PHYSICAL REVIEW B VOLUME 56, NUMBER 4 15 JULY 1997-II

Self-compensation in nitrogen-doped ZnSe

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(Received 10 March 1997; revised manuscript received 7 May 1997)

Nitrogen-doped and nitrogen-implanted ZnSe epitaxial layers grown by molecular-beam epitaxy are studied through photoluminescence (PL), selective PL, and PL-excitation spectroscopies. The results are compared with those obtained from samples implanted with other impurities. All N-containing samples, and only those, give rise to transitions corresponding to a dominant shallow donor with a binding energy of 29.1 meV. This donor is not a residual impurity in ZnSe but is associated with nitrogen. We propose that it involves nitrogen located on interstitial sites. In addition, the deep compensating donor is already present in lightly doped samples. Our results demonstrate that N doping of ZnSe is accompanied by the concomitant creation of N-related defects, both shallow and deep ones, from the onset of doping. An inescapable dramatic compensation of N acceptors ensues. [S0163-1829(97)51728-0]

The doping properties of wide-band-gap semiconductors are currently under focus driven by both the perspective to fabricate efficient short-wavelength optoelectronic devices and the aim to elucidate the intricate processes at work on a microscopic scale during doping and/or carrier compensation. ZnSe is a particularly enticing material in this respect since its p-type doping has been challenging for decades.[1,2] Indeed, only recently did plasma-activated nitrogen emerge as the (still) unique dopant suitable for the growth of p-type ZnSe by molecular-beam epitaxy (MBE),[3,4] which remains the only technique allowing to reproducibly grow stable p-type ZnSe films. The highest free-hole concentration reported so far is $N_a - N_d \sim 1-2\times10^{18}$ cm^{-3}.[5] N-doped layers, however, are always at least partially compensated, even at low doping levels.[6] Compensation manifests itself in the low-temperature photoluminescence (PL) spectra of ZnSe:N layers by the presence of two distinct series of donor-acceptor pair (DAP) bands.[7–9] The first series, D^{s}AP, with a zero-phonon line at about 2.70 eV arises from recombinations between a shallow donor (D^s) and the nitrogen acceptor, while the second series, D^{d}AP, with a zero-phonon line at about 2.68 eV arises from recombinations between a deep donor (D^d) and the nitrogen acceptor.[7–9]

Most studies of carrier compensation in ZnSe:N material have focused up to now on the deep compensating donor. Many theoretical models have been proposed[10–13] but experimental results agree well with a deep donor consisting of a N-related complex involving Se vacancies.[7,9,14] We have precisely determined its electronic structure and deduced a binding energy of 45.2±0.3 meV.[15] The shallow compensating donor responsible for the presence of the D^{s}AP bands in the PL spectra, on the other hand, has attracted very little attention and in the absence of detailed investigations it is commonly assumed to be a residual impurity in ZnSe.[7–9,16] Consequently, it is generally supposed that N would initially incorporate exclusively as an acceptor on Se substitutional sites, the presence of residual donors giving rise to the D^{s}AP bands in the PL spectra. Above a carrier concentration of about 10^{17} cm^{-3} N would get involved in the formation of deep compensating donors leading to D^{d}AP bands taking over in the PL spectra.[16] Eventually, all additional N atoms would generate deep donors resulting in total compensation. Recently, however, we reported that a shallow donor with a binding energy of 29.1 meV is created during N doping of ZnSe by MBE,[15] which raises serious doubts about this mechanism. Nevertheless this early study did not allow us to conclude whether this donor is a N-related defect or rather an unidentified impurity coming from plasma doping. In this paper, we discuss the N-doping properties of ZnSe epitaxial layers, which leads to a reassessment of the doping and compensation mechanisms.

