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Heavily p-Type Doped ZnSe and ZnBeSe

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Modulation growth techniques (δ-doping) with the use of Te and N co-doping have been investigated to enhance the p-type doping of ZnSe and ZnBeSe. The highest net acceptor concentration achieved was 6×10^{18} cm^{-3} in ZnSe and 1.5×10^{18} cm^{-3} for ZnBeSe when a triple δ-doping technique was used. The resultant layers have an average Te content of less than 3% and as low as 0.5% in some of the epilayers. We present results of C–V, I–V, and photoconductivity measurements that suggest high free carrier concentrations and low acceptor activation energy. We also discuss low temperature photoluminescence (PL) studies, which show that while the dominant PL is due to N impurities and of donor–acceptor pair type, some emission peaks related to Te_2 clusters and/or $Te_{n \geq 3}$ clusters are also present.

Introduction The best laser diode (LD) based on II–VI semiconductors works for about 500 h with the major problem being the degradation due to defect formation in the active region [1]. However, p-type doping levels [2] are also inadequate for successful device operation with one of the problems being the lack of Ohmic contacts. This results in relatively high threshold currents (the heat generated by relatively high resistivity may well contribute to the fast degradation); it has been shown that reduction of such currents increase LD lifetime [3]. The problem of Ohmic contacts is being addressed via use of a graded ZnSe/ZnTe superlattice inserted between the ZnSe:N bulk and the ZnTe:N cap layer [4]. However, these contacts are not very stable due to (i) N diffusion into ZnSe:N layer, where it forms compensating defects [5, 6], and (ii) large lattice mismatch between ZnTe and ZnSe, resulting in formation of extended defects [7]. The problem of inadequate doping of the device structure has not been addressed up to now.

In this paper we report results of δ-doping techniques in molecular beam epitaxial (MBE) growth of p-type ZnSe and ZnBeSe. Two approaches were employed [8]: single δ-doping and so-called triple δ-doping (δ^3-doping). In both cases N with Te, as co-dopant, was used. We emphasize that our samples have mole Te concentrations (0.5%–3%), which are substantially lower than the 9% Te in previously reported δ-doped ZnSe/ZnTe:N superlattices [9]. Low temperature (11 K) photoluminescence (PL), photoconductivity, I–V and electro-chemical C–V measurements were used to characterize the samples.

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Table 1
The net acceptor concentrations

samples & doping	spacer (ML)	$N_A - N_D$ (cm^{-3})	Te conc. (%)
uniform ZnSe:N	N/A	3.0×10^{17}	N/A
δ-ZnSe:N	N/A	5.6×10^{17}	N/A
δ-ZnSe:(Te,N)	10	1.5×10^{18}	~ 0.5%
δ^3-ZnSe:(Te,N)	12	4.0×10^{18}	< 3%
δ^3-ZnSe:(Te,N)	7	6.0×10^{18}	< 1.8%
uniform ZnBeSe:N	N/A	2.0×10^{17}	N/A
δ-ZnBeSe:(Te,N)	10	4.0×10^{17}	~ 0.5%
δ^3-ZnBeSe:(Te,N)	10	1.5×10^{18}	~ 0.5%

Growth, Doping and Electrical Growth was performed in a Riber 2300 molecular beam epitaxy (MBE) system. Atomic N was produced by an rf-discharge N source. All samples were grown on (001) p-type GaAs substrates and ZnBeSe samples were nearly lattice matched to GaAs (with mole Be concentration of 2.8%–2.9%). Prior to the growth of the δ-region, undoped or uniformly N-doped ZnSe was grown as a buffer layer in most of ZnSe:(Te,N) samples. For ZnBeSe, in order to avoid the formation of Ga_2Se_3 at the III–V/II–VI interface we performed Be–Zn co-irradiation before the growth of a 5 nm ZnSe buffer layer. The growth rate was about 0.8 μm/h. The shutter control sequence used during the growth is described elsewhere [8].

Only small enhancements in the net acceptor concentrations were obtained in the single δ-doped case; however, a significant increase was obtained with δ^3-doping (Table 1). We also have to add that these doping levels must be considered in the context of uniformly doped ZnSe:N, where concentrations are significantly lower (Table 1).

We studied the temperature dependence of the critical voltage ($U_{critical}$), i.e. the voltage that corresponds to the barrier height of the contacts [10] for one of the δ-ZnSe:(Te,N) samples. (We note that the improvements in the $I-V$ characteristics were reported previously [8]). In Fig. 1 we plotted $\ln[U_{critical}]$ vs. $-1/\sqrt{T}$. This shows almost a perfect straight line above 84 K, which is consistent (see e.g. Ref. [10]) with constant carrier concentration in the bulk of the semiconductor in this temperature range. This type of behavior can occur if the acceptor activation energy is low, like that of N in ZnTe. Similar results, showing carrier saturation at temperatures below 70 K, were also observed by Jung et al. [9] in δ-doped ZnSe/ZnTe:N. To further confirm high hole concentrations we

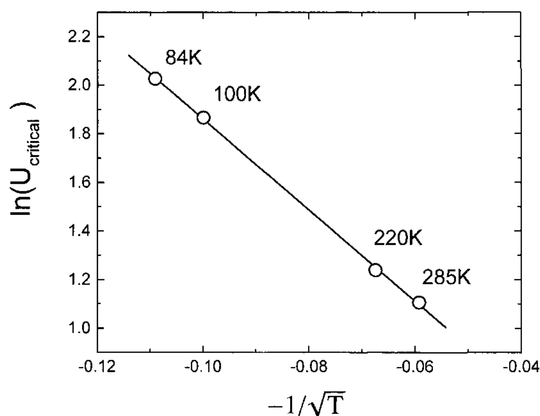

Fig. 1. $U_{critical}$ as a function of the temperature for a δ-ZnSe:(Te,N) sample

looked at the photocurrent (PC) at temperatures above 84 K. As we expected, there was no appreciable PC, which is consistent with high dark hole concentrations. We plan to check this hypothesis with Hall effect measurements.

