

Anomalous Mg Incorporation Behavior in InGaAlP Grown by Metalorganic Chemical Vapor Deposition

Yukie NISHIKAWA, Hideto SUGAWARA, Masayuki ISHIKAWA
and Yoshihiro KOKUBUN

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

Mg incorporation behavior in InGaAlP grown by metalorganic chemical vapor deposition has been investigated. A large Mg-doping delay between turning on the Mg-dopant source in the reactor and the Mg incorporation into the InGaAlP layer was observed. The Mg-doping delay in InAlP increased with increasing substrate temperature (T_s). The Mg-doping delay for InGaP was about twice as long as that for InAlP at the same Cp_2Mg introduction. The calculated effective Mg amount, which corresponded to the total amount of Mg on the growth surface between turning on the Cp_2Mg and the Mg incorporation, was almost constant for all samples, independent of T_s and Al composition in the InGaAlP layer. It was found that Mg incorporation does not occur until the effective Mg amount exceeds a certain critical value.

1. Introduction

InGaAlP alloys are used in the fabrication of visible-region lasers. In order to improve device performance, it is desirable to grow high concentration p-type layers.¹⁾ Magnesium and zinc are widely used p-type dopants in metalorganic chemical vapor deposition (MOCVD). The maximum hole concentration in Mg-doped InAlP is $1 \times 10^{18} \text{ cm}^{-3}$.²⁾ This is about five times higher than the concentration in Zn-doped InAlP²⁾, indicating a dominant property of Mg compared with Zn. However, it has been reported that control of the abrupt doping profile in Mg-doped GaAs was difficult, due to adsorption of Mg-dopant precursors on the internal walls of the reactor; the memory-effect.³⁻⁵⁾ Several factors would influence the control over the Mg-doping profile. However, there have been no reports on detailed investigations about Mg incorporation behavior on the growth surface.

In this study, we investigated the Mg-doping delay in InGaAlP, especially at the

moment the Mg-dopant source is turned on in the reactor. The Mg-doping delay strongly depended on the substrate temperature and the Al composition in the InGaAlP, and this finding is not explained by the memory-effect. It was found, instead, that this Mg-doping delay was related to the essential mechanism of Mg incorporation on the growth surface.

2. Experiment

The materials investigated here were prepared by low-pressure MOCVD, using trimethylindium, trimethylgallium, trimethylaluminum, PH_3 and AsH_3 . The dopant source was (bis)cyclopentadienylmagnesium (Cp_2Mg). The reactants were injected into the reactor through a high speed vent/run gas switching manifold. The substrate temperature (T_s) values ranged from 670°C to 760°C . The total pressure was 25 Torr and the growth rate was about $3 \mu\text{m/h}$.

Samples consisted of a $0.5 \mu\text{m}$ -thick undoped InGaAlP, followed by a $1 \mu\text{m}$ -thick InGaAlP layer grown with Cp_2Mg on the (100)

GaAs substrate. Al composition, x , in $\text{In}_{0.5}(\text{Ga}_{1-x}\text{Al}_x)_{0.5}\text{P}$ was either 0 or 1.0. The Mg-doping profiles in InGaAlP were measured by secondary ion mass spectroscopy (SIMS). Absolute Mg concentration was examined, using ion implanted samples.²⁾

3. Results

Figure 1 is an example of an Mg-doping profile in InAlP. Cp_2Mg was introduced into the reactor at 1 μm depth from the surface. Cp_2Mg introduction, the Cp_2Mg molar fraction divided by the total molar fraction for group-III sources ($[\text{Cp}_2\text{Mg}]/[\text{III}]$), was 3.4×10^{-4} and T_s was 730°C . Mg was incorporated into the InAlP layer from 0.6 μm depth. Thus, there was a large Mg-doping delay between turning on the Mg-dopant source into the reactor and the Mg incorporation into the InAlP layer. The 0.4 μm delay corresponds to eight minutes of growth time.

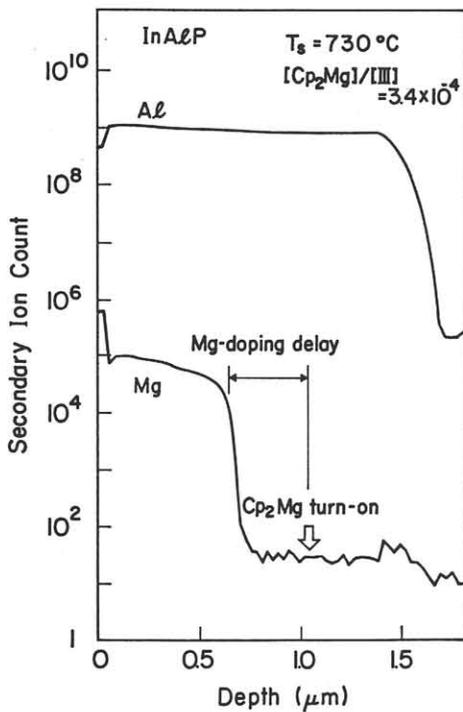


Fig.1 Mg-doping profile in InAlP measured by SIMS. Cp_2Mg introduction ($[\text{Cp}_2\text{Mg}]/[\text{III}]$) was 3.4×10^{-4} and substrate temperature (T_s) was 730°C .

