

Photoluminescence of δ -doped ZnSe:(Te,N) grown by molecular beam epitaxy

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We have studied the low temperature photoluminescence (PL) of a δ -doped ZnSe:(Te,N) system using two different types of samples, one with single δ layers separated by undoped spacers and the other with three adjacent δ layers in each doping cycle. We have concluded that both Te and N participate in radiative recombination. We observe a relatively low PL efficiency (compared to samples without N) for these samples, and we suggest that Auger recombination is a likely mechanism, although a role of slow donor–acceptor pair PL and consequent nonradiative processes cannot be ruled out. © 2001 American Institute of Physics. [DOI: 10.1063/1.1389483]

I. INTRODUCTION

Recently, most of the efforts toward fabrication of light emitting devices has been concentrated on InGaN/GaN systems. Use of these materials led to the fabrication of short wavelength-ultraviolet and violet (390–420 nm)-laser diodes (LDs) and a wide variety (450–530 nm) of bright light emitting diodes (LEDs).¹ However, this approach has so far failed to produce long-lived LDs in the blue and green spectral regions ($\lambda \geq 450$ nm) because of very high threshold current densities required for lasing.² Besides, LEDs show a “spectral gap” in the green–yellow, i.e., between 530 and 590 nm.³ Therefore, devices based on II–VI wide band gap semiconductors (e.g., ZnSe and related alloys) are still preferred in these spectral regions, particularly as the possibility of fabricating three color emitters on one substrate has recently been demonstrated using II–VI ZnMgCdSe alloys.⁴ However, successful device fabrication, among other problems, is tempered by the lack of relatively good bipolar conductivity of these materials,⁵ by carrier induced nonradiative defect formation,⁶ and/or by defect diffusion into the active region of devices.⁷

To improve p -type doping of ZnSe based materials, the use of Te in ZnSe (e.g., ZnSe_{1-x}Te_x alloys) has been of interest, since it was expected that in addition to relatively easy n -type doping, good p -type doping could be achieved in this alloy system (ZnSe is easily doped n -type while ZnTe is easily doped p type). While little has been reported on p -type doping of ZnSe_{1-x}Te_x (see, e.g., Ref. 8), extensive studies have been done on the ZnSe/ZnTe:N superlattice (SL) system (see, e.g., Ref. 9), which is used as a contact layer in ZnSe based devices. However, while such a structure gives high hole concentrations, the stability of such contacts is not very good due to a large mismatch between the ZnSe and

ZnTe lattice constants ($\sim 7.4\%$). Specifically, the diode structures are usually relaxed, which leads to creation of dislocations, which in turn enhance nitrogen diffusion out of the contact layers.¹⁰

Jung *et al.*¹¹ have reported hole concentrations in ZnSe up to $7 \times 10^{18} \text{ cm}^{-3}$ by using a δ -doped SL of ZnSe/ZnTe:N with a reduced average Te concentration of about 9%. This results in about 0.7% lattice mismatch to ZnSe. Interestingly, this p -type doping level is significantly higher than those of uniformly N-doped ZnSe/ZnTe short period SLs and ZnSe_{1-x}Te_x alloys⁸ with a similar Te concentration (9%).

We have recently improved on this approach, using a modulation doping technique¹² that allowed us to achieve a net acceptor concentration $[N_A - N_D] \sim (4 \div 6) \times 10^{18} \text{ cm}^{-3}$ with average Te concentrations less than 3%, and as low as 0.5% in some samples. In this article we report photoluminescence (PL) studies of the role of nitrogen in this δ -doped ZnSe:(Te,N) system. We have investigated two types of samples: (1) consisting of one (Te,N) containing layer and (2) consisting of three adjacent such layers embedded into an undoped ZnSe matrix. We use the notation: δ -ZnSe:(Te,N) or “single δ doped” for the former and δ^3 -ZnSe:(Te,N) or “triple δ doped” for the latter. The details of the growth procedure have been reported elsewhere.^{12,13} Specifically, we shall show the data from two typical samples: sample A is δ -ZnSe:(Te,N) with 14 undoped ZnSe monolayers (MLs) per doped δ layer and sample B is δ^3 -ZnSe:(Te,N) with 12 undoped ZnSe MLs per doped δ^3 layer. Schematic drawings for both samples are shown in Fig. 1.

