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Compensation processes in nitrogen doped ZnSe

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We have examined the compensation processes in nitrogen doped ZnSe grown by molecular beam epitaxy. Two independent donor–acceptor pair emission processes have been observed in photoassisted grown layers and detailed temperature dependence measurements have allowed us to conclude that a deep compensation donor with a binding energy of 44 meV exists in more heavily doped material. We propose that the compensating donor is a complex involving a native defect such as the (V_{Se}-Zn-N_{Se}) single donor and this suggestion is supported by the observation of changes in the carrier concentration profile with time.

The use of a plasma source for nitrogen doping of ZnSe by Ohkawa *et al.*[1] and Park *et al.*[2] has resulted in *p*-type material with active acceptor concentrations up to 10^{18} cm^{-3}.[3] The developments have led to the demonstration by Haase *et al.*[4] of II-VI laser diodes which operate in a pulsed mode at 77 K. However, a comparison by Qiu *et al.*[3] of the active acceptor concentration (N_A-N_D), measured by *C-V*, with the nitrogen concentration [N], as determined by secondary-ion-mass spectrometry (SIMS), shows that, typically (N_A-N_D) reaches a value of $\sim 5 \times 10^{17}$ cm^{-3} quite quickly but then saturates as compensation by donors occurs.

The use of UV radiation during growth has a dramatic effect on the growth and doping of ZnSe epitaxial layers and, in particular, it has been shown that the doping of ZnSe with iodine can be reduced by up to 20× with UV.[5] This letter reports the first examination of photoassisted nitrogen doping in ZnSe where samples were grown using a constant flux of nitrogen and a part of the ZnSe epilayer substrate was illuminated. Thus, comparisons of the doping levels and the photoluminescence could be made for the irradiated and nonirradiated regions of each epilayer.

ZnSe epitaxial layers were grown using a Vacuum Generators MBE 288 system and details are given elsewhere.[6] Nitrogen doping was carried out using an Oxford Applied Research plasma source and the photoassisted growth was carried out with UV radiation from a krypton ion laser with levels up to 4 W cm^{-2}. For these measurements a part of the layer with a diameter of approximately 5 mm was illuminated through a heated quartz window.

Figure 1 shows the PL spectra for the three regions of a ZnSe:N layer grown at 280 °C. The lowest curve (a) shows the results for the unirradiated part of the layer where the emission is characterized by two donor-acceptor pair (DAP) recombination series with zero-phonon transitions at 2.696 and 2.678 eV, each with LO phonon replicas. Electrochemical profiling of this unirradiated part of the layer showed that $(N_A-N_D) \simeq 1 \times 10^{17}$ cm^{-3}. At these doping levels the dominant DAP band is at 2.696 eV corresponding to recombination involving the shallow donor and the nitrogen acceptor.

Curve (b) in Fig. 1 shows the PL for a region of the sample on the edge of the laser irradiated region where it can be seen that the occurrence of the two DAP series is very striking. The series with zero-phonon energy of 2.678 eV has increased in intensity while the higher energy emission has decreased. Finally, at the center of the laser irradiated region it can be seen in curve (c) that the lower energy DAP transitions now dominate the spectrum. The pair spectrum corresponds to that observed by Qiu *et al.*[3] for a nitrogen level of [N]$=1.5 \times 10^{18}$ cm^{-3}. In fact, our *C-V* profiling showed a value of (N_A-N_D) of 1.5×10^{17} cm^{-3}, slightly higher than measured in the unirradiated area.