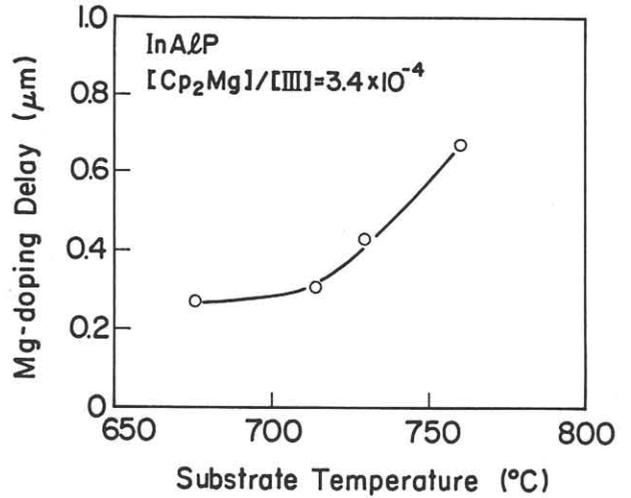


Fig.2 Mg-doping delay for InAlP versus substrate temperature (T_s). Cp_2Mg introduction ($[\text{Cp}_2\text{Mg}]/[\text{III}]$) was 3.4×10^{-4} .

The dependence of this Mg-doping delay on T_s for InAlP is shown in Fig.2. The flow rate for Cp_2Mg and the other sources were kept constant ($[\text{Cp}_2\text{Mg}]/[\text{III}] = 3.4 \times 10^{-4}$), and only T_s was varied. The Mg-doping delay increased with increasing T_s . The Mg-doping delay for $T_s = 760^\circ\text{C}$ was 0.7 μm . This was about twice as long as that for $T_s = 670^\circ\text{C}$ and 720°C values.

The relationship between Mg-doping delay and the Cp_2Mg introduction for InGaP and InAlP is shown in Fig.3. T_s was 730°C . The Mg-doping delay decreased with increas-

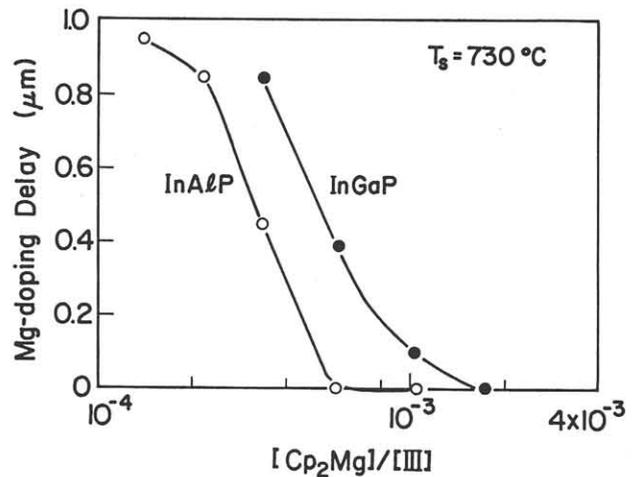


Fig.3 Mg-doping delay for InGaP and InAlP versus Cp_2Mg introduction ($[\text{Cp}_2\text{Mg}]/[\text{III}]$). Substrate temperature (T_s) was 730°C .

ing $[Cp_2Mg]/[III]$. The delay for InGaP was about twice as long as that for InAlP at the same Cp_2Mg introduction. For InAlP, large Mg diffusion into the undoped layer was observed for the Cp_2Mg introduction above 10^{-3} . It can be seen that the Mg-doping delay is not only determined by the Cp_2Mg introduction, but that is also depends on the Al composition in InGaAlP layers.

4. Discussion

Kuech et al. reported that the Mg-doping transient at turning on the Cp_2Mg into the reactor was caused by the removal of the dopant source from the growth ambient by the adsorption onto the internal surface of the reactor; the memory-effect, and that the adsorption continued until a steady state between the adsorbed species and the gas ambient was reached.³⁾ According to their model, T_s would have little influence on the Mg-doping delay, since the adsorption of the Mg-dopant source takes place upstream from the growth area. Al composition in InGaAlP layers would also have no effect on the Mg-doping delay, because the necessary time to reach the steady state is only determined by the Cp_2Mg introduction and the internal surface area. However, the Mg-doping delay strongly depended on T_s and Al composition in InGaAlP, as shown in Figs.2 and 3. These results indicate that the memory-effect is not the dominant cause of Mg-doping delay in InGaAlP.