We study through PL, selective PL (SPL), and PL excitation (PLE) spectroscopies N-doped and N-implanted ZnSe layers. All N-containing samples exhibit spectral signatures of a shallow donor with a binding energy of 29.1±0.1 meV. This finding is confirmed by a close inspection of spectra published by other groups. We show that this donor is N related. In addition, the presence of the deep donor is already detected at very low doping levels. Our results thus demonstrate that N doping is accompanied by the concomitant formation of compensating N-related defects, both shallow and deep ones, from the onset of doping.

The samples under investigations were grown directly onto (001) GaAs substrates by solid-source MBE. The growth temperature was 280 °C and the growth rate 1.4 Å/s. *In situ* N-doping was performed with a RFK 30 rf plasma cell purchased from Oxford Applied Research. All samples were grown under Se-rich conditions, as evidenced by the presence of the sole (2×1) reconstruction during growth. N ions were implanted in nonintentionally doped layers (residual carrier concentration $N_d - N_a \sim 5-10\times10^{14}$ cm^{-3}) with an energy of 50 keV resulting in a mean depth of about 1050 Å with a straggling of 500 Å.[17] Implanted doses are in the range from 5×10^{12} cm^{-2} to 10^{15} cm^{-2}. As implanted samples were annealed under a Zn atmosphere for 10 min at 500 °C in a vacuum-sealed ampoule. For low-temperature PL spectroscopy the samples were mounted on the cold finger of a closed-cycle He cryostat regulated at 9 K. PL was excited by the 325-nm line of a He-Cd laser and detected at the exit of a 64-cm spectrometer. SPL and PLE measure-

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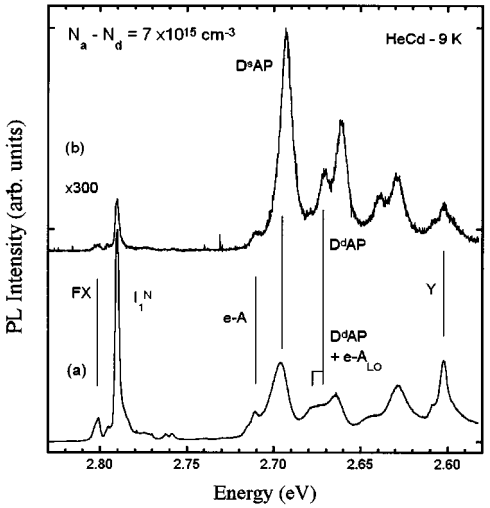

FIG. 1. Low-temperature PL spectra taken from a very lightly doped sample (EPI-548). $N_a - N_d = 7 \times 10^{15}$ cm^{-3}. Excitation conditions: 325-nm line of the He-Cd laser: (a) 5 W cm^{-2}, (b) 50 mW cm^{-2}.

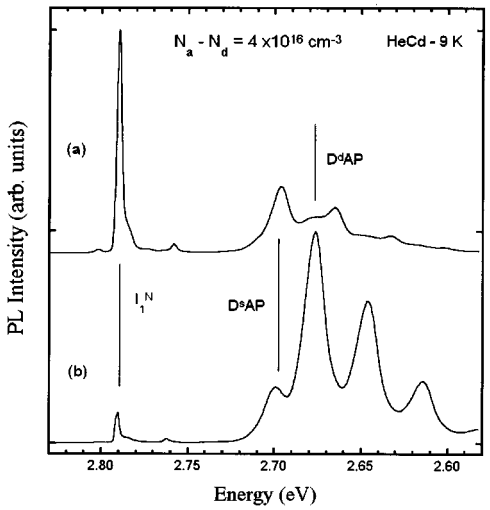

FIG. 2. Low-temperature PL spectra taken from (a) a lightly doped sample (EPI-552) and (b) a compensated sample (EPI-567). $N_a - N_d = 4 \times 10^{16}$ cm^{-3}. Excitation conditions: 325-nm line of the He-Cd laser: 5 W cm^{-2}.

ments were performed at 1.8 K in a He-bath cryostat. The samples were excited by a Stilbene-3 dye laser pumped by the UV lines of an Ar laser. PL was detected at the exit of a 1-m double spectrometer equipped with 1800 grooves/cm gratings blazed at 400 nm. In all experiments a CO_2-cooled GaAs photomultiplier was used as detector. Details on the principle of SPL and PLE techniques applied to impurity spectroscopy can be found in Ref. 15. In the following we study successively the deep- and shallow-compensating donors.

