

## Enhancement of *p*-type doping of ZnSe using a modified (N+Te) $\delta$ -doping technique

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Delta doping techniques have been investigated to enhance the *p*-type doping of ZnSe. Tellurium was used as a codopant for improving the nitrogen doping efficiency. The net acceptor concentration ( $N_A - N_D$ ) increased to  $1.5 \times 10^{18} \text{ cm}^{-3}$  using single  $\delta$  doping of N and Te (N+Te), while it was limited to  $8 \times 10^{17} \text{ cm}^{-3}$  by  $\delta$  doping of N alone. A promising approach was developed in which three consecutive  $\delta$ -doped layers of N+Te were deposited for each  $\delta$ -doping cycle. An enhancement in the ( $N_A - N_D$ ) level to  $6 \times 10^{18} \text{ cm}^{-3}$  has been achieved in ZnSe using this technique. The resultant layer has an average ZnTe content of only about 3%. This doping method shows potential for obtaining highly *p*-type doped ohmic contact layers without introducing significant lattice mismatch to ZnSe. Low-temperature photoluminescence spectra reveal some Te-related emissions. © 2000 American Institute of Physics. [S0003-6951(00)00816-0]

The success in *p*-type doping of ZnSe using a discharge nitrogen source has generated interest in wide band gap II–VI semiconductors for fabrication of blue-green lasers.<sup>1</sup> A net acceptor concentration ( $N_A - N_D$ ) of high  $10^{17} \text{ cm}^{-3}$  has been achieved, with rather lower free hole concentrations.<sup>2</sup> However, this *p*-type conductivity is still not sufficient for practical device applications such as the formation of ohmic contacts. It is well known that nearly all wide band gap semiconductors exhibit preference for one type of doping. For example, ZnSe can be readily doped *n* type with free electron concentration ( $n$ ) of  $3 \times 10^{20} \text{ cm}^{-3}$  and ZnTe can be highly *p*-type doped with free hole concentration ( $p$ ) of  $1 \times 10^{20} \text{ cm}^{-3}$ .<sup>3,4</sup>

To improve the *p*-type doping of ZnSe, Jung *et al.*<sup>5</sup> used delta doping with both N and Te, which gave a value of  $p$  of  $7 \times 10^{18} \text{ cm}^{-3}$ . The method they used results in the formation of a ZnSe/ZnTe:N superlattice where full atomic layers of highly N-doped ZnTe are separated by 10 monolayers (MLs) of undoped ZnSe. In that case, the average ZnTe content of the sample is about 9%, corresponding to  $\sim 0.7\%$  lattice mismatch to ZnSe. This *p*-type doping level is significantly higher than those of uniformly N-doped ZnSe/ZnTe short period superlattices<sup>6</sup> ( $p \sim 2 \times 10^{16} \text{ cm}^{-3}$ ) and ZnSeTe alloys<sup>7</sup> ( $p \sim 1 \times 10^{17} \text{ cm}^{-3}$ ) with similar Te content. The higher *p*-type doping by the method of Jung *et al.*<sup>5</sup> suggests that spatial isolation of incorporated N from ZnSe is useful for achieving high doping efficiencies.

Delta doping has been proposed to reduce complex-type defects.<sup>8–10</sup> For ZnSe:N, Zhu *et al.* have proposed that the  $N_{\text{Se}} - V_{\text{Se}}$  complex can be suppressed by  $\delta$  doping.<sup>8</sup> However, so far, ( $N_A - N_D$ )  $\sim 1 \times 10^{18} \text{ cm}^{-3}$  is the highest *p*-type doping level achieved in ZnSe by  $\delta$  doping with N alone. This suggests that other mechanisms besides complex formation may be limiting the *p*-type doping level of ZnSe:N.

