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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 $In_{0.5}(Ga_{1-x}Al_x)_{0.5}$ 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 alkoxy such 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_D) in Zn-doped InGaAlP. Zn electrical activity (η) was calculated as $\eta=(N_A-N_D)/N_{Zn}$.

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 $x\leq0.4$ was almost constant ($1.5X10^{17}cm^{-3}$), which is close to the detection limit for oxygen in SIMS measurements ($1X10^{17}cm^{-3}$). N_O rapidly increased for x>0.4. N_O in InAlP was one order of magnitude higher than that for $x\leq0.4$. Since Al-oxide is nonvolatile at ordinary growth temperatures[1,3,8], oxygen incorporation may increase in InGaAlP with higher Al composi-

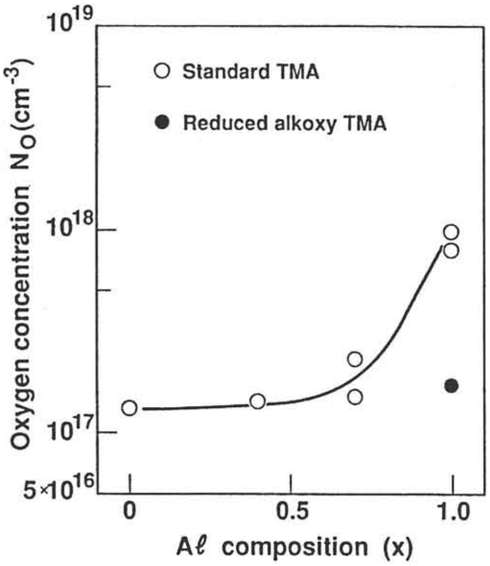

Fig.1 Oxygen concentration (N_O) vs. Al composition (x) in $In_{0.5}(Ga_{1-x}Al_x)_{0.5}P$. The V/III ratio was 450 and T_S was 730°C. The black dot indicates InAlP grown by using reduced alkoxy TMA.

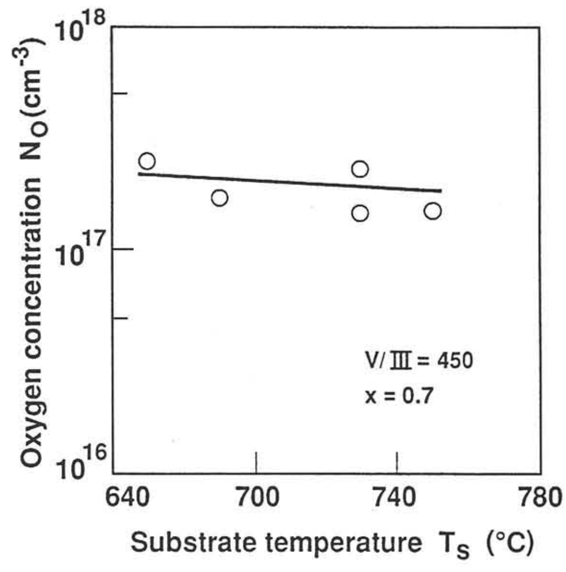

Fig.3. Oxygen concentration (N_O) vs. substrate temperature (T_S) for x=0.7. The V/III ratio was 450.

tion. Keuch[7)] reported that N_O in $Ga_{1-x}Al_xAs$ increased superlinearly with x. The dependence of N_O on Al composition in InGaAlP is somewhat different from that in GaAlAs.

Figure 2 shows the relationship between the V/III ratio and N_O for x=0.7 and 1.0. T_S was 730°C. Remarkable decreases in N_O for both x=0.7 and 1.0 were observed as the V/III ratio increased. N_O 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_O with increasing V/III ratio was also observed in $Ga_{0.3}Al_{0.7}As$[3)]. This result suggests the possibility that PH_3 and/or

