red with the increasing delay time, confirming the DAP origin of the PL. Third, to further understand the role of the potential fluctuations we performed the following experiment. We have excited PL with a pulsed laser with ~ 3 ns pulse width and 20 Hz repetition rate, but have employed a cw detection scheme, using a photon counter with a gate of 0.4 s. The results are shown in Fig. 3 for all three samples (the cw PL results obtained with the lowest excitation intensity are shown for comparison). Such an experiment allows one to detect the part of an emission band that has the slowest decay. In the case of DAP PL it means the emission from the most distant pairs [8]. From Fig. 3 we see that the samples with stronger potential fluctuation show the PL peak obtained with the pulsed laser excitation at higher energies than that obtained using the cw excitation, and the energy separation increases with increasing compensation. It is important to note that such a blue shift does not arise from higher excitation intensity of the pulsed laser, since at the long times the concentration of photo-generated carriers is severely depleted, and the quasi-Fermi levels are expected to be close to those in the cw case.

To understand these data one has to remember that in the presence of the potential fluctuations, different DA pairs can emit light at the same wavelength [2]. However, the decay time of a given pair is determined, for the most part, by the distance between the donor and the acceptor, if the radiative recombination rate, W_{max} , is constant. Therefore, there will be pairs that decay very slow but emit light corresponding to the high energy side of the spectra.

In the absence of fluctuations the emitted photon energy and a pair separation are uniquely related [8] so that distant pairs emit light at longer wavelengths. Thus, if there are no potential fluctuations (or they are small), cw spectra under low excitation and the pulsed laser induced PL should coincide since both correspond to the photons emitted by the slowest (the most distant) pairs. On the other hand, in the presence of the potential fluctuations the cw detected pulsed laser induced PL should be shifted to the higher energies, since, due to “wavelength mixing” [2] some distant pairs, which contribute to the slow decay, will emit at higher energies. Obviously, the energy difference between two types of spectra would be larger in samples with the stronger fluctuations. We indeed observe such a behavior (Fig. 3).

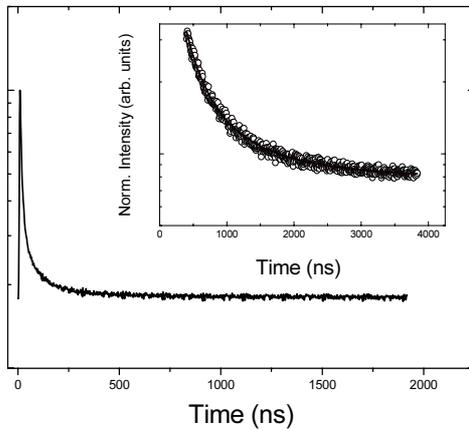


Fig. 4 Time-resolved PL from sample C. The inset shows the long times tail with the fit using Eq. (4) (solid line).

shown in the inset in Fig. 5 is obtained with the following parameters: $W_{max} = 2.74 \times 10^9 \text{ s}^{-1}$ and $(N_D - N_A)R_B^3 = 0.0098$. Taking $R_B = 36 \text{ \AA}$, we obtain the net donor concentration of $N_D - N_A = 2.1 \times 10^{17} \text{ cm}^{-3}$, which is in good agreement with that obtained from cw PL (see above) and ECV measurements (see Table 1).

4 Conclusions This work has allowed us to better understand the following issues: (1) the magnitude of fluctuations depends on the doping levels and the compensation; (2) ionized impurities “contribute” to both the recombination and the potential fluctuations; (3) the slow decay arises from the “wavelength mixing”, confirming the model given in Ref. [2]; (4) at low excitation intensities the PL peak shift as square root of logarithm of excitation intensity, confirming the model given in Ref. [4]; (6) both models (for TRPL and CW PL) are mutually consistent.

References

- [1] P. Baume, J. Gutowski, D. Wiesmann, R. Heitz, A. Hoffmann, E. Kurtz, D. Hommel, and G. Landwehr, *Appl. Phys. Lett.* **67**, 1914 (1995).
- [2] I. Kuskovsky, G. F. Neumark, V. N. Bondarev, and P. V. Pikhitsa, *Phys. Rev. Lett.* **80**, 2413 (1998).
- [3] M. Behringer, P. Baume, J. Gutowski, and D. Hommel, *Phys. Rev. B* **57**, 12869 (1998).
- [4] I. Kuskovsky, G. F. Neumark, V. N. Bondarev, and P. V. Pikhitsa, *Appl. Phys. Lett.* **75**, 1243 (1999).
- [5] If we assume that at lower excitation intensities deep donor associated with N is responsible for the PL, then in the absence of the potential fluctuations the lowest possible DAP emission energy will be 2.666eV if we take N acceptor energy of 111 meV (Dean et al., *Phys. Rev. B* **27**, 2419 (1983)) and the deep donor ionization energy of ~45 meV (Hauksson, et al., *Appl. Phys. Lett.*, **61**, 2208 (1992); Morhain, et al., **54**, 4714 (1996)). Moreover, considering that concentration of Cl donors exceeds that of the deep donor, we shall assume that only donor impurity in our material is Cl.
- [6] C. F. Klingshirn, *Semiconductor Optics* (Springer-Verlag, Berlin, 1997).
- [7] P. Y. Yu and M. Cordona, *Fundamentals of Semiconductors*, second edition (Springer-Verlag, Berlin, 1999).
- [8] D. G. Thomas, J. J. Hopfield, and W. M. Augustyniak, *Phys. Rev.* **140**, A202 (1965).
- [9] G.-J. Yi and G. F. Neumark, *Phys. Rev. B* **48**, 17043 (1993).
- [10] P. T. Landsberg and M. J. Adams, *Proc. Roy. Soc. London A* **334**, 523 (1973).

We next show the time-dependent PL obtained from the sample C which is characterized by the strongest fluctuations (Fig. 4). The decay is non-exponential and it has a very long tail as predicted for samples with strong potential fluctuations and as observed in heavily doped and compensated ZnSe:N [2]. The material parameters then can be obtained from the asymptotic formula [2] and then compared with those obtained from cw PL. Thus, we use the following expression [2]:

$$I_{PL} \sim \frac{(\ln \tilde{t})^2}{\tilde{t}} \exp \left[-0.483(N_D - N_A)R_B^3 (\ln \tilde{t})^3 \right], \quad \tilde{t} \rightarrow \infty, \quad (4)$$

where $\tilde{t} = tW_{max}$ and R_B is the Bohr radius of the shallowest impurity (Cl donor in our case). We shall define the “start” of asymptotic behavior at $t = t_0 + 500 \text{ ns}$, where t_0 corresponds to the peak of the laser pulse. Such a choice is appropriate since for ZnSe the theoretical radiative recombination rate is $W_{max} = 2.7 \times 10^9 \text{ s}^{-1}$ [9, 10]. The fit