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.
limit. An increase of the excitation density from 3 mW/cm$^2$ (lowest curve) to 1 kW/cm$^2$ (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 broad-band, even for larger excitation densities. A striking confirmation of this behavior is seen in Fig. 2 for a ZnSe:N sample with $N_A - N_D = 1.8 \times 10^{17}$ cm$^{-3}$ and high nitrogen concentration. The time-integrated luminescence after nanosecond-pulse excitation at 430 nm with 1.5 and 40 kW/cm$^2$ 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. 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 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 nonbended 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...
GaAs:Li, 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., 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^{-3} 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 responsible for the large differences in the estimation of the binding energy of any nitrogen-correlated donor complex ranging from 35 to 55 meV. 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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