

Low-Pressure OMVPE of GaAs Using a Triethylgallium Source

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Growth of undoped GaAs layers by low-pressure organometallic vapor phase epitaxy (OMVPE) was investigated using triethylgallium (TEG) and arsine (AsH_3). All layers, grown at pressures from 0.1 to 20 Torr and $[\text{AsH}_3]/[\text{TEG}]$ ratios from 1 to 30, showed n-type conductivity and nearly constant carrier concentrations. In 4.2K photoluminescence spectra, the carbon acceptor peaks were very weak in comparison with the bound exciton peaks. The reaction products were analyzed in-situ by a quadrupole mass spectrometer (QMS). Ethylarsine compounds were detected at growth pressures below 1 Torr. The formation of hydrocarbons seems to be effective in suppressing carbon incorporation into GaAs layers.

1. Introduction

Organometallic vapor phase epitaxy (OMVPE) of GaAs and other III-V semiconductors has been developed for the preparation of microwave and optoelectronic devices. Low-pressure OMVPE has desirable features such as interface abruptness, reduced autodoping and lower growth rate. In OMVPE of GaAs, trimethylgallium (TMG) has been generally used as a Ga source.^{1,2)} Previous work has shown that the properties of undoped GaAs layers grown using TMG depend very sensitively on growth conditions such as growth pressure, V/III ratio, and substrate temperature.³⁾ One of the reasons for this is heavy carbon incorporation into grown layers.⁴⁾ It has been suggested that carbon incorporation can be reduced by using TEG instead of TMG.⁵⁾

In this paper, undoped GaAs layers were grown by low-pressure OMVPE using TEG and arsine. We present results on the effects of growth conditions with special emphasis on the difference between the TEG and TMG system, and discuss preliminary results of in-situ gas analysis using a quadrupole mass spectrometer (QMS).

2. Experimental Procedures

The apparatus, shown in Fig. 1, had a vertical, water-cooled, quartz growth chamber containing a graphite susceptor coated with SiC. Growth pressure is adjusted by a conductance

control valve between the growth chamber and the pumping system. Flow rates are regulated by mass flow controllers (MFC).

Epitaxial layers were grown on (100) Cr-O doped, GaAs substrates etched in $4\text{H}_2\text{SO}_4 : 1\text{H}_2\text{O}_2 : 1\text{H}_2\text{O}$ at 60°C for 2 minutes. The growth chamber was pumped to 2×10^{-6} Torr prior to growth. TEG and

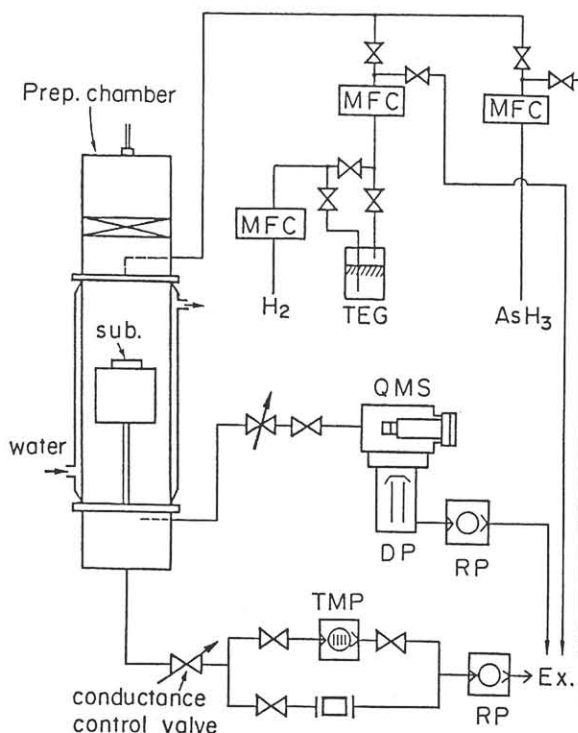


Fig. 1 Schematic diagram of the low-pressure OMVPE system.

AsH₃ diluted to 10% with H₂ are used as Ga and As sources. Pd-diffused H₂ is used as a carrier gas. Growth was performed at pressures varying from 0.1 to 20 Torr and at [AsH₃]/[TEG] ratios from 1 to 30. Substrate temperature was 650°C, and total flow rate 300 sccm. Growth rates were about 1 μm/h.

Carrier concentrations and mobilities of epilayers were measured at 77 K by the van der Pauw method. Also, the layers were characterized by low temperature (4.2K) photoluminescence (PL), using the 514.5 nm line of an argon ion laser. The excitation intensity was about 1 W/cm².

