Effects of Growth Parameters on Oxygen Incorporation into InGaAlP Grown by Metalorganic Chemical Vapor Deposition

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Oxygen incorporation into In$_{0.5}$(Ga$_{1-x}$Al$_x$)$_{0.5}$P grown by metalorganic chemical vapor deposition has been quantitatively investigated as a function of growth parameters. The oxygen concentration (N$_O$) increased with increasing Al composition (x). An remarkable decrease in N$_O$ for x=0.7 and 1.0 was observed as the V/III ratio was increased, although N$_O$ for x=0.7 was almost unrelated to the substrate temperature. Since N$_O$ for x=1.0 was strongly affected by the amount of oxygen-containing species in trimethylaluminum (TMA), the origin of the oxygen in InGaAlP is thought to be TMA. Zn electrical activity decreased with increasing N$_O$. Oxygen may act as a deep donor, compensating for Zn acceptors.

1. Introduction
Oxygen incorporation has been a serious problem in the growth of Al-containing layers by metalorganic chemical vapor deposition (MOCVD), since Al reacts vigorously with oxygen to form strong bonds. Degradation of the optical and electrical properties of GaAlAs due to oxygen has been reported[1-3]. Deep levels relating to oxygen have been found in GaAs[4,5] and Ga$_{0.5}$Al$_{0.5}$As[6]. Recently, the oxygen concentration in GaAlAs has been determined as a function of the growth parameters[7].

The InGaAlP quaternary alloy has been investigated extensively used in the fabrication of visible-light-emitting devices. Since InGaAlP layers with a high Al composition are usually used in device applications, their electrical properties may be affected by the existence of oxygen. However, there have been no reports of residual oxygen incorporation into InGaAlP. We present here the first report on quantitative oxygen incorporation into InGaAlP in terms of growth parameters. The origin of the oxygen and the electrical compensation of Zn acceptors by oxygen are also investigated.

2. Experiments
Undoped and Zn-doped In$_{0.5}$(Ga$_{1-x}$Al$_x$)$_{0.5}$P layers were prepared by low-pressure MOCVD, using methyl precursors and PH$_3$. The dopant source was dimethylzinc (DMZ). The growth parameters of Al composition (x), V/III ratio (molar flow rate ratio of group-V to group-III sources), and substrate temperature ($T_S$) were varied. The total pressure was 25 Torr and the growth rate was about 3µm/h.

In order to examine the origin of the oxygen, two kinds of trimethylaluminum (TMA) containing different amounts of alkoxysuch as -OCH$_3$ were used for InAlP growth. Since TMA is an alkyl which is highly reactive with oxygen, it is considered to be a likely source of oxygen.

The oxygen concentration (N$_O$) and Zn concentration (N$_{Zn}$) were examined by secondary ion mass spectroscopy (SIMS). SIMS measurements were carried out with a high sputter rate under high vacuum conditions in order to improve the background detection limits. These concentrations were calibrated using ion-implanted samples. Capacitance-voltage (C-V) measurements were used to determine the net acceptor concentration (N$_A$-N$_p$) in Zn-doped InGaAlP. Zn electrical activity (η) was calculated as η=(N$_A$-N$_p$)/N$_{Zn}$.

3. Results and discussion
3.1 Effects of growth parameters
Open circles in Fig.1 show the dependence of N$_O$ on x in undoped In$_{0.5}$(Ga$_{1-x}$Al$_x$)$_{0.5}$P grown by using standard TMA. The V/III ratio was 450 and $T_S$ was 730°C. N$_O$ for x<0.4 was almost constant (1.5×10$^{17}$/cm$^3$), which is close to the detection limit for oxygen in SIMS measurements (1×10$^{17}$/cm$^3$). N$_O$ rapidly increased for x>0.4. N$_O$ in InAlP was one order of magnitude higher than that for x<0.4. Since Al oxide is nonvolatile at ordinary growth temperatures[1,3,8], oxygen incorporation may increase in InGaAlP with higher Al composi-
Fig. 1 Oxygen concentration \( N_0 \) vs. Al composition \( x \) in \( \text{In}_{0.5}(\text{Ga}_{1-x}\text{Al}_x)_{0.5}\text{P} \). The V/III ratio was 450 and \( T_s \) was 730°C. The black dot indicates InAlP grown by using reduced alkoxyn TMA.

The dependence \( \text{Ga}_1-\text{Al}_x\text{As} \) on \( N_0 \) in GaAlAs increased superlinearly with \( x \). The dependence of \( N_0 \) on Al composition in InGaAlP is somewhat different from that in GaAlAs.