We show in Fig. 1 the low-temperature PL spectra taken from a N-doped sample under different excitation densities, namely 5 W cm^{-2} [Fig. 1(a)] and 50 mW cm^{-2} [Fig. 1(b)]. Its thickness is ~ 1 μm and its net carrier concentration measured by the capacitance-voltage technique is $N_a - N_d = 7 \times 10^{15}$ cm^{-3}. This sample is very lightly doped, as evidenced by the presence of (i) the N neutral-acceptor bound-exciton line I_1^N, (ii) the well-resolved free-exciton line EX, and (iii) the defect-related Y line. Since this line is very sensitive to sample purity,[18] its reminiscence in the PL spectra of this sample confirms its low impurity content. At high excitation density, excitonic-recombination channels are favored and the spectrum is dominated by the neutral-acceptor bound-exciton I_1^N [Fig. 1(a)]. In the DAP band region, the free electron to acceptor recombination line (e-A) and the D^sAP bands are easily identified. Note that the two-LO-phonon replica of the D^sAP band overlaps with an unidentified band near 2.63 eV that we always observe to be a companion of the Y line. Another band emerges in the 2.67–2.68 eV range. Its intensity is too high to only be the one-LO-phonon replica of e-A. When decreasing the free-electron population by reducing the excitation density the e-A band and its replica are extinguished while DAP emissions are favored. The spectrum than provides evidence for the presence of the so-called D^dAP band [Fig. 1(b)]. This figure thus reveals that the deep donor is generated into the samples as soon as N doping sets in, and not above a given carrier concentration as previously suggested.[16] We point out that our samples have been grown under Se-rich conditions which should prevent—or at least reduce—the formation of Se vacancies believed to be involved in the deep donor.[7,9,14] Indeed, we do observe that under these conditions the D^dAP bands are dramatically reduced as compared to near-stoichiometry growth. However it appears improbable to find proper growth conditions allowing to totally avoid the formation of the deep donor at low doping levels.

We now turn to the shallow compensating donor in ZnSe:N layers. For this purpose, two samples with identical net carrier concentrations ($N_a - N_d = 4 \times 10^{16}$ cm^{-3}) and thicknesses (~ 3 μm) but different impurity contents have been thoroughly characterized. Their PL spectra (taken with an excitation density of 5 W cm^{-2}) displayed in Fig. 2 reveal that sample EPI-552 is lightly doped while the other, EPI-567, is compensated but not overdoped. Note again the presence of D^dAP bands in the lightly doped sample.

We have investigated the DAP band emission by means of SPL. We obtain results qualitatively similar to our previous work performed on different samples. We thus refer the reader to Ref. 15 for details. Briefly, DAP resonances related to the dominant shallow-donor clearly appear in the SPL spectra. The striking result is that *all* these resonances agree very well with the electronic spectrum expected for a donor with a 29.1-meV binding energy and obeying the effective-mass law. In the present work, we obtain highly resolved spectra and in particular we could detect resonances in excellent agreement with excited transitions up to the $1s$-$5p$ transition.

In order to corroborate this finding we have performed complementary experiments. We show in Fig. 3 a series of SPL spectra taken from the lightly doped sample (EPI-552) by exciting from 2.8142 to 2.8170 eV, i.e., in the vicinity of the $n=2$ free exciton and of excited states of the neutral-donor–bound-exciton complex. Under such conditions, a giant enhancement of the electronic Raman scattering has been evidenced in various materials systems.[19,20] Indeed, we observe very intense resonant electronic Raman replicas allowing to identify the donors present in the sample. The replicas stemming from the common Al, Cl, In residual impurities in

