

Crystal Growth of GaAs by Metalorganic Molecular Beam Epitaxy Using Trimethylgallium and Triethylgallium

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The metalorganic molecular beam epitaxial (MOMBE) growth of GaAs using trimethylgallium and triethylgallium has been studied. The results of introducing hydrogen in this system are also described. Introducing ionized hydrogen in TMG-As₄ system, reduced the carrier concentration from $1 \times 10^{20} \text{cm}^{-3}$ to $1 \times 10^{18} \text{cm}^{-3}$. Using TEG as a Ga source, epitaxial layers grown at temperatures below 580°C showed n-type conduction and the carrier concentration was about $1 \times 10^{17} \text{cm}^{-3}$, while those grown at higher temperatures showed p-type conduction.

I. Introduction

Recently, some publications have appeared on the use of gas sources in molecular beam epitaxy (MBE) such as AsH₃ and PH₃^{1),2)}. We have already reported metalorganic molecular beam epitaxial (MOMBE) growth of GaAs using trimethylgallium (TMG) as a Ga source³⁾. The epitaxial layers grown from TMG and As₄ showed p-type conduction with high carrier concentration ($\sim 10^{20} \text{cm}^{-3}$). This high carrier concentration might be due to the residual carbon. It has been reported that introducing hydrogen during MBE growth improves the quality of GaAs⁴⁾. Since hydrogen is highly reactive with carbon and oxygen, the presence of hydrogen during MOMBE growth can be expected to reduce the incorporation of these impurities. In this work, the introduction of molecular and ionized hydrogen in the MOMBE system has been studied, for the purpose of reducing the residual carbon.

It has been also reported that the residual carbon concentration can be reduced by using triethylgallium (TEG) as a Ga source in the metalorganic chemical vapor deposition (MOCVD)⁵⁾. It is assumed that the bond strength between Ga and the methyl group is stronger than that between Ga and the ethyl group, because of the difference of electron affinities. For this reason, the crystal growth of GaAs using TEG instead of TMG is

also described in this paper.

II. Experimental apparatus

Figure 1 shows the schematic representation of the MOMBE apparatus used in this work. This apparatus is similar to that reported earlier³⁾, and no liquid-nitrogen shroud nor cryo-panel were used in this work. It consists of a stainless steel chamber with a 250 l/s turbomolecular pump (T.M.P). High purity 99.9999% TMG or TEG was introduced into the growth chamber through a UHV leak valve and directed towards the substrate. As an arsenic source, a usual arsenic effusion cell was used to produce As₄ flux.

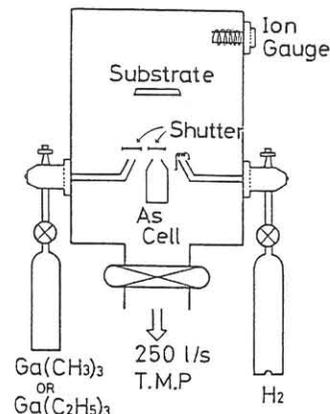


Fig. 1 Schematic representation of the MOMBE apparatus used in this work.

Hydrogen gas was also introduced into this chamber through a variable leak valve. The schematic representation of the apparatus used to ionize hydrogen is illustrated in Fig. 2. A tantalum filament was arranged in the outlet of the tube and the ionized hydrogen was obtained by thermal electrons which accelerated by ionization voltage (V_i).

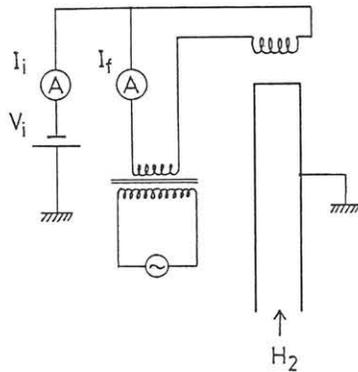


Fig. 2 Schematic representation of the hydrogen ionizer.

III. Results and Discussion

(III-I.) Introducing H_2 gas in the TMG- As_4 system

GaAs epitaxial layers were grown on (100) Cr-doped semi-insulating substrates. The typical growth conditions were as follows; $T_{sub} = 560^\circ C$, $T_{As} = 250^\circ C$, P_{MO} (partial pressure of TMG) = 1.5×10^{-5} Torr. The partial pressure of hydrogen was 2×10^{-5} Torr and ionization voltage V_i and ion current I_i were 350V and 1mA, respectively. Three types of samples were grown; one with molecular hydrogen, the second without molecular hydrogen, and the third with ionized hydrogen. The other growth parameters were kept constant. The growth rate of these layers were all about $0.5 \mu m/h$.