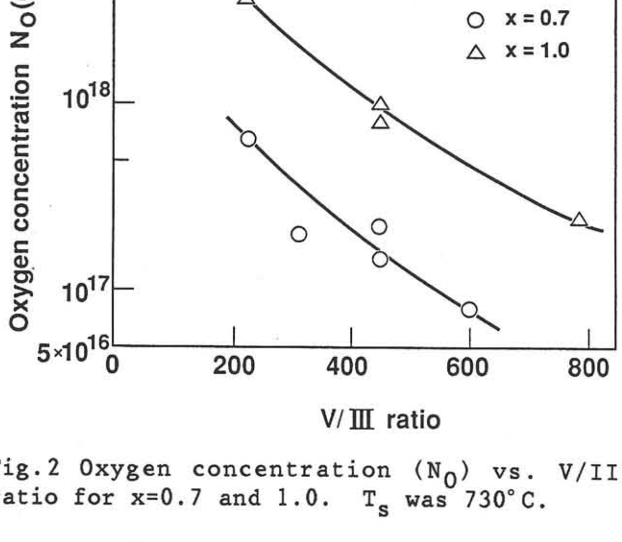

Fig.2 Oxygen concentration (N_O) vs. V/III ratio for x=0.7 and 1.0. T_s was 730°C.

decomposition products of 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_O 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_O 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 H_2 and AsH_3 in GaAlAs growth[3)]. Since highly purified H_2 and 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 alkoxy TMA is considered to contain less alkoxy, such as $-OCH_3$, than the standard TMA. As shown in Fig.1, N_O in InAlP grown by TMA with reduced alkoxy 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_O 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

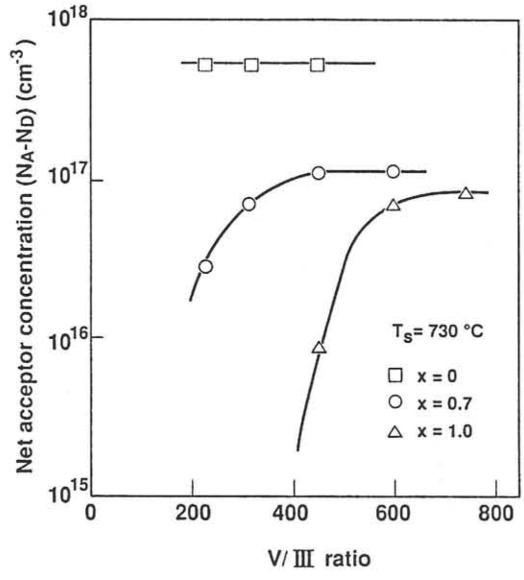

Fig.4 Net acceptor concentration (N_A-N_D) vs. V/III ratio for x=0, 0.7 and 1.0. T_S was 730°C and DMZ introduction ([DMZ]/[III]) was kept at 0.74.

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=0.7 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[9]. Thus, the decrease in net acceptor concentration for x=0.7 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_O as shown in Figs.2 and 4.

The dependence of Zn electrical activity on N_O for x=0.7 and 1.0 is shown in Fig.5. N_{Zn} was about $6X10^{17}cm^{-3}$ for all samples. With increasing N_O, 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[4-6]. The oxygen-related donors in InGaAlP may then compensate for Zn acceptors, so the Zn electrical activity may decrease with increasing N_O. Not only is the low Zn electrical activity in Zn-doped InGaAlP explained by oxygen compensation, but it is found that oxygen greatly affect Zn electrical activity. We have detected deep donor levels in InGaAlP using DLTS measurements. The relationship between oxygen and the deep donor levels will be clarified in a separate paper.

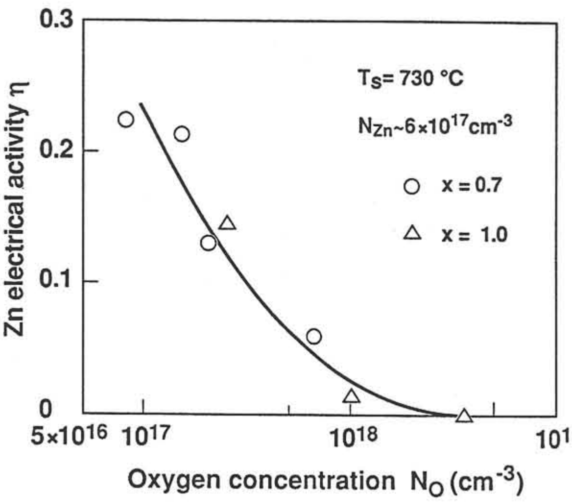

Fig.5 Zn electrical activity vs. oxygen concentration (N_O) for x=0.7 and 1.0. T_S was 730°C.

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_O in InGaAlP increased with x. N_O in InAlP was one order of magnitude higher than that for $x\leq0.4$. A remarkable decrease in N_O for x=0.7 and 1.0 was observed as the V/III ratio increased, although N_O 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_O 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_O. Oxygen in InGaAlP may act as a deep donor, compensating for Zn acceptors.

Acknowledgments

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