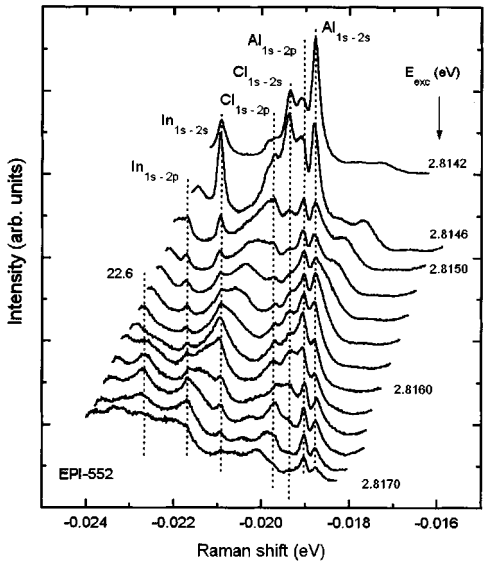

FIG. 3. Electron Raman scattering spectra taken from the lightly doped sample (EPI-552). Between 2.8170 and 2.8150 eV the excitation energy was varied in 0.2-meV steps.

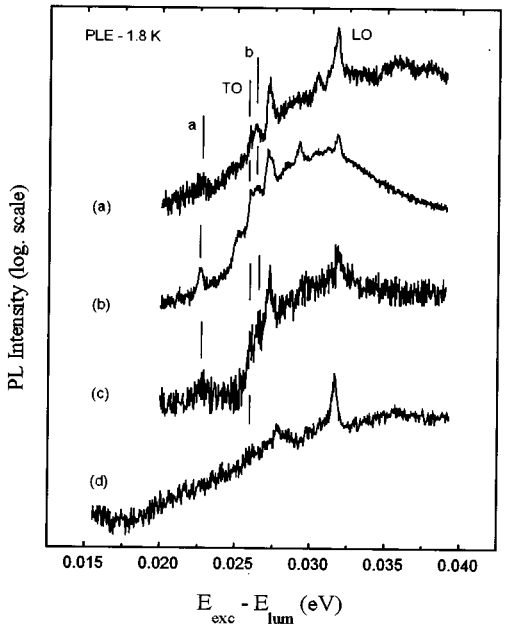

FIG. 4. PLE spectra taken from (a) the lightly doped sample (EPI-552), (b) the compensated sample (EPI-567), (c) a N-implanted sample, and (d) a P-implanted sample. Implantation doses are equal to 5×10^{12} cm^{-2}. Detection was set to 2.734 eV for (a)–(c) and to 2.744 eV for (d).

ZnSe are clearly detected (Fig. 3).[21–23] Furthermore, another resonance at 22.6 meV appears on these spectra which is well separated from the residual-donor lines and cannot be misinterpreted. This resonance does not correspond to any transition energy of any known residual donor in ZnSe and thus confirms the presence of an ''other-than-residual'' donor in the ZnSe:N samples. On the other hand, this line corresponds well to the $1s$-$2p$ transition energy of a donor with a 29.1-meV binding energy which is not detected in nonintentionally doped samples grown in our MBE system.[15] We note that a donor with a binding energy of 26.8 meV has recently been detected in ZnSe:N samples and ascribed to a N-doping related donor.[24] However, a donor with a 26.8-meV binding energy has previously been detected in ZnSe material[25,26] and attributed by Dean *et al.*[26] to residual Br impurity.