In order to explain the dependences of the Mg-doping delay on T_s and Al composition, we propose a new model for Mg incorporation mechanism, wherein the accumulation of a certain amount of Mg on the growth surface is required before Mg incorporation. At first, Mg is built up gradually on the growth surface with turning

on the Cp_2Mg . Then, Mg incorporation into the InGaAlP layer occurs when the effective Mg amount, which is accumulated on the growth surface, exceeds a certain critical value.

To examine this model, we calculated the effective Mg amount as a product of distribution coefficient, Cp_2Mg flow rate in vapor phase and doping delay time. It corresponds to the total amount of Mg on the growth surface between turning on the Cp_2Mg in the reactor and the Mg incorporation into the InGaAlP layer. The distribution coefficient was determined by the ratio of Mg concentration in the InGaAlP layer near the surface to the Cp_2Mg concentration in vapor phase. The relationship between the Mg-doping delay and the effective Mg amount is shown in Fig.4. Effective Mg amount is independent of the Mg-doping delay. It is also independent of T_s and Al composition, and almost constant for all samples. This means that the total Mg amount, which is accumulated on the growth surface before Mg incorporation occurs, is the same for all

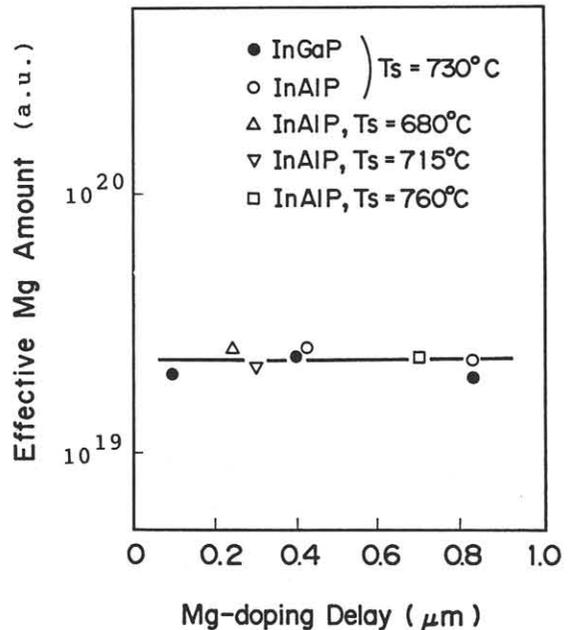


Fig.4 Effective Mg amount versus Mg-doping delay for InGaP and InAlP.

samples. These results support our model, in that Mg incorporation does not occur until the effective Mg amount exceeds a certain critical value.

5. Summary

Mg incorporation behavior in InGaAlP grown by MOCVD has been studied and a new understanding of Mg incorporation mechanism was presented. There was a large Mg-doping delay between turning on the Cp_2Mg in the reactor and the Mg incorporation into the InGaAlP layer. The Mg-doping delay in InAlP increased with increasing T_s . The Mg-doping delay for InGaP was much longer than that for InAlP at the same Cp_2Mg introduction. These Mg-doping delay dependences on T_s and Al composition were not explained by the memory-effect. The Mg-doping delay was considered relating to the essential mechanism of Mg incorporation on the growth surface. The calculated effective Mg amount, which corresponded to the total Mg amount accumulated on the growth surface before Mg incorporation occurred, was independent of T_s and Al composition and almost the same for all samples. This

result suggests that Mg incorporation into InGaAlP starts after the effective Mg amount exceeds a certain critical value.

Acknowledgment

The authors would like to thank Dr. Y. Ohba and C. Nozaki for helpful discussions, and Drs. A. Hojo, Y. Uematsu, T. Beppu and G. Hatakoshi for their continual encouragement.

References

- 1) H. Okuda, M. Ishikawa, H. Shiozawa, Y. Watanabe, K. Itaya, K. Nitta, G. Hatakoshi, Y. Kokubun and Y. Uematsu; IEEE J. Quantum Electron. 25(1989)1477.
- 2) Y. Ohba, Y. Nishikawa, C. Nozaki, H. Sugawara and T. Nakanisi; J. Cryst. Growth 93(1988)613.
- 3) T. F. Kuech, P. J. Wang, M. A. Tischler, R. Potemski, G. J. Scilla and F. Cardone; J. Cryst. Growth 93(1988)624.
- 4) M. Rask, G. Landgren, S. G. Andersson and A. Lundberg; J. Electron. Mater. 17(1988)311.
- 5) J. S. Roberts and N. J. Mason; J. Cryst. Growth 68(1984)422.