II. RESULTS AND DISCUSSION

We plot in Fig. 2(a) the 11 K PL spectra from the δ -ZnSe:(Te,N) sample. It consists of a broad PL band, which at high excitation intensity shows two maxima at 2.687 eV and at 2.656 eV, and a shoulder at 2.62–2.63 eV. (Note that the ZnTe band gap is only about 2.42 eV at low tempera-

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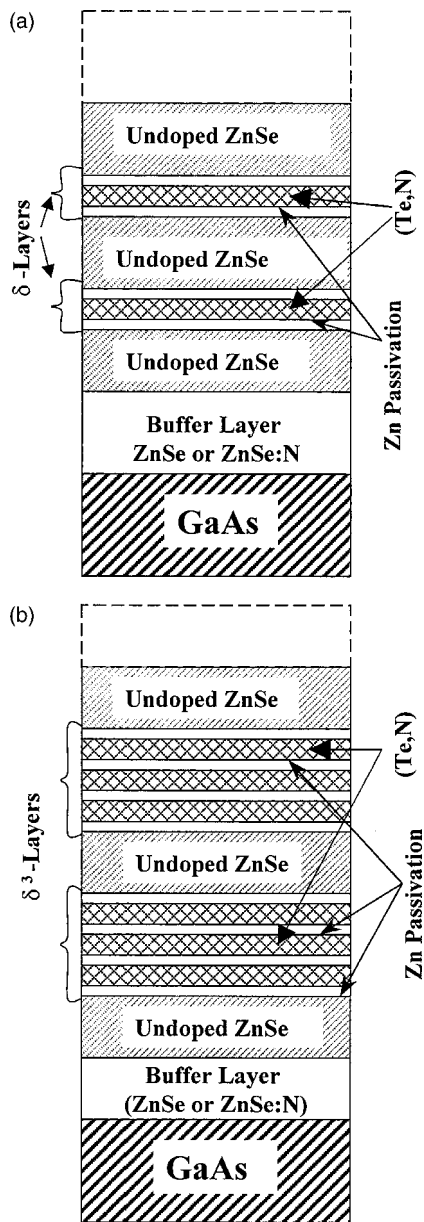


FIG. 1. Schematic representation of δ -doped samples. All layers are shown out of scale: each δ layer is less than 1 ML thick and the thickness of undoped ZnSe spacers is between 7 and 14 ML. Each δ layer is repeated many times. For exact growth sequence see Refs. 12 and 13.

tures.) Similarly, we plot in Fig. 2(b) data from a triple δ -doped sample; here there is one broad PL band with a maximum at about 2.454 eV (at high excitation intensity), which is also above the ZnTe band gap. The PL from both samples shifts to the red with decreasing excitation intensity (Fig. 2), where such shifts are usually considered a hallmark of donor-acceptor pair DAP PL (see, e.g., Ref. 14). We note that similarly grown samples without nitrogen did not show such a dependence on the excitation intensity, which is consistent with the previous assignment of this PL to excitons bound to various Te complexes.¹³

We now discuss the PL in more detail. We shall mainly discuss the PL for the single δ -doped case [Fig. 2(a)], since this PL does show some structure, whereas the triple δ -doped case [Fig. 2(b)], shows only one broad peak. For this (single

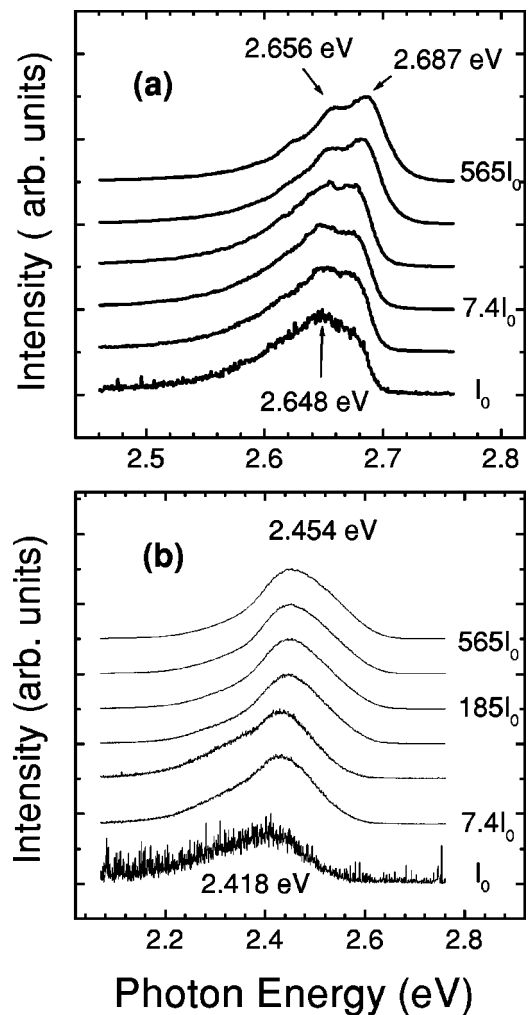


FIG. 2. Low temperature photoluminescence at different excitation intensities: (a) δ -ZnSe:(Te,N); (b) δ^3 -ZnSe:(Te,N).

