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Growth Conditions and Doping Control in GaInAsP/InP OMVPE

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Growth and doping conditions of the GaInAsP/InP OMVPE in the bandgap wavelength of 1.3-1.6μm were obtained. As for a p-type dopant DMZn was found to be an adequate source gas with better controllability of the concentrations in the range of $3x10^{16}-4x10^{17}cm^{-3}$. Lasing operation at the wavelength of 1.58μm was achieved.

1. Introduction

GaInAsP/InP is an interesting crystal system for opto-electronic devices in the wavelength range of 1.1-1.7μm(1),for low loss optical fiber communications as well as high-speed electronic devices, and there is an increasing demand for GaInAsP/InP epitaxial growth methods with high controllability and productivity.

An organometallic vapor phase epitaxy (OMVPE), is a new technique, and has been demonstrated better controllability in GaAlAs/GaAs(2), and GaInAsP/InP(3). Although there were some reports on GaInAsP/InP OMVPE(3)(4), lattice matching conditions were not clear enough and dopants are still in open question.

In this paper, growth conditions in GaInAsP/InP organometallic vapor phase epitaxy (OMVPE) for DH laser operation has been given experimentally,and DMZn was found to be an adequate p-type dopant.

2. Apparatus

Triethylindium(TEI), triethylgallium(TEG), arsine(AsH_3) and phosphine(PH_3) were used as source gases, while H_2 or $H_2+N_2(H_2:N_2=1:1)$ as carrier gas. The reactor was a horizontal water-cooled quartz tube with inductively heated susceptor. To avoid a parasitic reaction with TEI, PH_3 was cracked at 800 °C prior to the introduction into the reactor, and organo-metallic gases and hydride gases were separately introduced into the reactor. The growth pressure was 76 Torr.

Unique points of our system were as follows(Fig.1).

(i) To eliminate oxygen and water contamination, the whole gas control system was sealed in a vacuum chamber,and a load-lock system for wafer loading was equipped.

(ii) Mixing of source gases and bubbling of TEG and TEI were made at reduced pressure to get quick gas-exchange in gas tubes.

(iii) Materials on the reactor wall deposited during epitaxial growth were cleaned by combination of hot-wall type baking and PCl_3 etching at 850°C without exposing to air.

3. Lattice Matching Conditions

In order to study the relation between mole flow rates of source gases and lattice mismatch, quaternary layers were grown on (100) InP at 640°C. The mole flow ratio of (TEG/TEI) was dominant parameter for lattice match rather than other parameters, (As_3/PH_3),(V/III) and growth temperature. This tendency agrees with previous

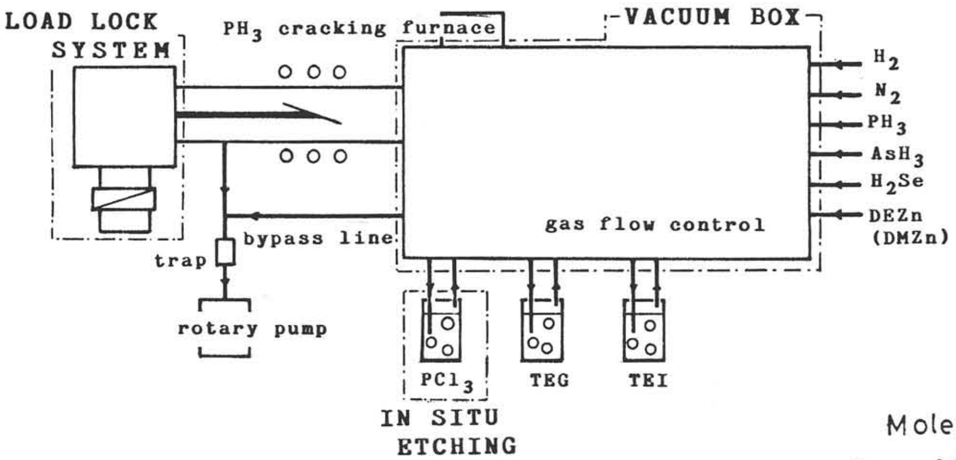

Fig.1 A schematic of our apparatus.

report(3). So we adjusted the flow rate of TEG so that the lattice matched, while we adjusted AsH_3 so that desired bandgap wavelength was obtained.