During growth, reaction products were analyzed by a quadrupole mass spectrometer. The ambient gas was sampled from the bottom of the growth chamber as shown in Fig. 1.

3. Results and Discussion

3.1 Effects of Growth Pressure

Figure 2 shows the 77 K Hall mobility and carrier concentration of undoped GaAs layers versus growth pressure. The [AsH₃]/[TEG] ratio was kept at 20. All layers, grown at pressures from 0.1 to 20 Torr, showed n-type conductivity. Carrier concentration decreases slightly as growth pressure is decreased, but Hall mobility shows no significant change. The broken lines in Fig. 2 show the corresponding results for growth using TMG.³⁾ The growth conditions were the same, except that V/III ratio [AsH₃]/[TMG] = 75. In the TMG-AsH₃ system, p/n conversion³⁾ occurs at about 0.5 Torr; layers show p-type conductivity below 0.5 Torr. This is in marked contrast with the present results for the TEG-AsH₃ system.

3.2 Effects of [AsH₃]/[TEG] Ratio

Figure 3 shows the 77 K Hall mobility and carrier concentration of undoped GaAs layers versus [AsH₃]/[TEG] ratio. The growth pressure was 10 Torr. All layers showed n-type conductivity, similarly to the results on the effect of growth pressure (Fig. 2). The Hall mobilities and carrier concentrations are nearly constant at 40,000 cm²/V·sec and 3 × 10¹⁵ cm⁻³, respectively. Again, this is in marked contrast with the results of the TMG-AsH₃ system,⁶⁾ where undoped layers grown at 8 Torr show p- or n-type conductivity according as [AsH₃]/[TMG] ratio is

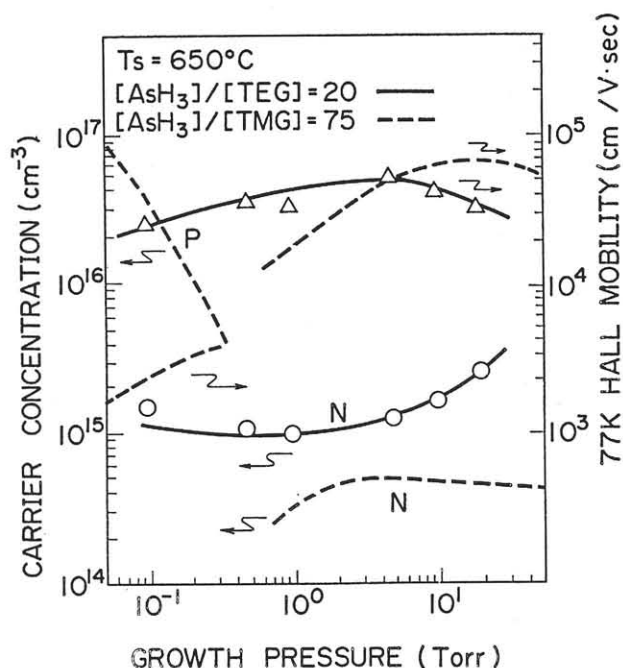


Fig. 2 Effect of growth pressure on carrier concentration and Hall mobility at 77 K. Solid and broken lines represent for TEG and TMG systems, respectively.

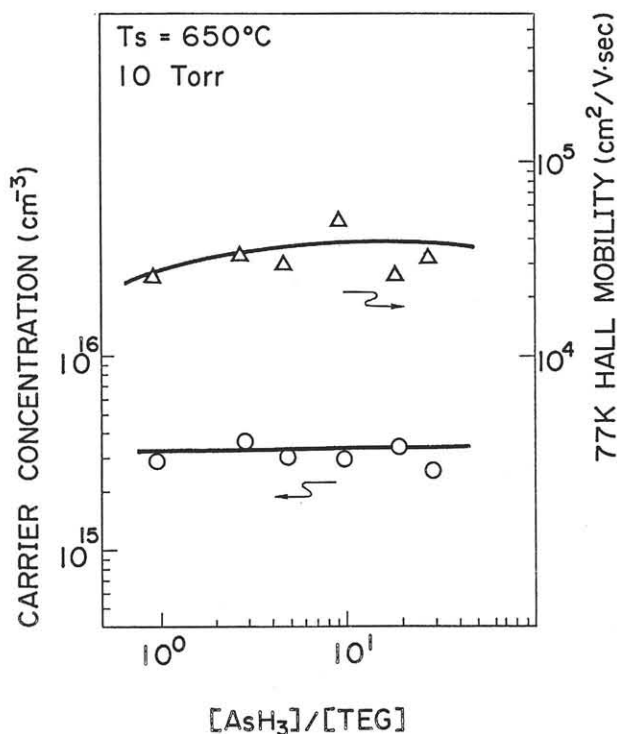


Fig. 3 Effect of [AsH₃]/[TEG] ratio on carrier concentration and Hall mobility at 77 K.

