Extended Abstracts of the 1993 International Conference on Solid State Devices and Materials, Makuhari, 1993, pp. 757-759

# Realization of High-Concentration p-Type Layers in Zn-Doped InAlP by Substrate Misorientation

## Mariko Suzuki, Kazuhiko Itaya, and Masaki Okajima

Research and Development Center, Toshiba Corporation, 1 Komukai Toshiba-cho, Saiwai-ku, Kawasaki 210, Japan

High-concentration p-type layers were achieved in Zn-doped InAlP alloys grown by metalorganic chemical vapor deposition (MOCVD) with off-axis substrate. The highest net acceptor concentration  $(N_A-N_D=1.3X10^{18} \text{ cm}^{-3})$ , obtained with the off-axis substrate, was one order of magnitude higher than the previous maximum. The electrical resistivity reached down to 0.68  $\Omega$ ·cm. It was found that substrate misorientation improves not only Zn incorporation efficiency but also Zn electrical activity. Furthermore the high device performance was obtained for the laser diodes (LDs) and the LEDs fabricated with this Zn-doped InAlP as a p-cladding layer.

### 1. Introduction

InGaAlP alloys are widely used for visible-region LDs and LEDs. Use of InAlP alloys, which have the widest band-gap energy of all members of the InGaAlP system, is desirable as the cladding layers to achieve short wavelengths and high-power operation. Low resistivity and high carrier concentration are the most desirable characteristics for these p-type cladding layers. However it is difficult to fabricate p-type InAlP layers with high concentration. Mg and Zn are the widely used p-type dopants in metalorganic chemical vapor deposition (MOCVD), and though high acceptor concentrations  $(1X10^{18} \text{ cm}^{-3})$  have been obtained in Mg-doped InAlP layer<sup>1)</sup>, Mg is known to be difficult as regards achieving a sharp doping profile at the layer interface<sup>2)</sup>. On the other hand, the maximum acceptor concentration in Zn-doped InAlP has been limited to 2X1017  $cm^{-3}$  <sup>(1)</sup>, since the Zn incorporation efficiency was saturated at a low level and Zn electrical activity was low.

In this study, we have investigated the Zn doping characteristics and the electrical characteristics of InAlP with a nominal (100) substrate and an off-axis substrate (a (100) substrate tilted 15° off towards [011]). The maximum net acceptor concentration obtained in this study  $(1.3X10^{18} \text{ cm}^{-3})$ , obtained with the off-axis substrate, was one order of magnitude higher than the previous one  $(2X10^{17} \text{ cm}^{-3})$ . The activation energy of Zn acceptor was from 58 to meV in the InAlP layer with maximum net acceptor concentration. It has been demonstrated that substrate misorientation improves not only Zn

incorporation efficiency, as shown for  $In_{0.5}(Ga_{1-x}Al_x)_{0.5}P$  (x≤0.7)4,5), but also Zn electrical activity in InAlP.

2. Experiment

The materials investigated here were grown by low-pressure MOCVD, using trimeth-(TMI), trimethylgallium ylindium (TMG), trimethylaluminum (TMA), PH3, and AsH3. Alkoxy-reduced TMA was employed to reduce oxygen incorporation<sup>6</sup>). The dopant source was dimethylzinc (DMZ). Epitaxial layers were grown in a reaction chamber with a total pressure of 25 Torr and a growth rate of 3 µm/h. The substrate temperature, TS, and the V/III ratio were varied from 650°C to 730°C and from 225 to 900, respectively. A 1.0-µm GaAs layer and 0.5-µm undoped InAlP layer were grown as buffer layers, prior to forming of a 2.5-µm Zn-doped InAlP layer on the GaAs substrate. The substrates were cut at 0° and 15° off the (100) plane toward the [011] direction. An n-type cap layer was grown on the Zn-doped InAlP layer to avoid hydrogen passivation<sup>7</sup>). The undoped InAlP was n-type (4.0X10<sup>16</sup> cm<sup>-3</sup>), independent of the growth condition in this study.

Capacitance-voltage (C-V) measurements were carried out to determine the net acceptor concentration  $(N_A-N_D)$ . Secondary-ion mass spectroscopy (SIMS) was used to investigate the Zn concentration  $(N_{Zn})$  and the residual oxygen concentration. Electrical resistivity ( $\rho$ ), mobility ( $\mu$ ), and carrier concentration (p) were determined by employing Van der Pauw-Hall effect measurements. 3. Results and discussion

3.1 Zn doping characteristics

Figure 1 shows NZn and NA-ND as a function of the DMZ mole fraction divided by the total mole fraction of group III. sources ([DMZ]/III) in InAlP for both types of substrate. the NZn increased with increasing [DMZ]/[III] for both types of substrate. The Zn incorporation efficiency in InAlP with off-axis substrate four was times greater than that with (100)substrate almost independent of [DMZ]/[III]. The NA-ND increased with increasing [DMZ]/[III] for both types of substrate and it rapidly decreased at low [DMZ]/[III] for (100)substrate.

Both the  $N_{\rm Zn}$  and the  $N_{\rm A}-N_{\rm D}$  increased with decreasing  $T_{\rm S}$  for both types of sub-

strate as shown in Fig.2. The  $N_A-N_D$  was tended to saturate at about  $1X10^{18}$  cm<sup>-3</sup> with off-axis substrate and it rapidly decreased with increasing the substrate temperature.