The optical and *C-V* data from these ZnSe:N layers

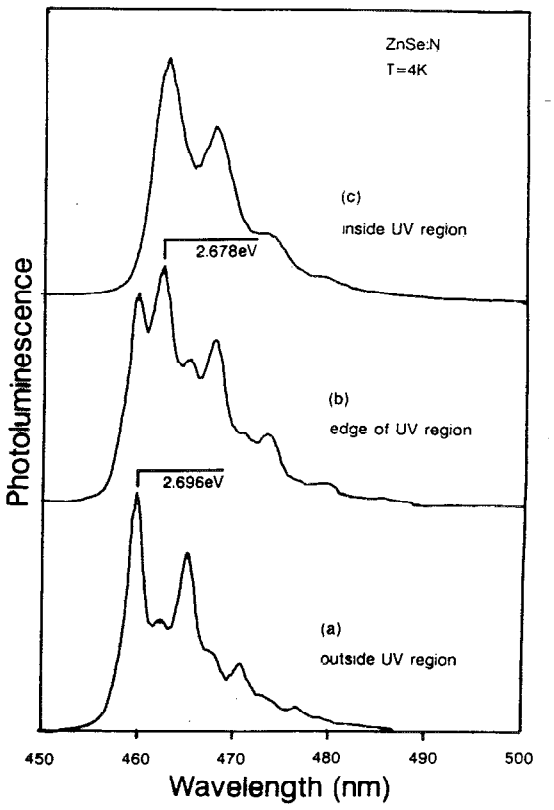

FIG. 1. Photoluminescence spectra at 4 K of ZnSe:N showing the DAP spectra from a sample grown with UV laser radiation on one section. (a) Outside the UV irradiated region, (b) On the edge of the UV region, (c) Inside the UV region.

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show that laser irradiation during growth is equivalent to increasing the nitrogen flux from the plasma source for a fixed substrate temperature and Se/Zn ratio. At 280 °C the irradiated part of the sample shows a reduction of growth rate by 30% consistent with earlier results where the growth rate is controlled by the Se incorporation; the radiation effectively changes the Se/Zn ratio to a Zn rich condition which enhances the nitrogen incorporation. We have confirmed these results by examining a series of samples with the same nitrogen flux and varying the Se:Zn ratio from 0.68:1 to 3.7:1, but without UV irradiation. The shallow donor-to-acceptor spectrum [curve (a) in Fig. 1] dominates the spectrum for Se:Zn ratios $>0.85:1$ and the deep donor–acceptor bands occur at lower ratios. Both spectra are observed near the ratio of 0.85:1.

The PL spectra clearly show that the DAP emission does not just shift to longer wavelengths as the nitrogen concentration increases as suggested by Qiu *et al.*[3] but there are two distinct DAP series shifted by 18 meV. In order to determine whether two donors or two acceptors are involved we have carried out detailed temperature dependence measurements of the DAP spectra from material with different doping levels and the results show that as the temperature is increased from 4 K the deeper DAP band reduces in intensity more slowly than the shallow pair transitions consistent with the presence of two donors, namely, the shallow residual donor and a deep-donor which we label as D^N. At temperatures around 100 K both donor-to-acceptor transitions are replaced by a single series of free electron-to-acceptor (FA) transitions with a zero phonon transition at 2.707 eV consistent with the nitrogen acceptor binding energy of 110 meV.

The exciton emission region of the spectrum changes drastically with increased nitrogen concentration as well. In the lightly doped material the emission is dominated by a sharp acceptor bound exciton due to the nitrogen but as the doping increases a second bound exciton line at 784 eV is observed and at high doping levels this transition broadens to encompass most of the exciton region. As the temperature is raised the new exciton transition reduces in intensity much more quickly than the acceptor bound exciton and the results are consistent with the second exciton emission being due to the deep donor bound exciton.

Figure 2 shows the basic model for recombination processes in nitrogen doped ZnSe. At low temperatures the shallow DAP band occurs with a no-phonon transition at 2.696 eV. As the temperature is raised, the free electron-to-acceptor (FA) transition at 2.707 eV is observed followed by, at approximately 150 K, the shallow donor-to-free hole (DF) emission at 2.689 eV. The deep DAP band has a no-phonon transition at 2.678 eV and the energy shift of 18 meV corresponds to a deep donor binding energy of 44 meV if the same coulomb energy as the shallow DAP transitions is assumed. Therefore, this value of the binding energy must be taken as a lower limit. In considering the nature of the deep donor we note that $(N_A\text{-}N_D)$ increases as the substrate temperature decreases and the deep pair band is increased with increased Zn:Se flux ratios. These results are consistent with a native defect being involved in