Figure 3 shows photoluminescence (PL) spectra of the samples grown in TMG- As_4 , TMG- As_4 - H_2 and TMG- As_4 -ionized H_2 system. Introducing molecular hydrogen affected the quality of the epitaxial layers as shown in Fig. 3. Although luminescence intensity was improved by a factor of 10, the luminescence peak at room temperature was still observed at 1.37eV. It was found by van der Pauw Hall measurements that carrier

concentration slightly decreased from $1 \times 10^{20} cm^{-3}$ to $5 \times 10^{19} cm^{-3}$. Increasing the partial pressure of hydrogen had no significant effect on the carrier concentration. On the other hand, the films grown with ionized hydrogen still showed p-type conduction, but the carrier concentration was drastically reduced to $1 \times 10^{18} cm^{-3}$ and luminescence peak at room temperature was observed at 1.43eV.

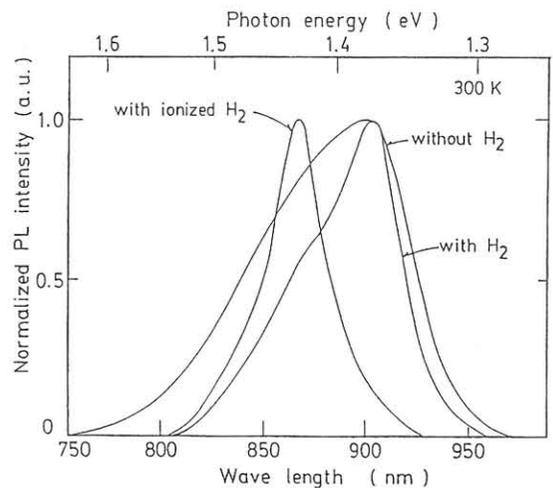


Fig. 3 Photoluminescence spectra of GaAs epitaxial layers grown in TMG- As_4 , TMG- As_4 - H_2 and TMG- As_4 -ionized H_2 system.

It was found from secondary ion mass spectrometry (SIMS) analysis that the carbon concentration of the films grown with molecular hydrogen and ionized hydrogen were $3 \times 10^{19} cm^{-3}$ and $1 \times 10^{18} cm^{-3}$, respectively, which agreed with the values obtained from the Hall measurements. These results may be because ionized hydrogen is more reactive with carbon than molecular hydrogen. The presence of ionized hydrogen during growth reduced the incorporation of carbon more than that of molecular hydrogen.

To see the effect of ionized hydrogen on surface damage, reflection high energy electron diffraction (RHEED) patterns were examined. It showed that epitaxial layers were all monocrystalline. Also, surface defects of these samples were observed by microscope and scanning electron microscope. No additional surface defect was observed on the films grown with ionized

hydrogen. These results indicate that ionized hydrogen made no damage on the epitaxial layers.

(III-II.) Using TEG as a Ga source

We have also tried to use TEG as a Ga source to reduce carbon concentration. The dependence of the growth rate on the substrate temperature for the metalorganic gas pressure of 2×10^{-5} Torr is shown in Fig. 4. Epitaxial layers were grown on (100) Cr-doped semi-insulating substrates and the temperature of the arsenic cell = 250°C. In the range of 620°C to 540°C, no difference in growth rate can be seen between TMG and TEG. In this range, the growth rate increased linearly with increasing the partial pressure of TEG as well as that of TMG. Below 540°C, the growth rate in TMG-As₄ system dropped rapidly, whereas in TEG-As₄ system only a slight decrease occurred. Therefore, in this temperature range, the growth process is believed to be limited by metalorganic gas decomposition, and TEG decomposes more easily than TMG at low temperatures.

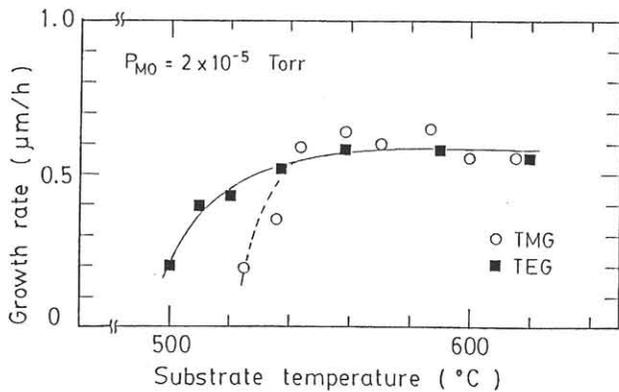


Fig. 4 Temperature dependence of the growth rate for the metalorganic gas pressure of 2×10^{-5} Torr.