In this letter, we investigate the *p*-type doping of ZnSe with N by several  $\delta$ -doping techniques. Both  $\delta$  doping of N alone and  $\delta$  doping of N with Te as codopant were employed. Only a small enhancement (up to  $1.5 \times 10^{18} \text{ cm}^{-3}$ ) was obtained by N and Te codoping. Finally, a variation of the  $\delta$ -doping sequence, in which three consecutive  $\delta$ -doping layers of N and Te were deposited [(N+Te)  $\delta^3$ -doping], was developed. By this approach, the ( $N_A - N_D$ ) level increased to  $6 \times 10^{18} \text{ cm}^{-3}$ . An average ZnTe concentration of only 3% was obtained in these samples. These results suggest the possibility of forming an ohmic contact layer for ZnSe, with a relatively small lattice mismatch, using the (N+Te)  $\delta^3$ -doping technique. Low temperature photoluminescence (PL) measurements reveal several broad emissions, deeper than the typical donor-acceptor-pair emissions of ZnSe:N, which are considered to be Te related emissions.

Growth was performed by molecular beam epitaxy (MBE). Atomic N was produced by an radio-frequency (rf)-discharge N source. All samples were grown on (001) *p*-type GaAs substrates. Prior to the growth of the  $\delta$ -doped layer, uniformly N-doped ZnSe was grown as a buffer layer. The growth rate was  $0.8 \mu\text{m/h}$ . The optimum discharge conditions for the N source, which produced a ( $N_A - N_D$ ) level of mid  $10^{17} \text{ cm}^{-3}$  in uniformly doped ZnSe:N, were used. These are an rf power of 400 W and a pure N (6N) flow corresponding to a chamber background pressure of  $8 \times 10^{-6}$  Torr. For the growth of the N  $\delta$ -doped region, the conditions were kept the same. Figure 1 shows the shutter control sequence used during  $\delta$  doping. A ZnSe undoped spacer region was first grown for  $t_{\text{ZnSe}}$  seconds and then the Se shutter was closed for  $t_{\text{Zn}}$  seconds to interrupt the growth and to produce a Zn-terminated surface. Then, all shutters were closed for  $t_{\text{all}}$  seconds to desorb excess Zn from the surface, after which the N shutter was opened to deposit N onto the Zn-terminated surface for  $t_{\text{N}}$  seconds. After another interruption time of  $t_{\text{all}}$  seconds, Zn was evaporated onto the N containing surface for  $t_{\text{Zn}}$  seconds followed by opening the

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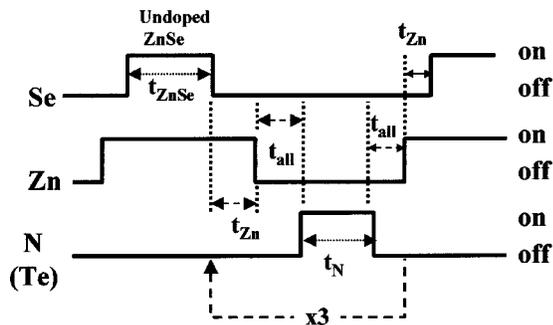


FIG. 1. Shutter control sequence of conventional  $\delta$ -doping, single (N+Te)  $\delta$ -doping, and (N+Te)  $\delta^3$ -doping techniques.

Se shutter for growth of the next undoped ZnSe spacer region. This sequence was repeated over a hundred times in order to obtain layers thick enough to perform electrical measurements. The thickness of the undoped ZnSe spacing is determined by  $t_{\text{ZnSe}}$ . Since it was reported that the deposition of N on the Se-terminated surface degrades the N-doping efficiency,<sup>11</sup> only the Zn-terminated surface was used for our experiments. The shutter control of the single (N+Te)  $\delta$ -doping technique is the same as the one above except that the Te shutter is opened and closed along with the N shutter. Various  $t_{\text{N,Te}}$  and undoped spacing thickness ( $t_{\text{ZnSe}}$ ) were employed. The results for some of the samples are listed on Table I. For these,  $t_{\text{all}}$  and  $t_{\text{Zn}}$  were kept at 5 s while  $t_{\text{N,Te}}$  and  $t_{\text{ZnSe}}$  were varied. The optimum results were obtained when  $t_{\text{Zn}} = t_{\text{all}} = t_{\text{N}} = 5$  s, while a shorter  $t_{\text{N,Te}}$  (3 s) gave less enhancement and a longer one (10 s) decreased the  $p$ -type doping. For the growth of the (N+Te)  $\delta^3$ -doped samples, the shutter control sequence was similar to that of the single (N+Te)  $\delta$ -doping sequence except that the (N+Te) codoping steps were repeated three consecutive times, as shown in Fig. 1 by the dashed arrow.