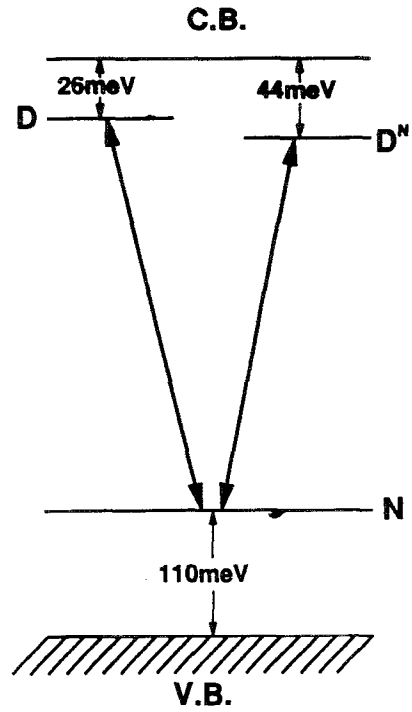

FIG. 2. Recombination model for nitrogen doped ZnSe showing the origin of the two DAP bands related to the shallow donor (26 meV) and the deep donor (44 meV). The nitrogen acceptor is labelled N.

a complex with nitrogen. We note that the vacancy V_{Se} is a double donor which is 300 meV deep[7] but the complex (V_{Se}-Zn-N_{Se}) where nitrogen and V_{Se} are in the next-nearest neighbor positions as shown in Fig. 3 is a single donor and we propose that this is the most likely candidate for the deep donor, D^N.

The involvement of a native defect such as V_{Se} in the compensation donor complex is supported by our observation that the $(N_A\text{-}N_D)$ profile through a 2 μm nitrogen doped layer has changed over a period of 4 months as shown in Fig. 4. Curve A was obtained immediately after growth using the electrochemical profiling technique which we have developed[8] and shows a constant value of 2×10^{17} cm^{-3} throughout the layer. However, after a pe-

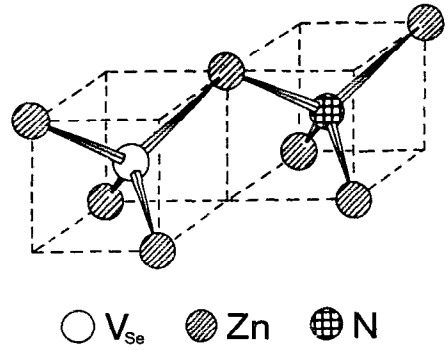

FIG. 3. Model for the deep donor complex in ZnSe:N involving the association of the V_{Se} double donor and a nitrogen acceptor.

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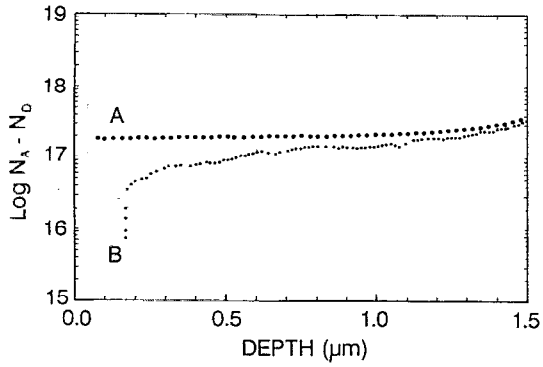

FIG. 4. Electrochemical *C-V* profile of the carrier concentrations in a ZnSe:N sample as grown (A) and after 4 months at room temperature (B) showing the formation of a surface depletion region.

riod of 4 months the profile (curve B) shows that a surface depletion layer has formed. No such changes in carrier concentration profiles have ever been observed in *n*-type material. The observed change in the *p*-doping level clearly originates from the surface and is consistent with the role of native defects in the compensation process and supports our proposed defect model since the surface is a source of V_{Se} centers which could diffuse to nitrogen acceptor centers.

In conclusion, we have observed two distinct DAP recombination processes in nitrogen doped ZnSe corresponding to shallow donors with a binding energy of 26 meV and deep donors with a binding energy of 44 meV. This deep donor we suggest is a (V_{Se}-Zn-N_{Se}) complex which is a single donor and compensates the material at high nitrogen concentrations.

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