below 25 or above 70. This p/n conversion arises from the carbon incorporation which depends sensitively on $[AsH_3]/[TMG]$ ratio.⁶⁾

To investigate the carbon incorporation, we studied the effect of $[AsH_3]/[TEG]$ ratio on 4.2 K PL spectra of GaAs layers (Fig. 4). In the PL spectra, carbon acceptor peaks were very weak in comparison with bound exciton peaks, and the peak intensities had no marked dependence on the $[AsH_3]/[TEG]$ ratio. This shows that the main acceptor in undoped GaAs layers is carbon, and carbon incorporation is very low, irrespective of the $[AsH_3]/[TEG]$ ratio.

These results indicate that high-quality GaAs layers can be grown using TEG over a wide range of growth conditions.

3.3 Gas Analysis

Figure 5 shows typical mass spectra for the TEG- AsH_3 system at 5 and 0.5 Torr. We note peaks due to hydrocarbons, AsH_3 and As_2 in the spectrum for 5 Torr. In addition, peaks due to ethylarsine compounds appear in the spectrum for 0.5 Torr.

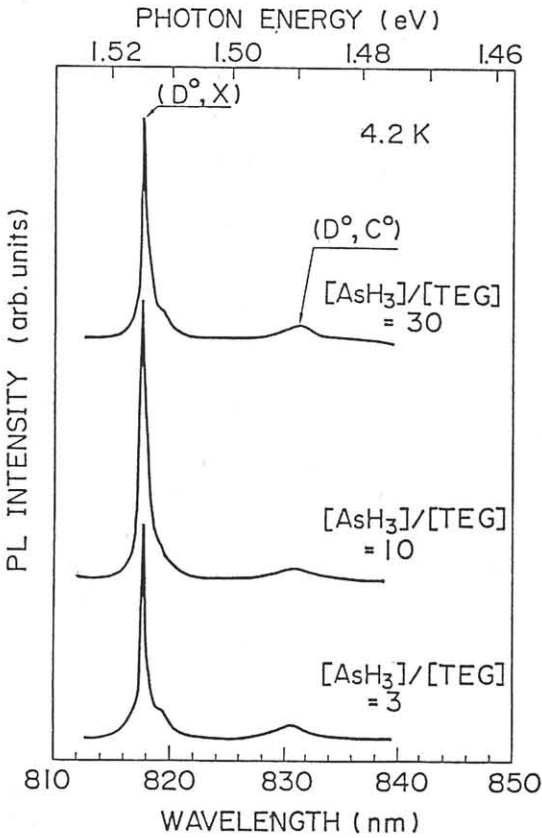


Fig. 4 Effect of $[AsH_3]/[TEG]$ ratio on the 4.2K PL spectra.

The relative peak intensities of AsH_3 and hydrocarbons are shown versus growth pressure in Fig. 6, where the intensities have been normalized to the hydrogen peak. The AsH^+ peak intensity increases as growth pressure is decreased, indicating that the AsH_3 decomposition becomes increasingly incomplete at lower pressures. The peak intensities of hydrocarbons remain insensitive to growth pressure.

The relative peak intensities for the TMG- AsH_3 system are shown in Fig. 7. In this case, the only hydrocarbon observed is methane. The intensity of methane decreases by about one order of magnitude as the pressure is decreased below 1 Torr. We note that carbon incorporation increases sharply below 0.5 Torr in the TMG- AsH_3 system.³⁾ Thus, the decrease of methane in Fig. 7 is correlated with the increase of carbon incorporation. In contrast, in the TEG- AsH_3 system, for which carbon incorporation is low, hydrocarbons remain at high concentrations over a wide range of growth pressure (Fig. 6). These results suggest that the formation of hydrocarbons is effective in suppressing the carbon incorporation.

