

Growth of GaAs by Chemical Beam Epitaxy Using Unprecracked Arsine and Trimethylgallium

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ABSTRACT

Undoped GaAs has been successfully grown by chemical beam epitaxy (CBE) via surface decomposition process using arsine (AsH_3) and trimethylgallium (TMG). Three distinct regions of temperature-dependent growth rates were identified in the range of temperatures from 570 to 690°C. The growth rates were found strongly dependent on the V/III ratio between 5 and 30. The growth rate at low V/III ratio seems to be determined by arsenic produced on the surface, whereas at high V/III ratio it shows dependence on the adsorption of TMG. Hall measurement and photoluminescence (PL) analysis show that the films are all p-type and that carbon impurities are primarily responsible for the background doping. Carbon concentrations have been found to be reduced by two orders of magnitude as compared to those of epilayers grown by CBE which employs TMG and arsenic obtained from precracked AsH_3 in a high temperature cell. It was also found that hydrogen atoms dissociated from unprecracked AsH_3 play an important role in removing hydrocarbon-containing species resulting in a significant reduction of carbon impurities.

I. INTRODUCTION

Chemical beam epitaxy (CBE) is essentially a metalorganic vapor phase epitaxy (MOVPE) process conducted in an ultrahigh vacuum (UHV) growth chamber. In essence, it combines the versatility of the vapor sources of MOVPE with the molecular beam properties of molecular beam epitaxy (MBE). In the growth of GaAs, AsH₃ and trimethylgallium (TMG) have been normally used in CBE. However, AsH₃ must first be pre-cracked in a cracking cell at high temperature prior to growth to be used in the CBE process. As a result of this precracking, however, the actual arsenic species arriving at the growth surface, usually in the form of As₂ or As₄ may not be suitable for use with TMG as the gallium reagent species because they may not offer the proper reaction path for the reduction of carbon which is anticipated to result from the decomposition of TMG on the growing surface. On the other hand, in the CBE growth of epitaxial layers, hydrogen has been recognized to play an important role in obtaining high quality materials. It has been shown that the use of AsH₃ and elemental Ga for the growth of GaAs repeatedly produces high quality epilayers [1], [2]; this was considered to be due in part to the hydrogen ambient resulting from the thermal cracking of AsH₃ in the cell. Calawa [3] also demonstrated that a hydrogen ambient during GaAs growth significantly reduces the incorporation of carbon and oxygen in the epilayer. Furthermore, the partially

cracked species of AsH₃ were demonstrated to be responsible for improved characteristics of GaAs at low AsH₃ cracking temperatures [4].

E. Veuhoff et al. first attempted to grow GaAs by using TMG and unpredecomposed AsH₃ in an ultrahigh vacuum chemical vapor deposition (UHVCVD) system [5]. The observed GaAs growth was attributed to the thermal decomposition of AsH₃ by radiation from the sample heater. Furthermore, they later concluded that it is not possible to grow GaAs using this technique because cracking of AsH₃ into arsenic at the substrate surface alone is negligible and thus not sufficient for achieving growth [6]-[8].

In this study, we have found that GaAs epilayer can be grown by CBE using unprecracked AsH₃ and TMG via surface decomposition process. The feasibility of growing GaAs in UHV system was confirmed by avoiding the possible predecomposition of AsH₃. To avoid the potential decomposition of AsH₃ in the gas tube by radiation from the hot susceptor, we kept the temperature of the gas tube at 118°C which is far below the decomposition temperature of AsH₃. Furthermore, from the observation of low carbon impurity in GaAs, it was suggested that hydrogen atoms dissociated from AsH₃ play an important role in the reduction of carbon impurities in GaAs epilayer grown using unprecracked AsH₃ and TMG.

