Compensation mechanisms in ZnSe:N and codoped ZnSe:N:Cl

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Codoping experiments in ZnSe with Cl and N have been performed and the photoluminescence as well as the carrier concentrations have been studied to investigate the reason for compensation in ZnSe:N. Evidence could be given that not crystalline defects but rather potential fluctuations cause the often observed redshifted and broadened donor-acceptor-pair band in compensated layers. In addition, a quantitative study on these potential fluctuations could be performed by varying the chlorine concentration in p-type doped ZnSe:N:Cl. It has been shown that a chlorine concentration of 6×10^{17} cm^{-3} in the codoped layers already causes a shift of the main donor-acceptor-pair band emission energy of about 120 meV. By investigating the photoluminescence spectra of samples with different chlorine concentrations, a relation between the amount of ionized impurities and the redshift in emission energy has been given. [S0163-1829(98)07719-4]

I. INTRODUCTION

With the demonstration of efficient p doping in ZnSe:N in 1990 (Refs. 1, 2) the physics of optoelectronic devices in II-VI semiconductors got a new incentive, which led to the realization of light emitting devices and laser diode structures.[3] In spite of lifetimes of more than 100 h for laser structures[4] p-type doping still remains a performance limiting factor,[5] especially for shorter-wavelength emission. The physics of nitrogen as a dopant has been intensively investigated [Refs. 6–8, and references therein] to understand and to expand the existing doping limits. However, it soon became apparent that above a limit of $N_A-N_D\leqslant 2\times10^{18}$ cm^{-3} (Ref. 9) additionally incorporated nitrogen does not further increase the net carrier concentration.[10] When further increasing the nitrogen concentration, the free carrier concentration first saturates and than even a reduction of the amount of free holes in the layers is observed.[11]

The transition from increasing to saturating carrier concentrations in the electrical characteristics is accompanied by a change in photoluminescence (PL) of doped ZnSe. PL investigations revealed that by incorporating nitrogen not only acceptor states are created but also donorlike complexes,[12,13] which cause the self-compensation and thus determine the doping limits in p-ZnSe. For carrier concentrations below 1×10^{17} cm^{-3} and low compensation, a clear donor-acceptor-pair (DAP) recombination band involving a shallow donor (D^S) is detected[14] with the zero-phonon emission peak at 2.687 eV. For higher doping levels, a second DAP band peak appears at a lower energy of about 2.68 eV, indicating a second, deeper donor (D^D) to be present. Both donors appear to be created in connection with nitrogen.[14] Recently it was shown that they are formed in p-type doped ZnSe even with low nitrogen concentrations.[15] It is thought to compensate the N acceptor and thus to hamper increasing doping levels. In even more highly doped, strongly compensated samples, the zero-phonon peak of the DAP is shifted to lower energies between 2.5, and 2.65 eV,[10,16,17] and the phonon replicas are no longer resolvable. With increasing excitation densities, the broadened DAP becomes structured again and is blueshifted back to an energy known from uncompensated samples.[17] This behavior could not be explained by the simple DAP theory taking only into account the effects of high excitation densities. Some authors assumed additional donor acceptor transitions or deep-level luminescence[16] and a different intensity dependence of these transitions.[18] In an alternative model potential fluctuations due to a statistical distributions of ionized impurities were considered,[17,19,20] as reported earlier for the case of GaAs:Li.[21]

To determine the total amount of nitrogen, secondary ion mass spectrometry (SIMS) measurements were performed. It was shown that the doping efficiency of the incorporated nitrogen could be less than 10%, the remaining up to 1×10^{19} cm^{-3} nitrogen atoms were either inactive or compensated.[11] As SIMS does not determine the charge state of the detected nitrogen in the layer, it is not a suitable method for investigating expected potential fluctuations caused by charged nitrogen-related impurities.

In this study, we firstly intend to clear up whether deep levels or potential fluctuations are responsible for the redshifted broadened emission energy. Proving the latter case to be valid, we secondly are interested in the concentration of impurities being necessary to cause the degree of shift in DAP emission energy observed in compensated ZnSe:N.

To achieve this, we performed codoping experiments, such as were conducted in GaAs.[22] We intentionally introduced shallow donors in nitrogen-doped ZnSe samples by codoping with $ZnCl_2$ at different concentrations and compared the corresponding PL spectra with those of highly compensated, nitrogen-doped ZnSe layers.