δ -doped) case, it is however immediately apparent that one is not dealing with a “simple” DAP transition. Thus the lower-energy peak, at 2.656 eV at high intensity, is not just a phonon replica of the higher-energy peak at 2.687 eV, since the relative intensity of these two peaks changes with excitation intensity. It thus seems more likely that two different centers are involved in giving these two peaks. It is further worth noting that the two peaks show different shifts with intensity. The low-energy peak is at 2.648 eV at the lowest excitation intensity (where it is the dominant peak), which gives a shift of 8 meV from the lowest intensity to the highest, a change of about 2.5 orders of magnitude. It is apparent that there also is a similar intensity shift for the high energy peak; however, this shift is appreciably larger, with the peak location at about 2.674 eV at low intensity, i.e., a shift of about 13 meV over 2.5 orders of magnitude. These different shifts of course also show that the two peaks are associated with somewhat different defects.

We suggest an explanation for the above two peaks based on PL results in similar materials. First, we note that the high-energy peak, at 2.687 eV, is very close to the location of the “deep” DAP emission in ZnSe:N, with reported values of 2.683–2.686 eV, summarized for instance in Ref.

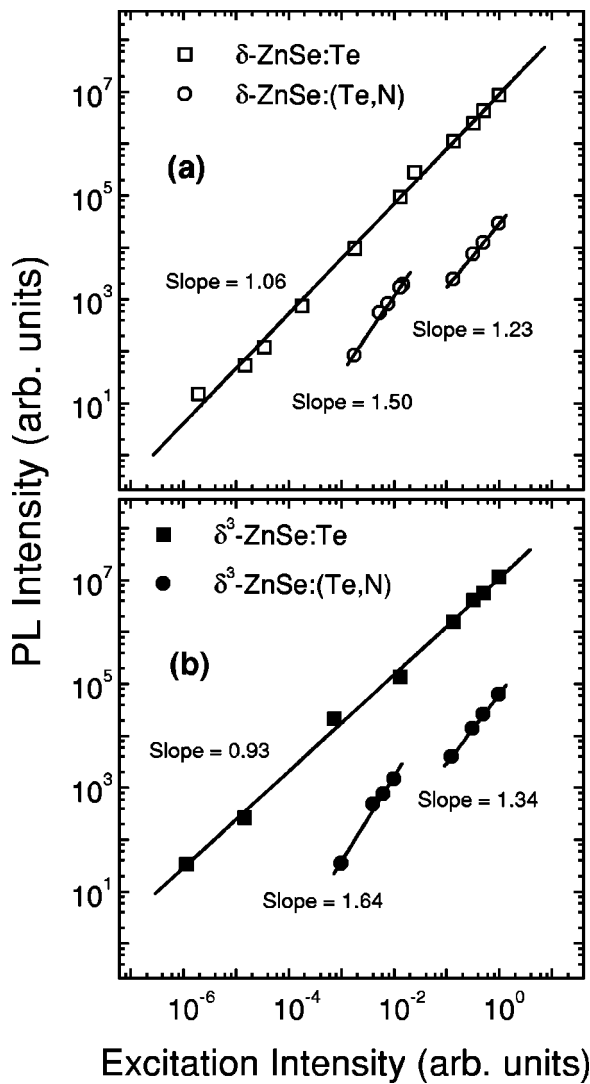


FIG. 3. Integrated PL intensity as a function of laser excitation intensity: (a) δ -ZnSe:(Te,N); (b) δ^3 -ZnSe:(Te,N); corresponding data for δ -ZnSe:Te and δ^3 -ZnSe:Te are also shown.