Figure 3 shows the Zn electrical activity ( $\eta$ ; ratio of N<sub>A</sub>-N<sub>D</sub> to N<sub>Zn</sub>) as a function of  $N_{Zn}$ . It is thought that the lowering of  $\eta$  at low N<sub>Zn</sub> is mainly due to relatively high concentration of the background donor. V/III ratio did not strongly influence on the NZn for both types of substrate. The 7 was higher with the off-axis substrate than with the (100) substrate at same level of Also, higher V/III ratio introthe N<sub>Zn</sub>. duced the higher  $\eta$  at same level of N<sub>Zn</sub>. The oxygen concentration of samples A, B, C and D is shown in table 1. It is found that the residual oxygen concentration, N<sub>O</sub>, in Zn-doped InAlP was reduced and  $\eta$  increased both by using off-axis substrate and by



Fig.1. Zn concentration and net acceptor concentration versus [DMZ]/[III]. Substrate temperature and V/III ratio were 730°C and 450, respectively.



Fig. 2. Zn concentration and net acceptor concentration versus substrate temperature. [DMZ]/[III] and V/III ratio were 0.30 and 450, respectively.

increasing V/III from the results of table 1. It is thought that these lowering of  $\gamma$ is caused by the compensation of Zn acceptor by residual oxygen. It was found that residual oxygen cases the low electrical activity of Zn as well as the low luminescence efficiency in InGaAlp<sup>8</sup>). These results show that the substrate misorientation improves not only the Zn incorporation efficiency but also the Zn electrical activity in Zn-doped InAlP.



Fig. 3 Zn electrical activity versus Zn concentration.  $T_S$  was 730°C. V/III ratio was 450 except for sample D. V/III was 900 for sample D.

| Sample | No (cm <sup>-3</sup> ) | η    | V/III Ratio | N <sub>zn</sub> (cm <sup>-3</sup> ) | Substrate   |
|--------|------------------------|------|-------------|-------------------------------------|-------------|
| А      | 1.4×10 <sup>17</sup>   | 0.67 | 450         | 7.2×10 <sup>17</sup>                | off-axis    |
| В      | 2.6×10 <sup>17</sup>   | 0.47 | 450         | 7.2×10 <sup>17</sup>                | (100) exact |
| С      | 2.6×10 <sup>17</sup>   | 0.05 | 450         | 2.2×10 <sup>17</sup>                | (100) exact |
| D      | 9.8×10 <sup>16</sup>   | 0.41 | 900         | 2.2×10 <sup>17</sup>                | (100) exact |

Table 1. Oxygen concentration  $N_{\rm O} versus$  net acceptor concentration  $N_{\rm A}-N_{\rm D}$  and Zn electrical activity  $\gamma$ , for both types of substrate.  $N_{\rm O}$  was determined by SIMS measurements.

### 3.2 Electrical characteristics

Figure 4 shows some electrical properties (A, M, P) of Zn-doped InAlP at 300K. The p was nearly consistent with ND-NA. The  $\mu$  was somewhat low (~12cm<sup>2</sup>/V·sec) and it almost independent of the p. This value of the µ for InAlP is nearly same The activation energy of Zn acceptor, determined by temperature dependence of the carrier concentration, decreased from 76 to 58 meV, as the net acceptor concentration at 300 K increased from 1.0X10<sup>17</sup>cm<sup>-3</sup> to 1.3X10<sup>18</sup>cm<sup>-3</sup>. The electrical resistivity decreased linearly with increasing p, and it reached down to 0.68 Q.cm. The distinction of the electrical properties between the samples with two types of substrate was not clear in this study.

# 3.3 Device performance using InAlP cladding layers

The LD with InAlP cladding layer



Fig. 4 Electrical resistivity and Hall mobility versus carrier concentration in both Zn-doped InAlP with a (100) substrate and with an off-axis substrate at 300 K.

 $(p=1.0X10^{18}cm^{-3})$  showed low threshold CW operation in 640nm band. Also, it was confirmed that the external quantum efficiency was 1.5 times higher in the LED (565nm) with InAlP cladding layer (6.0X10<sup>17</sup>cm<sup>-3</sup>) than in the LED with InGaAlP (x=0.7) cladding layer.

### 4. Summary

High concentration p-type layers ( $N_A$ - $N_D$ =1.3X10<sup>18</sup> cm<sup>-3</sup>) were achieved for Zn-doped InAlP by using the (100) substrate 15° off toward [011]. It was found that the substrate misorientation improves both Zn incorporation efficiency and Zn electrical activity. The results of this study indicate the high performance in InGaAlP light emitting devices with InAlP cladding layers.

# Acknowledgment

The authors would like to thank H. Sugawara and Y. Nishikawa for fruitful discussion. They also thank G. Hatakoshi, Y. Uematsu and M. Azuma for their encouragement throughout this work.

#### References

C. 1)Y.Ohba, Nishikawa, Nozaki, н. Y. Sugawara and T. Nakanisi; J. Cryst. Growth 93(1988)613. 2)Y. Nishikawa, H. Sugawara and Y. Kokubun; J. Cryst. Growth 119(1992)292. 3)Y. Nishikawa, Y. Tsuburai, C. Nozaki, Y. Ohba and Y. Kokubun; Appl. Phys. Lett. 53(1988)2182. 4)S. Minagawa and M. Kondow; Electron. Lett. 25(1989)413. 5)M.Suzuki, Y. Nishikawa, M. Ishikawa and Y. Kokubun; J.Cryst. Growth 113(1991)127. 6)Y. Nishikawa, M. Suzuki, M. Ishikawa and Y. Kokubun; J. Cryst. Growth 123(1992)181. 7)M. Ishikawa, M. Suzuki, Y. Nishikawa, K. Itaya, G. Hatakoshi, Y. Kokubun and Y. Uematsu; in :Proc. 16th Intern. Symp. on GaAs and Related Compounds, Karuizawa, 1989, Inst. Phys. Conf. Ser. 106(1990)575. 8)M. Suzuki, K. Itaya, Y. Nishikawa, H. Sugawara and M. Okajima; to be published in J. Cryst. Growth.