II. EXPERIMENTAL SETUP

ZnSe layers were prepared, exhibiting similar levels of nitrogen but different chlorine concentrations. The samples were grown in a twin chamber molecular-beam epitaxy (MBE) system EPI 930. Prior to growth, the n-GaAs substrates were etched in H_2O_2:NH_3:H_2O, and the oxide layers were removed by thermal etching in the growth chamber. The III-V chamber for GaAs buffer layer growth was equipped with cells for elementary Ga, As, and Si, the II-VI

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TABLE I. Measured carrier concentration of the investigated samples. The intended chlorine concentration in sample B was 3×10^{16} cm^{-3}.

Sample	$N_D - N_A$/cm^{-3} n-type layer	$N_A - N_D$/cm^{-3} codoped layer	$N_A - N_D$/cm^{-3} p-type layer
A	6×10^{17}	-5×10^{16}	4×10^{17}
B		3×10^{17}	
C	1×10^{17}	2×10^{17}	3×10^{17}
E	$3-4\times10^{17}$	5×10^{16}	$3-4\times10^{17}$

chamber was equipped with high-purity Se, Zn, and $ZnCl_2$. For p-type doping, radio-frequency (rf) activated nitrogen from a plasma source was used. All samples were nitrogen doped at an rf plasma power of 250 W, which leads to a free-hole concentration of about $(3-4)\times10^{17}$ cm^{-3}. The highest doping value of 6×10^{17} cm^{-3} was achieved in the system at a substrate temperature of about 290 °C and a power of $P=350$ W. The plasma power was chosen to 250 W to avoid a significant self-compensation with our growth conditions. For chlorine doping, the $ZnCl_2$ cell temperature was varied to yield chlorine concentrations between 3×10^{16} and 6×10^{17} cm^{-3}.

The samples typically consist of a triple-layer structure on top of the GaAs substrate and buffer. The first layer is purely n-type doped with chlorine, the second layer is codoped with chlorine and nitrogen, and the third layer is purely nitrogen doped. All layers had a thickness of 500 nm. For the codoped layer, the doping and growth parameters were kept identical to the conditions used for the n-type and the p-type doped layers. Growing these three layers, the chlorine concentration in the codoped layer could be determined by measuring the carrier concentration in the purely n-type layer, assuming no interdependence on chlorine and nitrogen doping. Similarly, the p-type doping could be checked by PL and capacitance-voltage (CV) measurements in the purely p-type doped top layer. Sample B was only a codoped layer with an intended chlorine concentration of 3×10^{16} cm^{-3}. The doping of the samples is summarized in Table I.

The samples were characterized in an electrochemical capacitance-voltage (ECV) profiler for determining the carrier concentrations.[23] The depth resolution was achieved by etching about 10 nm between two CV measurements. When the ECV measurement indicated that the etching completed the p-type doped layer, the measurement was interrupted and PL spectra in the underlying codoped layer were taken. Similarly, the measurement was stopped again after completely etching the codoped layer and PL measurements at the n-type doped layer were performed. Using this technique it could be ensured most easily that the above-lying layer(s) were removed before taking the PL data. The photoluminescence was taken at low temperature (1.6 K) under different excitation densities (0.1 W/cm^2 to 1 kW/cm^2) provided by a HeCd laser (441.56 nm).

III. RESULTS AND DISCUSSION

We first investigated the origin of the redshifted and broadened DAP. Therefore, the sample consisted of three layers as described above. The CV profile is depicted in the left part of Fig. 1. The y axis corresponds to the depth of the layer. The PL of the three layers at the same excitation density of 0.5 W/cm^2 is shown in the right part. The PL spectra of the layers and the corresponding measured carrier concentrations in these layers are horizontally aligned.

