

# Intensity-dependent energy and line shape variation of donor–acceptor-pair bands in ZnSe:N at different compensation levels

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We show that energy position and line shape of donor–acceptor-pair luminescence bands in ZnSe:N/GaAs epilayers depend very sensitively on excitation density and compensation. A continuous development from structureless red-shifted broad to well structured donor–acceptor-pair (DAP) bands is observed for increasing excitation density. The red shift is explained by the fluctuating potential affecting the bands and impurity levels and is caused by random distribution of charged impurities in highly compensated samples. The shift is reduced when these charge fluctuations are diminished due to an increasing number of impurities being neutralized via light-induced carrier excitation. These effects have not been taken into account in previous work concerning doped II-VI materials; however, they have to be considered when evaluating the frequently used hypothesis of a deep donor in ZnSe:N as an explanation of low-energy broadband DAP emission. The influence of band fluctuations on the behavior of the DAP luminescence and excitation spectra is qualitatively discussed. © 1995 American Institute of Physics.

Donor–acceptor-pair (DAP) spectra in ZnSe and related materials that are applied to blue optoelectronic devices are widely explored to gain information on type, energy, and concentration of the impurities. For the most relevant *p*-doped ZnSe:N layers, unique features were found: in lightly N-doped samples, the zero-phonon donor–acceptor-pair band peaks at 2.698 eV and is followed by a clearly resolved series of LO-phonon replicas.<sup>1</sup> Both the line shape and the transient behavior of these DAP emission bands in lightly doped samples are well described by standard DAP theory without the need to take compensation into account.<sup>2–4</sup> For more heavily doped ZnSe:N samples, the DAP band broadens and shifts towards lower energies. In highly doped layers at a nitrogen concentration [N] in the range of  $\sim 10^{18}$ – $10^{19}$  cm<sup>-3</sup>, instead of the “normal” DAP band, broad and structureless bands, and structureless bands were reported being strongly redshifted with the peak positions in the range of 2.623 up to 2.670 eV.<sup>1,5</sup> In the case of our samples, a very large shift towards 2.53 eV was observed for a layer with a nitrogen concentration of  $1.5 \times 10^{19}$  cm<sup>-3</sup> and a very low net hole concentration of  $6 \times 10^{15}$  cm<sup>-3</sup>, indicating a very high degree of compensation.<sup>5</sup>

Although broadened, these bands still originate from donor–acceptor-pair transitions as shown by the DAP-like transient behavior in time-dependent luminescence. Since the occurrence of a doubled DAP series under increasing N doping of ZnSe had been attributed to the rising density of a deeper donorlike complex,<sup>6</sup> the red shift of the broadbands

was assigned to a respective deep donor being involved in the DAP transition.<sup>7</sup> However, this interpretation cannot explain the extremely strong red shift in luminescence with decreasing excitation density. The purpose of this letter is to demonstrate that for the assignment of particular donor and acceptor species to such DAP bands, one has to take into account the influence of excitation density and level of compensation on their position and line shape, as has not been done for the II-VI materials so far. This is a well-known phenomenon that has been observed in bulk GaAs doped with different shallow impurities.<sup>8,9</sup> In these reports, the growing red shift of luminescence bands originating from DAP transitions for increasing dopant concentration and compensation level, as well as their shift back to the blue for increasing optical excitation densities, were explained in the framework of the model of fluctuating potentials in doped semiconductors introduced by Shklovskii and Efros.<sup>10</sup> To our knowledge, such effects of fluctuating potential due to local variation in the distribution of charged and neutral impurities and their influence on the behavior of the DAP emission have not been considered in the interpretation of DAP transitions in II-VI materials so far, but will be shown in the following to be of decisive importance for the explanation of the characteristics of ZnSe:N layers.