The depth-dependent ( $N_A - N_D$ ) level of each sample was determined by electrochemical capacitance–voltage ( $EC-V$ ) measurements.<sup>12</sup> PL measurements were performed at 12 K using the 325 nm line of a He–Cd laser. In order to minimize Te-related emission centers and a change in lattice constant, the lowest Te incorporation that still produces high doping levels is preferred. Thus, the beam equivalent pressure of Te used was only  $2 \times 10^{-8}$  Torr. Current–voltage ( $I-V$ ) measurements were performed between two gold dots evaporated onto the layer surface at room temperature. The Au dots were 500  $\mu\text{m}$  in diameter and 3 mm in separation and there was no postdeposition annealing.

Figure 2(a) shows the depth-dependent ( $N_A - N_D$ ) level of the conventional  $\delta$ -doped ZnSe:N. This sample contains 500 nm of a uniformly doped ZnSe buffer layer and 150  $\delta$ -doped units ( $\sim 300$  nm) where each unit contains 5 MLs of

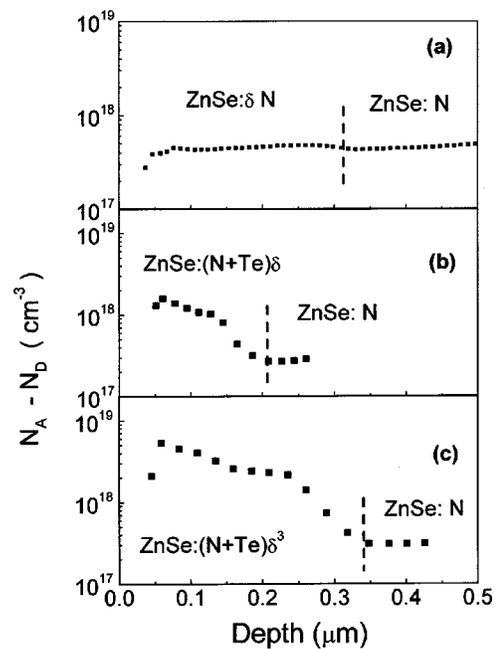


FIG. 2. Depth-dependent ( $N_A - N_D$ ) levels of a conventionally  $\delta$ -doped sample with 5 ML undoped spacer (a), a (N+Te)  $\delta$ -doped sample with 4 ML spacer (b), and a (N+Te)  $\delta^3$ -doped sample with 7 ML spacer (c).

the undoped ZnSe spacing and one N containing layer. The ( $N_A - N_D$ ) levels are nearly constant ( $\sim 5 \times 10^{17} \text{ cm}^{-3}$ ) in the  $\delta$ -doped and uniformly doped regions, suggesting that an ( $N_A - N_D$ ) level of high  $10^{17} \text{ cm}^{-3}$  could not be surpassed as previously observed.<sup>11</sup> We conclude that  $\delta$  doping with N alone does not produce any significant enhancement in the doping of highly N-doped ZnSe.