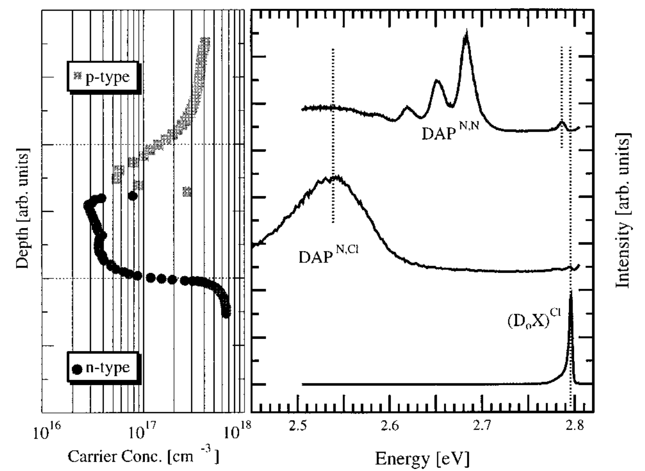

FIG. 1. CV profile and PL of a successively p-type doped, codoped, and n-type doped layer. The p-type doped layer shows the features of uncompensated samples. The codoped layer with nitrogen and 6×10^{17} cm^{-3} chlorine displays a broad and redshifted DAP emission band that is typical for a compensated sample. The n-type doped layer shows a strong donor bound exciton at 2.797 eV.

The lowest curve is typical for a chlorine-doped layer with a strong donor-bound-exciton line at about 2.797 eV. The full width at half-maximum (FWHM) amounts to 1.5 meV, i.e., this peak is broadened compared to low-doped samples. This indicates that the carrier concentration is close to the Mott density of about 4×10^{17} cm^{-3} in n-type ZnSe.[24] In the PL spectrum there is no indication of any crystalline defects or deep levels caused by the chlorine incorporation. CV profiling yielded a carrier concentration of $N_D-N_A=6\times10^{17}$ cm^{-3}. The middle curve obtained from the codoped layer shows a redshifted and broadened DAP emission band. The emission energy of the band is about 2.54 eV, and no phonon replica can be resolved. The top curve corresponds to the p-type doped layer showing a DAP band with clearly resolvable phonon replica. The zero-phonon energy is 2.683 eV and the phonon-replica spacings are about 31 meV. However, there is an underlying broadband present at about 2.5 eV which is attributed to the DAP emission from the codoped layer underneath. The origin of the signal at 2.787 eV is unclear. The energy is between the neutral-nitrogen acceptor-bound exciton at about 2.79 eV (Ref. 25) and an exciton bound to a complex at approximately 2.784 eV.[11,25] Like in the purely n-type doped layer, there is also in the purely p-type doped layer no indication for crystalline defects or deep levels caused by doping ZnSe with nitrogen. The carrier concentration of the p-type doped-layer was determined to be $N_A-N_D=4\times10^{17}$ cm^{-3}, and the codoped layer exhibited $N_D-N_A\approx5\times10^{16}$ cm^{-3}. Considering the difficulties of determining the carrier concentration at a p-n junction, this latter value corresponds fairly well with the difference between the carrier concentrations in the n-type and the p-type doped layers.

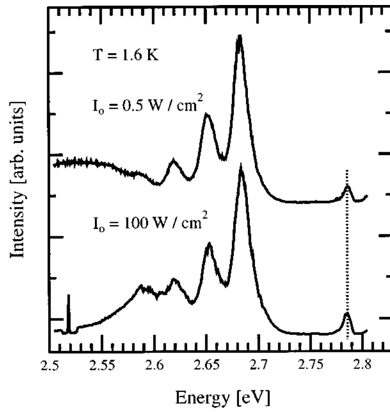

FIG. 2. DAP emission of the p-type doped layer at different excitation densities. The emission energy of the DAP shows hardly any shift. Only at energies below 2.6 eV, there is a change in the emission, originating in the underlying codoped layer.

Figure 2 shows the PL spectra of the p-type doped part of the structure at two different excitation densities. The upper spectrum was taken at an excitation density of about 0.5 W/cm^2, the lower spectrum at a density of 100 W/cm^2. The zero-phonon emission energy is almost unchanged for both excitations. This behavior was seen for almost all p-type doped samples, grown in our laboratory and is typical for uncompensated ZnSe:N layers. The signal only changes for energies below 2.6 eV. This part of the PL spectrum, however, originates from the underlying, codoped layer whose PL is depicted in Fig. 3 for excitation densities varied between 0.1 W/cm^2 and 1 kW/cm^2. The main emission peak shifts from 2.54 eV for lowest excitation to 2.66 eV at highest excitation density, but there are still no resolvable phonon replicas. These characteristics are rather similar to those observed for highly compensated nitrogen-doped samples.