15. The current value is somewhat toward the high end, but the present planar-doped system is expected to have a relatively strong Coulomb shift due to preferential DAP PL,¹⁵ which would account for this. As to the low-energy peak, we note that since the LO phonon energy in ZnSe is about 31–32 meV (see, e.g., Ref. 16) the first phonon replica of the 2.687 eV peak would be at about 2.655–2.656 eV, i.e., just coincident with the 2.656 eV peak. We thus suggest that the 2.656 eV peak has an additional contribution. We can envision two possibilities. The first one is a contribution due to excitons bound to clusters and/or pairs of Te (the emission for such pairs is known to be in the 2.6–2.7 eV range¹³) and the second one is a DAP recombination which involves either an electron or a hole level of a Te_n bound exciton. We believe the first is more likely, in view of the smaller shift with intensity of the lower energy peak.

Further evidence for (at least) two centers was also obtained by plotting the integrated PL intensity versus the excitation intensity (Fig. 3), which shows two distinct slopes for each of our samples. It can be shown¹⁷ that such a de-

pendence arises if two recombination centers (i.e., recombination paths) are present in the material. (For comparison we have also plotted in Fig. 3 the integrated intensity versus excitation intensity from δ -doped ZnSe:Te samples, which have only one slope, close to unity, as expected for a single excitonic recombination.) We would like to note that the slope at low excitation intensity is quite large, which is unexpected if the transition is due to excitonic recombination alone, so that we conclude some other recombination mechanism is very likely involved. For example, if Auger recombination (see below) is present, one could account for such slopes.

It is also of interest that the PL from the δ -doped ZnSe:(Te,N) samples is substantially weaker than that from δ -doped ZnSe:Te (compare, e.g., the excitation intensities in Fig. 3). Two different effects can cause such a reduction in PL efficiencies. First, since a DAP recombination process is substantially slower than an excitonic one, carriers have more time for thermalization and nonradiative paths, which would result in a lower efficiency. Second, there may well be a strong Auger effect (see, e.g., Refs. 18 and 19) possibly due to a high concentration of free carriers at high temperatures and/or impurity band conduction at low temperatures. Alternatively, there may well be a two-center Auger effect via the filled exciton levels and holes on the N acceptors; note that because of the (Te,N) δ geometry, the two centers would, on average, be much closer to each other than in a uniformly doped system, i.e., there would be appreciable wave-function overlap.

At the end we would still like to emphasize a point that is of general importance to the PL properties of all thin-layer materials. Jung *et al.*¹¹ reported observation of a ZnSe acceptor bound excitonic PL from their ZnSe/ZnTe system. Since we did not observe such a PL, even though our material contains substantially less Te, we decided to investigate this. We noticed that the layers described in Ref. 11 were only 500 Å thick, while the thickness of our films was greater than 3000 Å. We have etched one of our samples (with an initial thickness of 3500 Å grown over a ZnSe:N buffer layer), which showed predominantly Te related PL, and have recorded the luminescence after the sample was etched first to 2500 Å and then to 1500 Å. The results are shown in Fig. 4. It is apparent that the smaller the thickness of the ZnSe:(Te,N) layer, the stronger the PL from the ZnSe:N buffer layer [note that we observed very strong PL from the buffer layer from δ -doped ZnSe:(Te,N) samples with thicknesses less than 2000 Å]. These thicknesses are in agreement with the ZnSeTe light absorption coefficient $\alpha \geq 10^5 \text{ cm}^{-1}$ ^{20,21} that has been reported for photon energies above 3.5 eV. Therefore, we have concluded that the ZnSe acceptor bound exciton PL reported in Ref. 11 is due to nitrogen diffused into the buffer layer. These data also confirm our conclusion that the 2.656 eV peak has two contributions: from excitons localized at Te clusters and from ZnSe:N related DAP. It is clear that the relative intensity of the peak that corresponds to the position of the first phonon replica and the dominant peak changes as the thickness of the top layer is reduced. Therefore, the thinner the layer, the more phonon replica like this peak becomes.

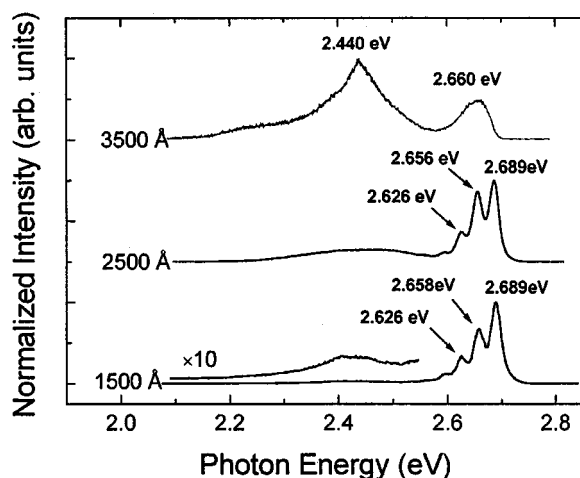


FIG. 4. Comparison of PL from a δ^3 -ZnSe:(Te,N) sample taken at different sample thicknesses.