From experimental results, the accuracy required in adjusting the ratio [TEG]/[TEI] is related to the desired lattice matching as follows:

$$\Delta a/a = -0.1\ \delta([TEG]/[TEI])/([TEG]/[TEI])$$
$$(\text{for } \lambda g = 1.55\mu m)$$

In our apparatus, errors of Mass-flow-controller(MFC) and thermo-bathes of TEG and TEI bubblers were 0.2% and 0.1°C, respectively. These errors caused lattice mismatch of 0.1% which agreed with experimental results. In order to achieve the lattice matching within 0.05%, the accuracy of MFC and stability of thermo-bath temperature must be improved to 0.1% and 0.05°C, respectively.

From experimental results about relations between gas flow ratios and alloy compositions (5), source gas flow ratios for the growth of GaInAsP/InP with desired bandgap wavelength are represented as in Fig.2, where points are experimental results. Based on the above results, we grew quaternary crystals with bandgap wavelength of 1.3-1.6μm on InP substrates with room temperature photoluminescence properties comparable to LPE-grown layers in intensity and spectral width, 45-63meV .

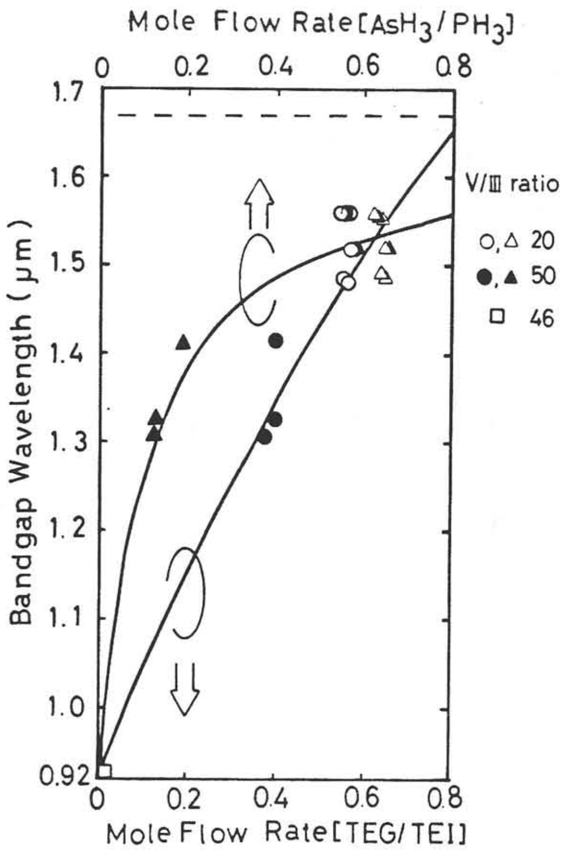

Fig.2 Growth conditions for lattice matched GaInAsP/InP with various bandgap energy.

4. Doping Conditions

We investigated p- and n-InP growth conditions, dopant, temperature and V/III ratio. Dimethylzinc (DMZn) and Diethylzinc (DEZn) were used for p-type doping, and hydrogen selenide (H_2Se) was used for n-type doping. All doping sources were introduced from gas cylinders. Concentrations of DMZn and DEZn in H_2 were 500ppm and that of H_2Se was 20ppm. To cover relatively wide range of mole flow rate, dopant gases were diluted by carrier gas in the gas flow control system.

Doped InP layers were grown on Fe doped semi-insulating InP substrates, and carrier concentrations were evaluated by van der Pauw method. Also we grew double-hetero structure wafers for laser diode as mentioned in detail later and carrier concentration of active layers and p-type InP layers were evaluated by C-V method(6). In the diodes, carrier concentration of n-type was larger than $10^{19}cm^{-3}$.