It has to be pointed out that, by introducing the shallow donor chlorine with an ionization energy $E_A = 26$ meV, the DAP emission is shifted by more than 100 meV. This shift cannot be due to crystalline defects and deep-level luminescence as it is not observed in the purely p-type or n-type doped layers above and below the codoped ZnSe. As the

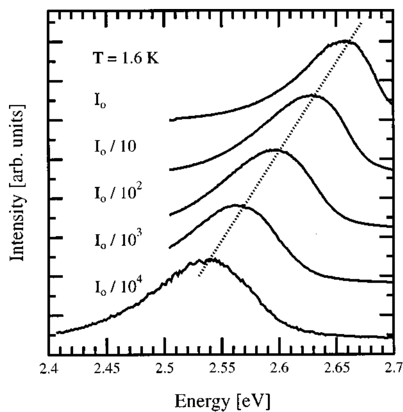

FIG. 3. DAP emission of the codoped layer at different excitation densities. The emission shifts to higher energies toward 2.66 eV with increasing excitation densities, as potential fluctuations are screened with increasing carrier generation by higher excitation densities.

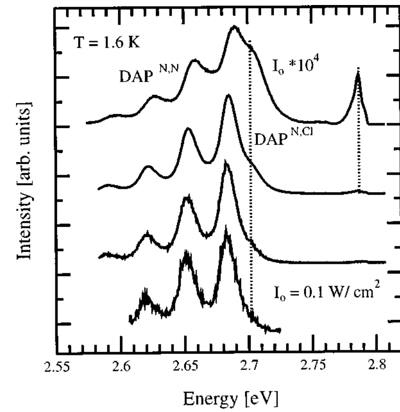

FIG. 4. PL spectra of a ZnSe:N:Cl sample. The chlorine concentration was 3×10^{16} cm^{-3} and the net carrier concentration was $N_A - N_D = 3\times10^{17}$ cm^{-3}. The DAP is hardly dependent on the excitation density and, only for highest excitation, a high-energy D^{S}AP shoulder appears at about 2.7 eV.

redshift is only observed in the layer containing both kinds of carriers, the origin of this shift must be due to the coexistence of chlorine donors and nitrogen acceptors. Both dopants compensate each other, leading to ionized charged impurities and thus causing potential fluctuations. Electron-hole recombination in such a system is redshifted and broadened. The large blueshift with increasing excitation density can be explained by screening of these potential fluctuations with increasing carrier generation at higher excitation densities.

To investigate the shift in dependence on the chlorine concentration quantitatively, the amount of chlorine was considerably reduced in sample B. The measured carrier concentration was $N_A - N_D = 3\times10^{17}$ cm^{-3}, which corresponds well to the difference of the intended doping levels for chlorine donors and nitrogen acceptors of 3×10^{16} and 4×10^{17} cm^{-3}, respectively. The PL of this sample for different excitation densities is shown in Fig. 4. For the lowest excitation density of 0.1 W/cm^2 a DAP band with several phonon replicas is clearly resolvable. The zero-phonon emission peaks at 2.682 eV indicating a transition between a deep donor level and an acceptor (D^{D}AP). With increasing excitation density there is a minor blueshift of the emission energy (about 5 meV) of the D^{D}AP transition observable that agrees well with the standard behaviour of the DAP in noncompensated samples.

At low excitation density, there is no indication of a transition between an acceptor and a shallow donor, normally seen in uncompensated samples doped so as to achieve $N_A - N_D$ below 1×10^{17} cm^{-3}, nor of the chlorine donor intentionally introduced in this system. The emission changes with increasing excitation: A shoulder develops on the high-energy side of the DAP and is clearly visible for an excitation density of 1 kW/cm^2 at about 2.705 eV. This shoulder is attributed to a D^{S}AP with the same nitrogen acceptor as in the D^{D}AP, mentioned above. The shallow donor could be nitrogen related or the chlorine donor. The appearance of only the D^{D}AP for low excitation densities can be explained by the relaxation of electrons located in energetically high-lying D^S states by hopping to energetically lower D^D states and subsequent recombination. Only for stronger excitation, when the D^D states are filled, will D^S states be considerably