In the single (N+Te)  $\delta$ -doping, the ( $N_A - N_D$ ) level was immediately increased to  $1.5 \times 10^{18} \text{ cm}^{-3}$ . Figure 2(b) shows the depth-dependent ( $N_A - N_D$ ) level of a (N+Te)  $\delta$ -doped ZnSe sample which has 500 nm of uniformly doped ZnSe:N buffer and 120 single (N+Te)  $\delta$ -doped units ( $\sim 200$  nm) where each unit contains 4 MLs of undoped ZnSe spacer and one (N+Te) containing layer. As shown in Fig. 2(b), the ( $N_A - N_D$ ) level in the (N+Te)  $\delta$ -doped region is in the range of  $1 - 1.5 \times 10^{18} \text{ cm}^{-3}$  while in the uniformly doped ZnSe:N layer it is  $3 \times 10^{17} \text{ cm}^{-3}$ . Several undoped spacer thicknesses were used. In all of them, the ( $N_A - N_D$ ) level was less than or equal to  $1.5 \times 10^{18} \text{ cm}^{-3}$  (see Table I) suggesting that the  $p$ -type doping efficiency cannot be further enhanced by increasing the average incorporated Te and N. It should be noted that Jung *et al.*<sup>5</sup> reported significantly higher doping levels ( $p \sim 7 \times 10^{18} \text{ cm}^{-3}$ ) in their (N+Te)  $\delta$ -doped samples. In our experiments two factors differ from theirs that may explain this difference: (1) our N plasma source efficiency may be lower due to differences in the experimental details and (2) in our  $\delta$ -doping sequence we purposely deposit less Te in each  $\delta$ -doped layer than was done in Ref. 5.

In an attempt to further enhance the  $p$ -type doping, a modified technique, (N+Te)  $\delta^3$  doping, was developed. Instead of a single (N+Te)  $\delta$ -doped layer, three consecutive (N+Te)  $\delta$ -doped layers were deposited. Each set of three (N+Te)  $\delta$  layers was separated from another by several MLs of an undoped ZnSe spacer. Figure 2(c) shows the depth-dependent ( $N_A - N_D$ ) level of a (N+Te)  $\delta^3$ -doped sample.

TABLE I. ( $N_A - N_D$ ) values for several (N+Te)  $\delta$ -doped samples.

Sample	ZnSe spacer (ML)	$t_{\text{N,Te}}$ (s)	$(N_A - N_D) \times 10^{18} \text{ cm}^{-3}$		Comment
			buffer	$\delta$ -region	
A	4	5	0.3	1.5	enhanced
B	7	5	0.7	1.1	enhanced
C	14	5	0.6	1.2	enhanced
D	7	10	0.3	0.09	decreased
E	6	3	0.3	0.5	less enhanced

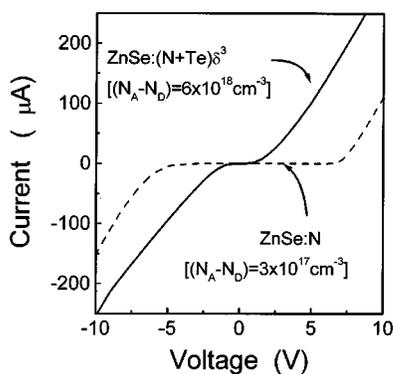


FIG. 3.  $I$ - $V$  characteristics between two Au contacts on a  $(N+Te)\delta^3$ -doped layer surface (solid curve) and on a uniformly doped ZnSe:N layer surface.