Figure 2 shows the relationship between the V/III ratio and \( N_0 \) for \( x=0.7 \) and 1.0. \( T_s \) was 730°C. Remarkable decreases in \( N_0 \) for both \( x=0.7 \) and 1.0 were observed as the V/III ratio increased. \( N_0 \) in InAlP for V/III=800 was more than ten times lower than that for V/III=200. It can be seen that high V/III ratios drastically reduce oxygen incorporation into InGaAlP. A decrease in \( N_0 \) with increasing V/III ratio was also observed in \( \text{Ga}_{0.3}\text{Al}_{0.7}\text{As} \). This result suggests the possibility that \( \text{PH}_3 \) and/or decomposition products of \( \text{PH}_3 \) such as -PH and -PH\(_2\), may react with oxygen-containing species either in the vapor phase or on the growth surface, resulting in decreased oxygen incorporation into the InGaAlP.

The dependence of \( N_0 \) on \( T_s \) for \( x=0.7 \) is shown in Fig. 3. \( T_s \) was varied between 650°C and 750°C. The V/III ratio was kept at 450. \( N_0 \) decreased slightly with increasing \( T_s \). Unlike the V/III ratio, \( T_s \) has little influence on oxygen incorporation into InGaAlP.

3.2 Origin of the oxygen

As described above, oxygen incorporation into InGaAlP is affected by the growth parameters. Primary sources of oxygen are considered to be gases such as \( \text{H}_2 \) and \( \text{AsH}_3 \) in GaAlAs growth\(^9\). Since highly purified \( \text{H}_2 \) and \( \text{PH}_3 \) are used for InGaAlP growth, however we believe the source of oxygen to be the metalorganic precursors, especially TMA. TMA is highly reactive with oxygen. InAlP was grown by using two kinds of TMA. The reduced alkoxyn TMA is considered to contain less alkoxyn, such as -OCH\(_3\), than the standard TMA. As shown in Fig. 1, \( N_0 \) in InAlP grown by TMA with reduced alkoxyn was a factor of five lower than in that grown by standard TMA. This result demonstrates that most of the oxygen comes from TMA.

3.3 Electrical compensation of Zn acceptors

Incorporated oxygen may influence the electrical properties of InGaAlP layers. We examined the relationship between \( N_0 \) and Zn electrical activity by varying the V/III ratio.

Figure 4 shows the net acceptor concentration as a function of the V/III ratio for
The net acceptor concentration \((N_a - N_p)\) vs. V/III ratio for \(x=0\), 0.7 and 1.0. The DMZ introduction \([(DMZ)/(III)]\) was maintained at a constant value of 0.74. \(T_S\) was 730°C. Net acceptor concentrations for \(x=0\) and 1.0 decreased with decreasing the V/III ratio, while that for \(x=0\) was unchanged. Zn concentrations \((N_{Zn})\) measured by SIMS did not change with the V/III ratio. Thus, the decrease in net acceptor concentration for \(x=0\) and 1.0 was due to the decrease in Zn electrical activity. The fall in net acceptor concentration with decreasing V/III ratio seems to correlate with the increase in \(N_0\) as shown in Figs. 2 and 4.

The dependence of Zn electrical activity on \(N_0\) for \(x=0\) and 1.0 is shown in Fig. 5. \(N_{Zn}\) was about 6x10^17 cm^-3 for all samples. With increasing \(N_0\), the Zn electrical activity decreased evenly independent of \(x\). It is thought that oxygen in the InGaAlP forms a deep donor level as in the case of GaAlAs.

4. Summary

The effects of the growth parameters of Al composition \((x)\), V/III ratio and \(T_S\), on oxygen incorporation into InGaAlP grown by low-pressure MOCVD have been quantitatively investigated for the first time. \(N_0\) in InGaAlP increased with \(x\). \(N_0\) in InAlP was one order of magnitude higher than that for \(x=0.4\). A remarkable decrease in \(N_0\) for \(x=0.7\) and 1.0 was observed as the V/III ratio increased, although \(N_0\) for \(x=0.7\) was almost independent of \(T_S\). Increasing the V/III ratio was found to be an effective way of reducing \(N_0\) instead of increasing of \(T_S\). The major source of the oxygen was considered to be TMA. The Zn electrical activity for \(x=0.7\) and 1.0 decreased with increasing \(N_0\). Oxygen in InGaAlP may act as a deep donor, compensating for Zn acceptors.

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References