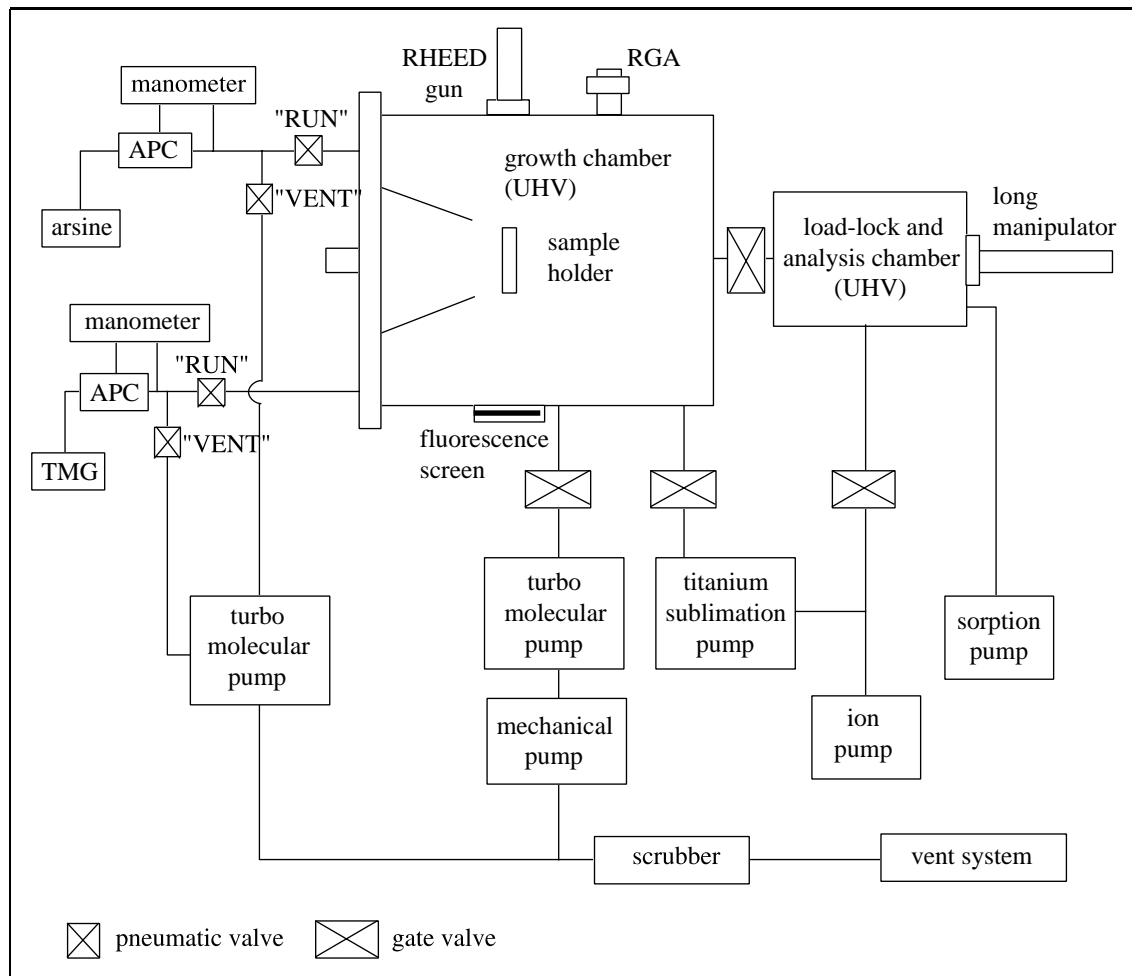


Fig. 1. Schematic diagram of the CBE growth system. APC, QMS, and RHEED denote automatic pressure controller, quadrupole mass spectrometer, and reflection high energy electron diffraction, respectively.

II. EXPERIMENT

The GaAs epilayers were grown in a CBE growth chamber which is schematically shown in Fig. 1. The UHV growth chamber is not equipped with a cryopanel and is evacuated with a 510 l/s turbo-molecular pump and titanium sublimation pump. The pump-

ing system could maintain the growth chamber at a pressure of less than 3×10^{-10} Torr after the system was baked out at 150°C. The gas flux was adjusted by means of a high precision automatic pressure controller which is essentially a closed-loop operated UHV leak valve. The typical total gas flow rate during growth was less than 10 SCCM.

TMG and AsH₃ were simultaneously injected into the growth chamber and directed towards the substrate through stainless steel tubes with a diameter of 1/4 inch without carrier gases. The temperature at the end of tube was 118°C when the substrate temperature was maintained at 610°C for 2 hours. This eliminated the possibility of decomposition of AsH₃ in the gas tube. The substrate temperature was monitored by a thermo-couple underneath a Mo block and also independently by an optical pyrometer. Commercially available "super-cleaned" semi-insulating (Cr-doped) GaAs(100) wafer (2° off (100) towards the nearest (110) plane) was used as substrate without wet cleaning process. After a 1.5cm × 1.5cm substrate was mounted on In-free molybdenum block, it was introduced into the load-lock chamber. Prior to growth the substrates and sample holder were outgassed at 200°C in the growth chamber for 15 min. The pre-growth annealing in the growth chamber was carried out at a temperature of 630°C for 20 min under an AsH₃ pressure of 10⁻⁴ Torr to obtain a clean surface. The gas pressure in the chamber during growth was maintained between 2 × 10⁻⁴ and 2 × 10⁻⁵ Torr depending on the growth temperature and V/III ratio.