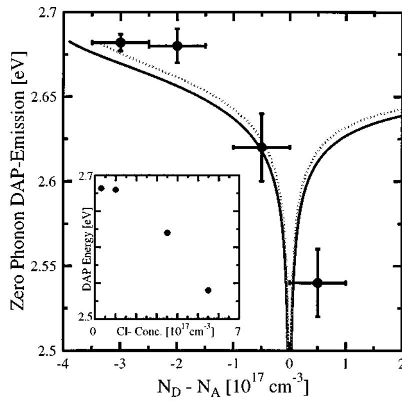

FIG. 5. Comparison of the main peak emission energy of the DAP band with the free carrier concentration. The lines correspond to calculations for acceptor concentrations of 3.5×10^{17} cm^{-3} (dashed line) and 4×10^{17} cm^{-3} (solid line). In the inset, the main peak emission is plotted in dependence on the intended chlorine concentration. Below 1×10^{17} cm^{-3}, hardly any difference from uncompensated p-ZnSe is detectable. For higher concentrations, the emission energy shifts very much to lower energies.

occupied, and thus contribute to the emission on the high-energy side of the D^DAP band.

The appearance of only the D^DAP at low excitation densities also implies that PL just gives an indication of the D^D concentration. The material could still contain a considerable amount of D^S without being detected by PL. Even if there is no D^SAP present in the spectrum, the D^S can contribute to the compensation process.

In Fig. 5, the energy of the main emission is plotted in dependence on the measured free carrier concentration in the codoped layer (see Table I). The nitrogen doping levels were identical for all samples and the PL spectra were taken at low excitation densities. The lines are theoretical calculations using a formalism developed by Morgan and stated in Refs. 26, 21, and 27, giving

$$E(\hbar\omega)\cong E_G-(E_D+E_A)-2\sigma \quad (1)$$

with

$$\sigma=\frac{e^2}{4\pi\varepsilon_0\varepsilon}\left[\frac{N_t^{2/3}}{n^{1/3}}\right].$$

Here N_t expresses the concentration of charged impurities and n the density of uncompensated carriers $|N_A-N_D|$. The dashed upper curve and the full lower line correspond to acceptor concentrations of 3.5×10^{17} and 4×10^{17} cm^{-3}, respectively. It is clearly visible that by increasing the amount of chlorine and thus reducing the amount of uncompensated N acceptors in the layers the DAP shifts to lower energies for a given excitation density. The experimental results and the theory are in qualitative agreement. The shift towards lower energies reaches a maximum for a perfect compensation of all incorporated acceptors. At that point the screening of the potential fluctuations is minimized. Due to the limited range for DAP recombination the calculated singularity will not be observed. There will be a saturation of the redshift instead. When further increasing the donor concentration beyond the acceptor concentration, the layers become n-type conductive. In the inset, the energy of emission is plotted versus the chlorine concentration. It is shown that with a chlorine concentration of about 6×10^{17} cm^{-3} the DAP is shifted by more than 120 meV. On the other hand, for chlorine concentrations below 1×10^{17} cm^{-3}, there is hardly any shift in the emission energy. This also gives un upper limit for the D^S concentration discussed above. The observed shift in codoped samples can be used to estimate the donor concentration in highly compensated layers that were doped by nitrogen only. The DAP in highly compensated samples is typically shifted by about 120 meV, leading to a donor concentration between 4×10^{17} and 6×10^{17} cm^{-3} in these layers. This indicates as well that the acceptor states are also limited to roughly the same order of magnitude.

IV. SUMMARY

In summary, we have grown ZnSe samples doped simultaneously with nitrogen and chlorine and have studied their PL spectra for various Cl concentrations. Samples slightly doped with Cl (3×10^{16} cm^{-3}) showed a clearly structured DAP band with a zero-phonon energy of 2.682 eV and a phonon replica spacing of 31 meV, as is typically seen in uncompensated ZnSe:N. More highly doped samples with chlorine concentrations above 3×10^{17} cm^{-3} displayed features typical for highly compensated p-ZnSe: the DAP emission spectra were broadened and shifted to lower energies. For chlorine concentrations of 3×10^{17} and 6×10^{17} cm^{-3} this shift was as high as 60 and 120 meV, respectively. By codoping ZnSe with chlorine and nitrogen, it could clearly be demonstrated that crystalline defects and deep levels are not responsible for the observed broadened and shifted DAP bands in compensated ZnSe:N, but rather charged ionized impurities, causing potential fluctuations within the crystal. In addition, by codoping with $ZnCl_2$ it was possible to give a precise number for the density of charged impurities in the ZnSe. It was shown that already comparably small amounts of impurities are sufficient to cause the same effects as there were observed in ZnSe:N with nitrogen concentrations above 1×10^{19} cm^{-3}. This result indicates that most of the incorporated nitrogen is active neither as an acceptor nor as a donor.

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