This work and Ref. 15 thus demonstrate the presence of a shallow donor with a binding energy of 29.1 meV in our ZnSe:N samples. The question of its origin remains open. Among the known impurities in ZnSe, none has been reported to have such a binding energy.[21–23] Since this donor is not present in the nonintentionally doped samples, it is introduced during N doping. We display in Fig. 4 PLE spectra taken from both samples investigated above [Figs. 4(a) and 4(b)], as well as from N-implanted [Fig. 4(c)] and P-implanted [Fig. 4(d)] samples. The crucial result is that lines *a* and *b*, corresponding to the $1s$-$2p$ and $1s$-$3p$ transitions of the shallow donor, are detected on the PLE spectra of all N-containing samples [Figs. 4(a)–4(c)], but not on the spectrum of the P-implanted sample [Fig. 4(d)]. Additional resonances between line *b* and the one-LO-phonon line are also detected. They are related to LO phonons bound either to the N acceptor or to the deep compensating donor.[15] Our results allow us to reassess similar SPL spectra which have been recently published.[27] Line *a* was ascribed to the emission of longitudinal-acoustic phonons at the Brillouin-zone boundary, and the lines between the TO-phonon and the LO-phonon peaks to local vibrational modes or phonons emitted at various points of the Brillouin zone other than the Γ point. The violation of the wave-vector conservation law was justified by a breakdown of the translational invariance which would be induced by the presence of impurities in doped samples.[27] This interpretation must be discarded since the P-implanted sample, which is surely seriously damaged, exhibits a spectrum markedly different from those of N-containing samples.[28] On the other hand we point out that we obtain the same results with heteroepitaxial, homoepitaxial, and implanted ZnSe:N layers, i.e., with all N-containing layers and only with these ones. Further, close inspection of Fig. 4 (and of SPL spectra not shown here) reveals that the higher the N content in the layer, the stronger the shallow-donor related resonances. This provides evidence for the direct correlation of the shallow-donor content with the N content. Finally, it is noteworthy that identical spectroscopic data are obtained with two different rf-plasma sources (Ref. 15 and this work) as well as with an electron-cyclotron resonance plasma source[27] which indicates that N-plasma doping of ZnSe is always accompanied by the formation of the new shallow donor. These results unambiguously demonstrate that the shallow donor is a N-related defect.

N atoms in ZnSe:N layers can sit either on Se- or Zn-substitutional sites, or on interstitial sites. Both Zn-substitutional and interstitial sites form donor levels. However, first-principle pseudopotential calculations reveal that N_{Zn} has a very high formation energy and is thus very unlikely to be generated during MBE growth.[12] On the other hand, a particular interstitial configuration, the so-called ''$\langle 100\rangle$ split interstitial'' has a low formation energy.[12] It involves a N interstitial bonded either to a Se host-atom or to a N_{Se} atom, the bond being aligned along the $\langle 100\rangle$ crystal

direction.[12,29,30] This configuration is predicted to form a shallow-donor level.[29] In addition, Na, a group-I acceptor when substituting Zn in ZnSe, has been demonstrated to readily incorporate at interstitial sites in the ZnSe matrix, giving rise to a shallow donor level.[31] Since N has a smaller covalent radius than Na, it is anticipated to be even more prone to interstitial incorporation. Finally, we have in complement characterized[32] oxygen-implanted ZnSe epitaxial layers in which we detected the presence of the O shallow-acceptor level.[33] Oxygen being isoelectronic to Se, it forms an acceptor level when located on interstitial sites.[30] This indicates that ion implantation leads to a significant incorporation on interstitial sites. Since the same shallow donor is detected in implanted and doped ZnSe:N layers, we suggest that it involves N located on interstitial sites.

In conclusion, we have presented data which lead to a reassessment of the compensation mechanisms during *p*-type doping of the ZnSe wide-band-gap material. We have confirmed that a shallow donor with a binding energy of 29.1 meV is generated during N-plasma doping of ZnSe epitaxial layers. This donor is a N-related defect and we propose that it involves N located on interstitial sites. Its concentration increases with the N content into the layers. In addition, the deep compensating donor is already present in lightly doped samples. Our results reveal that N doping of ZnSe is accompanied by the concomitant creation of N-related defects, both shallow and deep ones, from the onset of doping. An unavoidable dramatic compensation of N acceptors ensues.

We are indebted to M. Teisseire and A. Kozacki for expert help with the PLE/SPL experiments and to P. Brunet for electrical characterizations. We greatfully acknowledge J. Fontenille for sample implantations. We wish to thank N. Grandjean and M. Leroux for a critical reading of the manuscript.

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