Figure 5 shows the dependence of the carrier concentration on the substrate temperature. Epitaxial layers grown at the temperature below 580°C showed n-type conduction, while the films grown at the higher temperatures showed p-type conduction. This p-n conversion might be due to the change of TEG/As₄ ratio at high temperatures. The values for electron mobility of $1600 \text{ cm}^2/\text{Vs}$

and hole mobility of $150 \text{ cm}^2/\text{Vs}$ were obtained. These low Hall mobilities indicate a high degree of compensation.

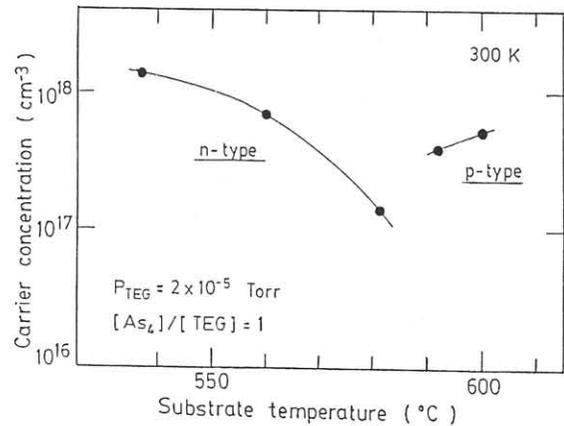


Fig. 5 Dependence of the carrier concentration on the substrate temperature in TEG-As₄ system.

The quality of these epitaxial layers were not enough for the electronic devices. Therefore, the effect of introducing hydrogen in TEG-As₄ system has been studied. Table 1 shows the minimum carrier concentration and the electron mobilities, varying the partial pressure of hydrogen. While introducing hydrogen had no effect on carrier concentration, the electron mobility significantly increased. These results indicate that the acceptor concentration in the epitaxial layer was decreased by introducing hydrogen.

H ₂ /TEG	n (cm ⁻³)	μ _n (cm ² /V.sec)
0	1x10 ¹⁷	1600
0.5	4x10 ¹⁷	2050
1	2x10 ¹⁷	2700

T = 300 K

Table 1 Dependence of electrical characteristics of the epitaxial layers grown in TEG-As₄-H₂ system on the partial pressure of hydrogen.

In addition to molecular hydrogen, we also investigated the effect of introducing ionized hydrogen in this system on the quality of epitaxial layers, by changing ionization voltage. The variation is shown in Fig. 6. The ion currents were kept constant at the value of 1.5 mA. The epitaxial layers grown at the ionization voltage below 40V, showed n-type conduction, whereas those grown at the higher voltage showed p-type conduction. Although the carrier concentration was reduced to $1 \times 10^{16} \text{ cm}^{-3}$, the electron mobility was not increased. Therefore, it is assumed that the ionized hydrogen makes the acceptor impurities in TEG-As₄ system. The reason for this p-n conversion is not clear at present. On the donor impurities, further study is presumed to be necessary.

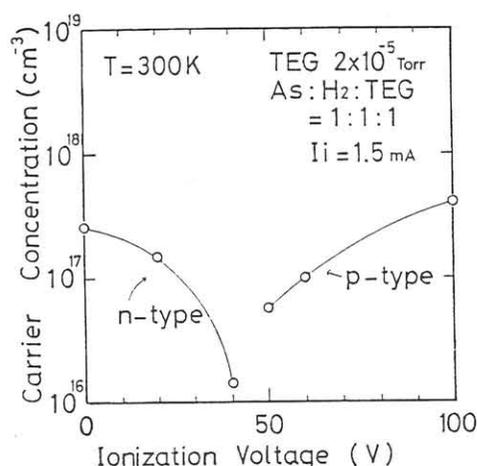


Fig. 6 Dependence of the carrier concentration on the ionization voltage for the substrate temperature of 560°C in TEG-As₄-ionized H₂ system.

Furthermore, it was observed that mono-crystalline GaAs only grew on the bare substrate and that no deposition took place on the SiO₂ masked region in the TEG-As₄ system, the same as in the TMG-As₄ system. This feature must be attributed to the surface catalyzed growth process.

IV. Conclusion

We have investigated the MOMBE growth of GaAs. The carrier concentration could be reduced by introducing ionized hydrogen in the TMG-As₄ system and the carrier concentration value $p = 1 \times 10^{18} \text{ cm}^{-3}$ was obtained. The crystal growth of GaAs using TEG was also examined. The undoped epitaxial layers grown at low temperatures showed n-type conduction and the films grown at higher temperatures showed p-type conduction. When using TEG as a Ga source, a carrier concentration of about 10^{17} cm^{-3} and an electron mobility of 2700 cm²/Vs were obtained.

Acknowledgement

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References

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