Firstly, using DEZn as dopant, acceptor concentrations of $0.5\text{-}1.5\times10^{18}cm^{-3}$ were obtained under conditions that [DEZn]/[TEI]=10%, [V]/[III]=29, Ts=565°C and carrier gas was pure H_2. The lowest doping level controllable by using DEZn was $5\times10^{17}cm^{-3}$. P-type InP could not be obtained for values of [V]/[III] high enough for mirror-like surface and growth temperature high enough for good quaternary layer. This phenomena might be attributed to parasitic reaction between DEZn and PH_3 or rediffusion of Zn in some volatile form with phosphorous atom at high phosphorous pressure. Compensation may not explain this phenomena because back ground carrier concentration of undoped InP was much less than $10^{17}cm^{-3}$.

On the other hand, about DMZn, under conditions that [V]/[III] ratio were high enough to obtain mirror-like crystal surface, acceptor concentrations in the range of $3\times10^{16}\text{-}7\times10^{17}cm^{-3}$ were obtained. The relations between carrier concentrations and mole flow ratios of DMZn/TEI is shown in Fig.3. The growth conditions were as follows: [V]/[III]=169, Ts=640°C, and carrier gas was H_2+N_2. In Fig.3, open triangles were data measured by C-V method, and open squares were data measured by van der Pauw method. Almost linear relation between the carrier concentration and the introduction of DMZn was obtained.

As the result of the comparison between DMZn and DEZn both from gas cylinders, we found that DMZn seemed better than DEZn for p-type dopant with respect to the efficiency of doping and controllable lowest doping level. This tendency is completely different from that of the OMVPE with adduct(7).

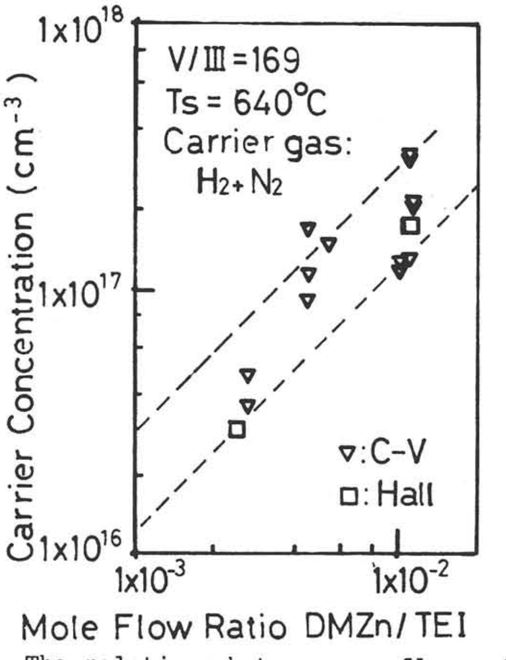

Fig.3 The relations between gas flow ratio DMZn/TEI and carrier concentrations of p-InP layer.

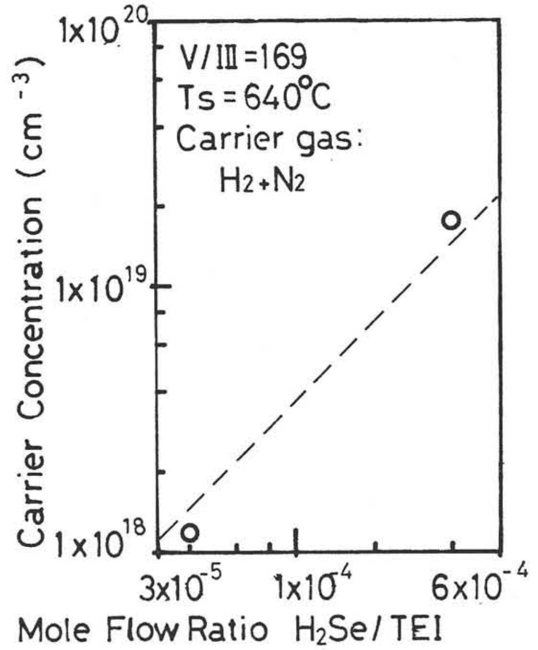

Fig.4 The relations betwwen gas flow ratio H_2Se/TEI and carrier concentrations of n-InP layer.