The sample contains 800 nm of uniformly doped ZnSe:N buffer layer and 120  $(N+Te)\delta^3$ -doped units ( $\sim 350$  nm) where each unit has 7 MLs of undoped ZnSe. As shown in Fig. 2(c), the  $(N_A - N_D)$  level was dramatically increased to  $3-6 \times 10^{18} \text{ cm}^{-3}$  by the  $(N+Te)\delta^3$ -doping technique while the level in the uniformly doped ZnSe:N buffer layer is  $3 \times 10^{17} \text{ cm}^{-3}$ . Another sample with 12 ML undoped ZnSe spacing for each  $(N+Te)\delta^3$ -doped unit was grown. The  $(N_A - N_D)$  level is also in the range of mid  $10^{18} \text{ cm}^{-3}$ , significantly higher than the  $1.5 \times 10^{18} \text{ cm}^{-3}$  maximum value of the single  $(N+Te)\delta$ -doped sample with 4 MLs undoped spacing. Although the average amounts of incorporated Te and N in the 12 ML- $(N+Te)\delta^3$ -doped and the 4 ML- $(N+Te)\delta$ -doped samples are expected to be equivalent (3/12:1/4), the  $p$ -type doping level is significantly increased in the  $(N+Te)\delta^3$  doped sample. It seems reasonable to assume that the higher  $p$ -type doping efficiency by the  $(N+Te)\delta^3$  doping technique originates from a more effective isolation of substitutional N by the Te atoms, which results in a reduction of compensating centers or in increased solubility.<sup>13</sup> The average Te content of the  $(N+Te)\delta^3$  sample is about 3% obtained from the measured lattice mismatch of 0.28% to ZnSe, assuming Vegard's law (in contrast with 9% Te in Ref. 5).

PL spectra at 12 K of our  $(N+Te)\delta^3$ -doped samples show broad emission bands at about 2.65 and 2.43 eV. Similar peaks have previously been attributed to emissions associated with Te centers.<sup>14</sup> Jung *et al.*<sup>5</sup> have reported that their highly  $\delta$ -doped (100 nm thick) ZnSe/ZnTe:N layers have 14 K PL spectra showing only bandedge emission at 2.792 eV. To understand the discrepancy between our results and theirs, the  $(N+Te)\delta^3$ -doped region in our sample was etched down to 150 nm in thickness. Once our sample was thinned, the broad Te-related emissions were suppressed and a donor-acceptor pair (DAP) emission with longitudinal-optical (LO) replicas from the ZnSe:N buffer layer became dominant. We propose that the PL spectrum of Ref. 5 originates from the ZnSe buffer layer rather than from the  $\delta$ -doped region which is only 100 nm thick, and that a thicker layer is needed for accurate PL measurements of the top  $(N+Te)\delta$ -doped layers.

Figure 3 shows the contact-to-contact  $I$ - $V$  characteristics of the sample in Fig. 2(c) (solid curve) and that of a uniformly doped ZnSe:N  $[(N_A - N_D) = 3 \times 10^{17} \text{ cm}^{-3}$ ,

dashed curve]. The solid curve exhibits a nearly ohmic behavior while the dashed one shows a nonohmic  $I$ - $V$  curve typical of uniformly doped ZnSe:N. This improvement of the  $I$ - $V$  characteristics is consistent with the increase of the  $p$ -type doping level. Thus, the  $(N+Te)\delta^3$ -doping technique has potential for achieving a highly doped  $p$ -type contact layer for ZnSe-based devices with only a small lattice mismatch to ZnSe. This is a large improvement over the ZnSe/ZnTe graded superlattice contact layer typically used in blue-green laser diodes, which introduces defects due to the presence of a very large lattice mismatch.<sup>15</sup>

In conclusion, increased  $p$ -type doping levels, up to  $6 \times 10^{18} \text{ cm}^{-3}$ , were achieved by a  $(N+Te)\delta^3$ -doping method in which three consecutive  $\delta$ -doped layers of N plus Te were deposited, separated by undoped spacer layers of ZnSe. The resultant  $p$ -type layer has an average ZnTe content of only 3%. These  $p$  doping levels are comparable to the highest reported values, which were achieved in samples where a monolayer of ZnTe was introduced for each  $\delta$ -doped period. The latter method results in 9% average ZnTe content and a significant lattice mismatch to ZnSe. Nearly ohmic contacts were achieved by nonannealed Au dots evaporated onto the layers. Thus, the  $(N+Te)\delta^3$ -doping technique has potential for achieving a highly  $p$ -type doped contact layer for ZnSe-based devices with only a small lattice mismatch to ZnSe. This approach may be applicable to other wide band gap materials where high doping levels are often difficult to achieve.

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