The set of seven samples investigated here was grown on GaAs substrates by molecular beam epitaxy. Their impurity content has been analyzed by SIMS, and the free carrier concentration has been determined by electrochemical CV profiling.<sup>5</sup> Figure 1 shows the DAP luminescence of a highly compensated N-doped ZnSe epilayer excited by the 441.5 nm emission of a continuous-wave HeCd laser. A strong influence of the excitation density on the shape of the DAP bands is seen even in the low-density

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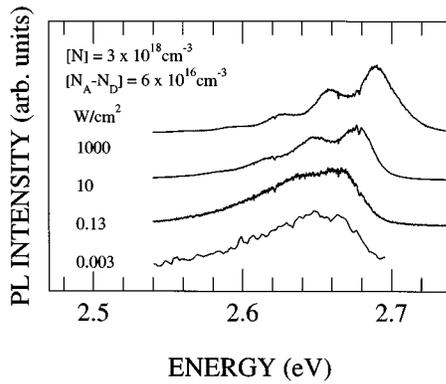


FIG. 1. Excitation-density dependence of the DAP luminescence at 2 K of a compensated ZnSe:N epilayer, excited by a HeCd laser at 441.5 nm.

limit. An increase of the excitation density from 3 mW/cm<sup>2</sup> (lowest curve) to 1 kW/cm<sup>2</sup> (uppermost curve) results in a striking but continuous change of the DAP feature from a structureless broad band into a well-structured pair band showing pronounced phonon replica. This development is accompanied by a strong blue shift of the peak by 25 meV. This change of shape cannot be caused by the evolution of a separate DAP series at higher excitation densities because it smoothly develops with increasing light density. Comparable ZnSe:N samples having a lower degree of compensation show a much smaller shift in DAP energy and well-structured pair bands even for the lowest excitation densities, whereas those samples with a higher doping level and extremely high compensation retain the structureless broadband, even for larger excitation densities. A striking confirmation of this behavior is seen in Fig. 2 for a ZnSe:N sample with  $[N_A - N_D] = 1.8 \times 10^{17} \text{ cm}^{-3}$  and high nitrogen concentration. The time-integrated luminescence after nanosecond-pulse excitation at 430 nm with 1.5 and 40 kW/cm<sup>2</sup> shows a broad DAP band peaking at about 2.62 eV and a somewhat structured band peaked at 2.690 eV, respectively (see inset). The accompanying excitation spectra (main part of Fig. 2) demonstrate a corresponding blue shift of the absorption edge with increasing excitation density.

Our interpretation is as follows: in highly compensated layers, most impurities are charged at low excitation densities, thus inducing Coulomb-potential fluctuations due to a random distribution of impurities.<sup>10</sup> They lead to spatially separated potential wells as well as to respective fluctuations of the absolute impurity level energies. The above stated red shift of the absorption edge (Fig. 2) may serve as a direct proof for this effect in unexcited samples. The situation is schematically depicted in Fig. 3. The randomly distributed band maxima and minima lead to a red shift in the absorption near the band edge as well as of the DAP emission. At lowest excitation densities, only a few donors are occupied by electrons. In this case, fast relaxation of electrons into energetically lowest-lying donor sites will occur before DAP recombination. This can be explained by the significantly larger mutual overlap of donor wave functions compared to the overlap of donor with acceptor wave functions, the latter being responsible for radiative DAP decay. Finally, DAP

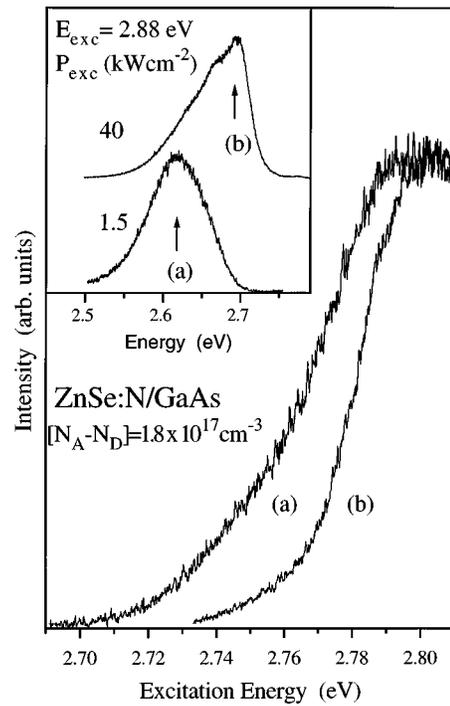


FIG. 2. Time-integrated excitation spectra of DAP luminescence (the luminescence is depicted in the inset with detection positions for excitation spectra marked by arrows) of a highly compensated ZnSe:N epilayer under nanosecond excitation with different excitation densities. For the luminescence spectra in the inset, excitation wavelength was 430 nm.