III. SUMMARY

In summary, we have investigated δ -doped ZnSe:(Te,N) samples using low temperature PL. We have found that the presence of N results in the appearance of DAP-like recombination, which reduces the effect of excitons bound to $\text{Te}_{n>2}$ centers. Furthermore, we have found that N reduces the efficiency of the PL over that in the absence of N.

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- ¹S. Nakamura, J. Cryst. Growth **201/202**, 290 (1999).
- ²S. Nakamura, M. Senoh, S. Nagahama, N. Iwasa, T. Matsushita, and T. Mukai, Appl. Phys. Lett. **76**, 22 (2000).
- ³R. Haitz, F. Kish, J. Tsao, and J. Nelson, Compd. Semicond. **6**, 34 (2000).
- ⁴M. C. Tamargo, W. Lin, S. P. Guo, Y. Guo, Y. Luo, and Y. C. Chen, J. Cryst. Growth **214/215**, 1058 (2000).
- ⁵G. F. Neumark, Mater. Lett. **30**, 131 (1997).
- ⁶S. Itoh, K. Nakano, and A. Ishibashi, J. Cryst. Growth **214/215**, 1029 (2000).
- ⁷H. Heinke, T. Passow, M. Behringer, H. Selke, and D. Hommel, J. Cryst. Growth **214/215**, 585 (2000).
- ⁸W. Lin, B. X. Yang, S. P. Guo, A. Elmoumni, F. Fernandez, and M. C. Tamargo, Appl. Phys. Lett. **75**, 2608 (1999).
- ⁹Y. Fan, J. Han, L. He, J. Saraie, R. L. Gunshor, M. Hagerott, H. Jean, A. V. Nurmikko, G. C. Hua, and N. Otsuka, Appl. Phys. Lett. **61**, 3160 (1992).
- ¹⁰W. Faschinger, J. Nürnberger, E. Kurtz, R. Schmitt, M. Korn, K. Schüll, and M. Ehinger, Semicond. Sci. Technol. **12**, 1291 (1997).
- ¹¹H. D. Jung, C. D. Song, S. Q. Wang, K. Arai, Y. H. Wu, Z. Zhu, T. Yao, and H. Katayama-Yoshida, Appl. Phys. Lett. **70**, 1143 (1997).
- ¹²W. Lin, S. P. Guo, M. C. Tamargo, I. Kuskovsky, C. Tian, and G. F. Neumark, Appl. Phys. Lett. **76**, 2205 (2000).
- ¹³I. L. Kuskovsky, C. Tian, G. F. Neumark, J. E. Spanier, I. P. Herman, W. Lin, S. P. Guo, and M. C. Tamargo, Phys. Rev. B **63**, 155205 (2001).
- ¹⁴J. L. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1974).
- ¹⁵G. F. Neumark, L. Radomsky, and I. Kuskovsky, Proc. SPIE **2346**, 159 (1994).
- ¹⁶H. Hartman, R. Mach, and B. Selle, *Wie Gap II-VI Compounds as Electronic Materials*, in Current Topics in Materials Science, Vol. 9, edited by E. Kaldis (North-Holland, Amsterdam, 1982).
- ¹⁷V. V. Serdyuk, G. G. Chemeresyuk, and M. Terek, *Photoelectrical Processes in Semiconductors* (Vischa Shkola, Kiev-Odessa, 1982) (in Russian).
- ¹⁸P. T. Lansberg, *Recombination in Semiconductors* (Cambridge University Press, Cambridge, 1991).
- ¹⁹G. F. Neumark, Phys. Rev. B **10**, 1574 (1974).
- ²⁰S. Ozaki and S. Adachi, Jpn. J. Appl. Phys., Part 1 **32**, 2620 (1993).
- ²¹M. M. El-Nahass, B. A. Khalifa, A. M. Abd El-Rahman, and R. El-Ariny, Appl. Phys. A: Mater. Sci. Process. **63**, 81 (1996).