As to n-type dopant H_2Se, donor concentrations in the range of $10^{18}\text{-}10^{19}cm^{-3}$ were obtained as shown in Fig.4 where [V]/[III]=169, growth temperature of 640°C, and carrier gas $=H_2$+N_2. The relations between carrier concentrations and mole flow ratio of H_2Se was linear as shown in Fig.4. Even for high doping level up to $10^{19}cm^{-3}$, mirror-like surfaces were obtained.

5. DH Laser Oscillation

The laser structure grown consisted of quaternary active layer (0.16-0.25μm),p-type cladding layer (1.5-2.0μm) and p-type quaternary cap layer. All layers were grown at 640°C.

The location of p-n junctions in DH structure was controlled by adjusting the start of introduction of DEZn to 6-8 minutes later than that of InP growth, and was checked by electron beam induced current (EBIC) measurement. This delay of doping canceled Zn diffusion from the cladding layer to active layer during the growth of the remainder, i.e. about 1-2 hours at 640°C. The thickness of this thin undoped InP layer was chosen to be 100-200nm. Fig.5 (a) and (b) show examples of the EBIC measurement and I-V characteristics of p-n junctions.

The grown wafers were polished to a thickness of 100-150μm, and were then coated with Au/Zn and Au/Sn by vacuum evaporation on p and n sides, respectively, followed by alloying to make ohmic contact. These wafers were cut into laser diode chips by cleavage with cavity length of 100-350μm.

Lasing properties of broad contact lasers were measured at room temperature under pulsed condition with repetition rate of 3kHz and the width of 200-300ns. Lasing wavelength was 1.58μm.

6. Conclusion

OMVPE growth conditions for 1.3-1.6μm GaInAsP/InP crystal which is lattice matched to InP substrate were obtained experimentally. Intensisties and widths of photoluminescence in grown crystals were good enough and comparable to those of LPE wafer. To achieve lattice matching for GaInAsP/InP, it was found that the mole flow ratio of (TEG/TEI) was dominant. The relation between lattice mismatch and mole flow ratio (TEG/TEI) was obtained.

We found that DMZn from gas cylinder was very adequate for p-type dopant in the accepter concentration from 3×10^{16} to $1\times10^{18}cm^{-3}$. DH laser operations at room temperature emitting at 1.58μm were obtained.

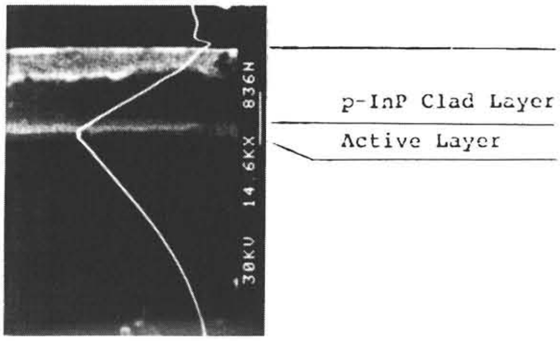

Fig.5(a) Direct observation of p-n junction in DH laser wafer by EBIC.

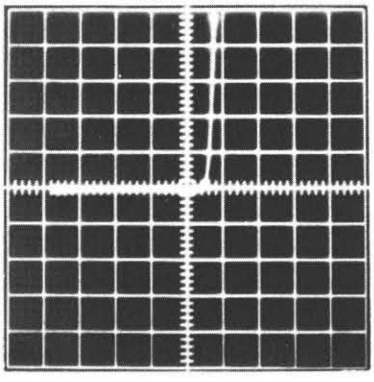

Fig.5(b) I-V characteristic of p-n junction. Horizontal 1V/div, vertical 1mA/div.

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