transitions from lowest donors into highest acceptors result in recombination energies being strongly red shifted (see arrows in Fig. 3) compared to the case of nonbanded bands. Additionally, a considerable Coulomb broadening of the donor-acceptor-pair luminescence occurs. Under growing excitation densities, the potential fluctuations are increasingly screened by light-induced electrons and holes, thus removing the band fluctuations. The well-known feature of the structured donor-acceptor-pair luminescence reappears.

This interpretation convincingly explains the striking dependence of the red shift of the DAP luminescence on the level of compensation, as stated in the description of experimental results, and is completely analogous to

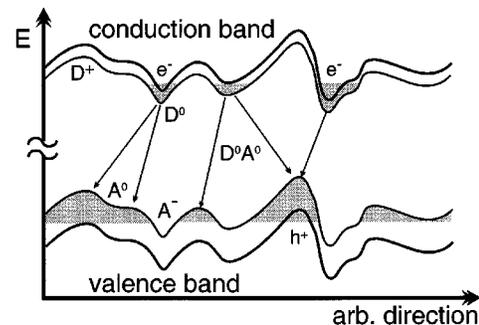


FIG. 3. Schematic plot of the fluctuating band structure in real space of a strongly doped and highly compensated semiconductor with conduction band (CB) and valence band (VB) as well as shallow impurity levels. The arrows indicate optical transitions from neutral donors to neutral acceptors, demonstrating the strong red shift of DAP emission of preferably occupied low-lying donors to high-lying acceptors.

GaAs:Li,<sup>9</sup> where the Li was taken as a suitable dopant tending to strong self-compensation. The application of this model to doped ZnSe:N also showing strong compensation effects allows one to reinterpret the data of Qiu *et al.*,<sup>1</sup> who explained the occurrence of the broadband DAP emission alone via the formation of minibands originating from impurity-level overlap. This may also play a role in the extremely heavily doped samples, but is not sufficient for the description of the behavior of samples with moderate nitrogen concentrations of less than  $10^{19}$  cm<sup>-3</sup> as observed by us. Further, it does not explain the reappearance of conventional DAP features at higher excitation levels.

In conclusion, we have applied a model involving impurity-induced potential fluctuations, introduced by Shklovskii and Efros, to explain the excitation-density dependent shape of DAP bands (Fig. 1) as well as the red shift of the absorption edge, as revealed in the DAP excitation spectra (Fig. 2). We have clearly demonstrated that the development of the line shape of the DAP emission into a broad, red-shifted band cannot be taken as proof for the formation of a new deeper donor. Instead, this broadband is due to the well-known donor-acceptor-pair emission distorted by the potential fluctuations and is strongly dependent on the particular excitation density. It most probably involves N acceptors on the Se site and the compensating or intrinsic donor. It should be noted that the effects of potential fluctuations are bound to both the degree of compensation and the total concentration of impurities.

The strong intensity-dependent blue shift of the DAP bands complicates the evaluation of the energy depths of the involved impurities from the DAP peak position at a particular excitation density. Instead, the calculation of donor and acceptor energies can only be successfully performed by a line shape analysis, taking into account the compensation level as well as the impurity and carrier densities. The lack of such a line shape analysis in previous work may be respon-

sible for the large differences in the estimation of the binding energy of any nitrogen-correlated donor complex ranging from 35 to 55 meV.<sup>5-7</sup> However, at this stage, we are not intending to make a final statement on the role of a deeper N-related donor in the described DAP luminescence. In general, the process leading to strong compensation at high nitrogen concentration in ZnSe is still not clear. Our future goal is to present a quantitative elaboration including the random potential fluctuations through charged donors and acceptors, from which reliable information about impurity energies and impurity concentrations may be obtained.

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