Photoluminescence In Fig. 2 we show photoluminescence (PL) from δ-ZnSe:(Te,N) and δ-ZnBeSe:(Te,N) (both have a Te content of ≈0.5%). We first discuss the δ-ZnSe:(Te,N). We note that the peaks shift with excitation intensity, a hallmark of donor–acceptor pair (DAP) PL. We also note that the high-energy peak, at 2.687 eV, is very close to the location of the "deep" [11] DAP emission in ZnSe:N. This 2.687 eV value is slightly high, but the present δ-doped system is expected to have a relatively strong Coulomb shift due to the proximity of the relevant species [12]. Furthermore, some other peaks seem to be phonon replicas of the 2.687 eV peak, since they are separated by about 32–33 meV [13]. However, it is clear that the peak at 2.654 eV does not scale with the intensity of 2.687 eV peak, dominating at lower excitation intensities and the shift, with intensity, of the 2.654 eV peak is about half that of the 2.687 eV peak. We thus suggest that the 2.654 eV peak has an additional contribution, possibly due to excitons bound to Te clusters [14].

In the case of δ-ZnBeSe:(Te,N) there is a main peak at ≈2.775 eV with a shoulder at ≈2.746 eV; it is unclear if the low energy shoulder belongs to Te clusters. However, it seems to dominate at lower excitation intensities and does not exhibit energy shift. This is similar to the above-discussed case of δ-ZnSe:(Te,N). So we assume that Te_n related PL also contributes to the spectra from ZnBeSe samples. We also note that for δ-ZnBeSe:(Te,N) the small peak at ≈2.844 eV is still present, similarly to uniformly doped ZnBeSe:N [15].

In addition, conclusions can be reached from Fig. 3, which shows PL from δ^3-ZnSe:(Te,N) and δ^3-ZnBeSe:(Te,N). Interestingly, the PL peak at 2.661 eV in the ZnBeSe sample corresponds to the PL generally related to Te_2 clusters [14]. The δ^3-ZnBeSe:(Te,N) low energy band (2.46–2.48 eV), which dominates at low excitation intensities, most likely involves $Te_{n\geq3}$ cluster (possibly with N), and it is about 30 meV higher in energy than similar bands in ZnSe (Fig. 3a). However, the bandgap of these ZnBeSe samples is about 2.9–2.92 eV, which is 80–100 meV larger than that of ZnSe.

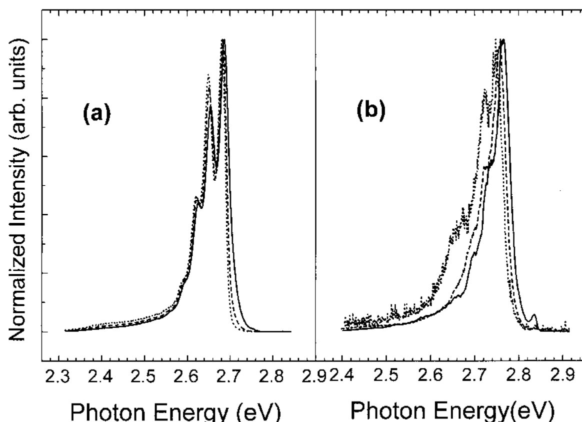

Fig. 2. Photoluminescence from a) δ-ZnSe:(Te,N) and b) δ-ZnBeSe:(Te,N); three curves are taken at different excitation intensities

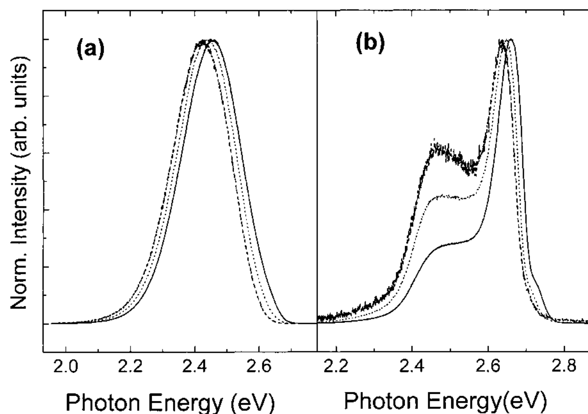

Fig. 3. Photoluminescence from a) δ^3-ZnSe:(Te,N) and b) δ^3-ZnBeSe:(Te,N); three curves are taken at different excitation intensities

Since all the samples show DAP like behavior, we conclude that N must be involved, in view of the fact that δ^3-ZnSe:Te did not show any intensity dependence [14].

Summary We have grown and studied several samples of δ-doped ZnSe and ZnBeSe which had N and Te as co-dopants. These samples show a substantial increase in the net acceptor concentrations, especially triple δ-doped samples, compared with uniformly doped ZnSe:N. PL data show that both N and Te are involved in the emission. We have obtained electrical data that suggest that free hole concentrations in such samples will be high and that the acceptor ionization energy is low.

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