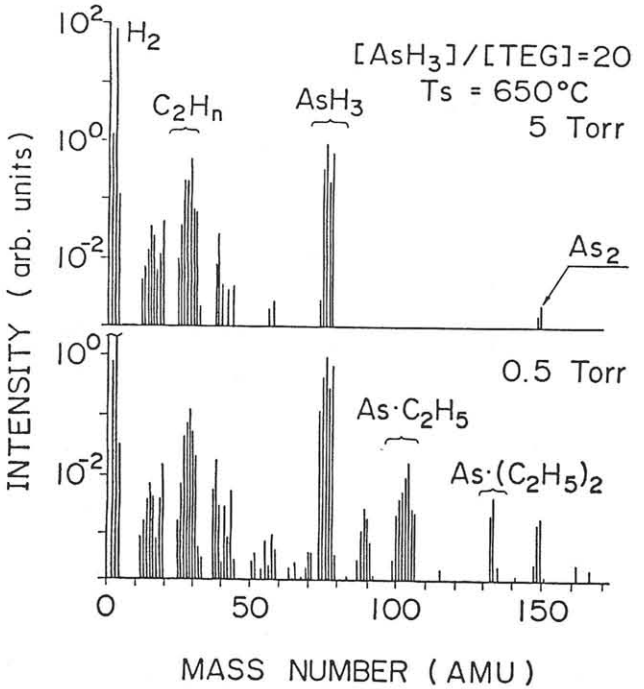


Fig. 5 Mass spectra for the TEG- AsH_3 system at 5 Torr and 0.5 Torr.

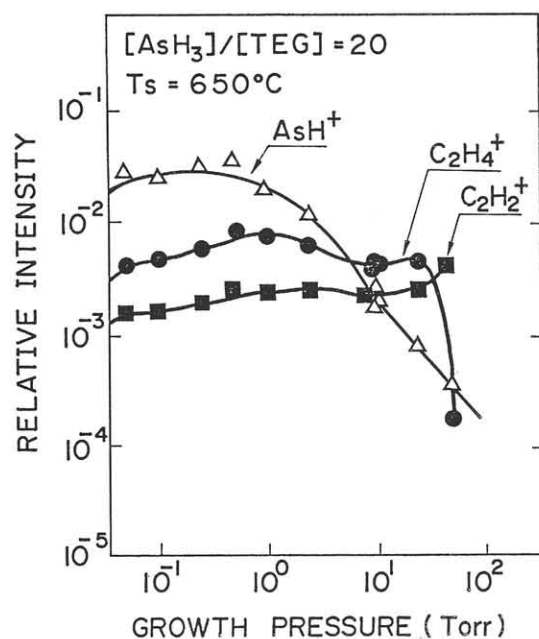


Fig. 6 Effect of growth pressure on the mass peak intensities for the TEG-AsH₃ system.

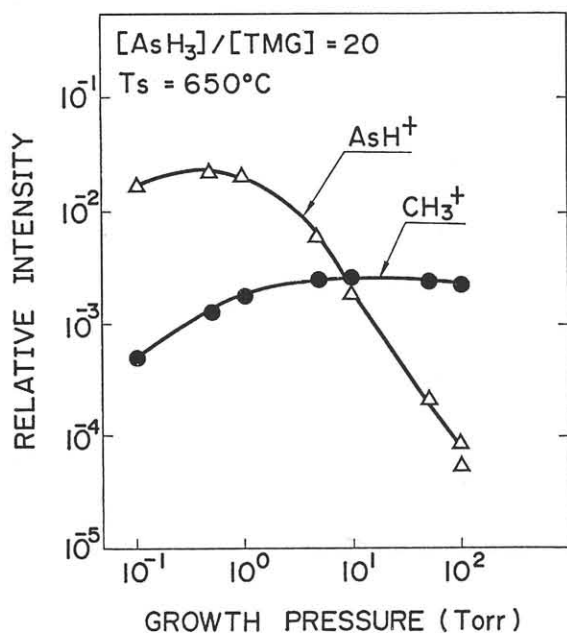


Fig. 7 Effect of growth pressure on the mass peak intensities for the TMG-AsH₃ system.

4. Summary

We have studied effects of growth pressure and [AsH₃] / [TEG] ratio on electrical and optical properties of undoped GaAs layers in low-pressure OMVPE using TEG and AsH₃. All layers showed n-type conductivity and nearly constant carrier concentrations. The carbon incorporation into GaAs layers was very low in comparison with the TMG-AsH₃ system.

In-situ gas analysis of OMVPE has been made. Peaks due to ethylarsine compounds and hydrocarbons were detected in the TEG-AsH₃ system. These hydrocarbons seem to be effective in reducing carbon incorporation in the TEG-AsH₃ system.

The present study is part of the national research and development project on optical measurement and control systems, conducted under a program set up by the Agency of Industrial Science and Technology, Ministry of International Trade and Industry.

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