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Highly Conductive p-type ZnSe Formation Using Li₃N Diffusion

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We have achieved a highly doped p-type ZnSe layer using Li₃N diffusion. The hole concentrations of the ZnSe:(Li, N) layers, grown on a GaAs substrate by metalorganic vapor phase epitaxy, are in the order of high 10¹⁷ cm⁻³. The averaged hole concentration \bar{p} of the p-type layer formed at the diffusion temperature of 470°C is as high as 1×10^{18} cm⁻³, with resistivity ρ =0.3 Ω ·cm and hole mobility μ_p =18 cm²/V·s. We made an ohmic contact to p-type ZnSe layer using the Li₃N-diffused ZnSe as a contact layer for the first time.

Recently, room temperature cw operation in ZnSe based laser diodes (LDs) have been demonstrated with the help of a high p-type conductivity control by molecular beam epitaxy (MBE).¹⁾ However, a difficulty in p-type doping still remains as a long standing problem in the fabrication of ZnSe based LDs by metalorganic vapor phase epitaxy (MOVPE).²⁾ A current issue in successful development of II-VI laser devices is to make a low resistance ohmic contact to p-type Zn(S)Se. Some techniques to achieve an ohmic contact to p-type ZnSe were reported.³⁾ However, most of them employed rather complicated multi-layer structures.

In this letter, we report a new approach for making a highly doped p-type ZnSe layer and solving the ohmic contact problem to p-type ZnSe. We employed Li_3N diffusion to an ZnSe layer, which is expected to act as shallow acceptors by forming Li_{Zn} and N_{Se} , respectively.

Two different layers, an undoped ZnSe and a nitrogen-doped ZnSe layer, were grown at the substrate temperature of 470° C on a (001) GaAs substrate by metalorganic vapor phase epitaxy (MOVPE). The diffusion of Li₃N was carried out in the vacuum sealed tube at 350 - 570°C for 30min. We studied the effect of the diffusion temperature on the optical and electrical properties of the samples using photoluminesence (PL), Hall effect and current-voltage (I-V) measurements.

Figure 1 shows PL spectra at 35K for an undoped ZnSe and Li₃N-diffused epilayers at 470 and 570°C. The PL spectrum of the undoped ZnSe layer exhibits a neutral donor bound exiton line (I₂) with a free exiton line (E_x). After Li₃N diffusion at 470°C, a neutral acceptor bound line (I₁) is clearly observed while I₂ line disappeares. The PL spectrum is dominated by the donor-acceptor pair (DAP) emission with phonon replica. This result indicates that high concentration of Li and N efficiently substitute for Zn and Se site as shallow acceptors in ZnSe. At diffusion temperature higher than 470°C, only a broad DAP emission peak is observed. We conclude from these results that the doping efficiency depends on the Li₃N diffusion temperature.

The electrical properties of Li₃N-diffused ZnSe epilayers were investigated at room temperature by means of I-V characteristics and Hall effect measurements. The I-V characteristic, measured between Au contacts on a Li₃N-diffused ZnSe, appears to be perfectly ohmic. Figure 2

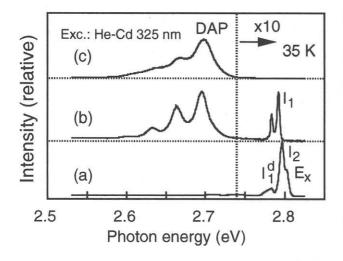
shows the dependence of the averaged free-hole concentration \bar{p} on the diffusion temperature. At diffusion temperature higher than 430°C, the hole concentrations and the hole mobilities of the p-type layers are in the order of 10¹⁷ cm⁻³ and 10 cm²/V·cm, respectively. The hole concentration increases as the diffusion temperature is increased. At 470°C, the diffusion of Li₃N on a nitrogen-doped ZnSe layer produces a highly conductive p-type ZnSe with the averaged hole concentration \bar{p} of 1x10¹⁸ cm⁻³, as shown in fig. 2 (b). This result is higher than the highest value reported for p-type ZnSe obtained by MBE. However, when the diffusion temperature is increased over 470°C, the hole concentration decreases to $6x10^{17}$ cm⁻³. The decrease of hole concentration at the high temperature is due to the self-compensation caused by extremely high doping of Li and N.

In conclusion, we demonstrate, for the first time, that Li_3N diffsion process can make a good ohmic contact to MOVPE-grown ZnSe. Hall measurement at room temperature reveals that a hole concentration and a resistivity of the ZnSe layer with Li_3N diffusion at 470°C are $1x10^{18}$ cm⁻³ and 0.3 Ω -cm. These values are comparable to those for the best quality nitrogen doped ZnSe layer obtained by MBE. Our experiments indicate that the Li_3N diffusion is effective to solve the ohmic contact problem for MOVPE-grown p-type ZnSe without any complicated material processing.

1) M. A. Haase, J. Qiu, J. M. DePuydt and H. Cheng: Appl. Phys. Lett. 59 (1991) 1272.

2) T. Yasuda, I Mitsuishi and H. Kukimoto: Appl. Phys. Lett. 52 (1988) 57.

 F. Hiei, M. Ikeda, M. Ozawa, T. Miyajima, A. Ishibashi and K. Akimoto: Electron. Lett. 29 (1993) 878.



- Fig. 1. PL spectra at 35K for a) undoped ZnSe, b) ZnSe diffused at 470°C and
 - c) ZnSe diffused at 570°C.

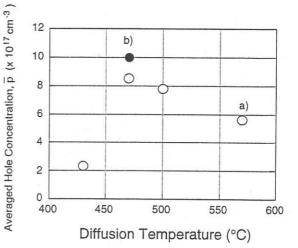


Fig. 2. Averaged hole concentration at room temperature vs diffusion temperature. The wafers used are a) as-grown undoped ZnSe and b) as-grown nitrogen-doped ZnSe.