III. RESULTS AND DISCUSSION

A film grown at a growth temperature below 650°C with a V/III ratio of 10 showed gallium droplets on the surface. The forma-

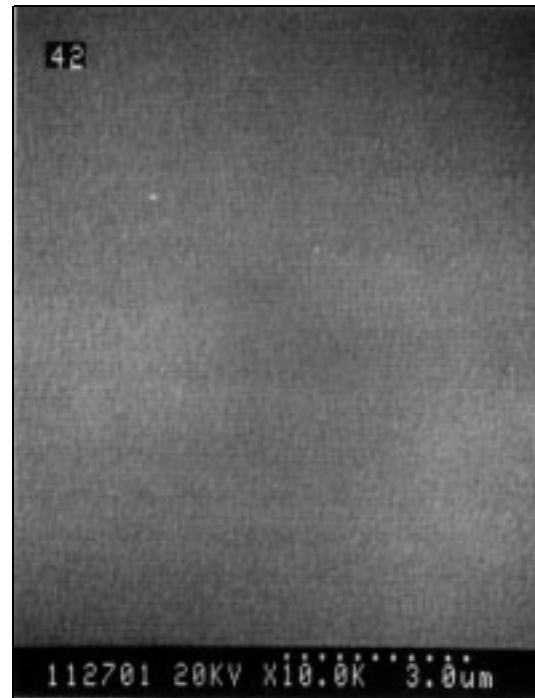


Fig. 2. SEM micrograph of surface of CBE grown GaAs epilayer ($P = 5 \times 10^{-5}$ Torr, $T = 650^\circ\text{C}$, and $V/\text{III} = 10$).

tion of gallium droplets is attributed to an insufficient supply of arsenic to produce GaAs on the surface. At a temperature higher than 650°C for the same V/III ratio, the density of gallium droplets decreased drastically giving a smooth surface. This suggests that the decomposition of AsH₃ is much easier at high temperature. It was also found that the film morphology improves rapidly and mirror-like surface is obtained at higher V/III ratios. Furthermore, it was observed that the surface morphology tends to become smooth with decreasing gas pressure in the range of gas pressure from 10⁻⁵ to 10⁻⁴ Torr. Fig. 2 shows a SEM micro-

graph of specular surface of epilayer which was grown at a lower pressure of 5×10^{-5} Torr for the same temperature and V/III ratio.

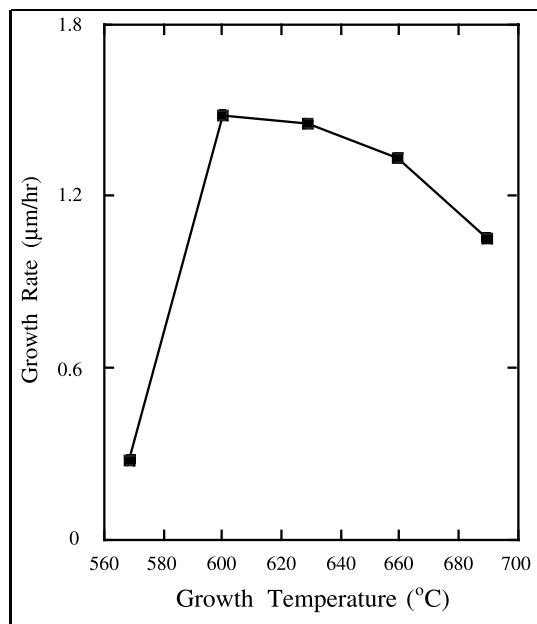


Fig. 3. Effect of growth temperature on growth rates ($P = 1.2 \times 10^{-4}$ Torr, V/III=10).

Figure 3 represents the temperature dependent growth rate measured by SEM using a cleave-and-stain method. The growth rates shown in Fig. 3 seem to be divided into three regions: below 600°C , the growth rate increases with growth temperature; between 600 and 630°C , the growth rate is constant; and above 630°C , the growth rate decreases with increasing temperature. Below 600°C , the growth rate is believed to be limited by the decomposition process of TMG on the surface. Between 600 and 630°C , the surface temperature is high enough to completely dissociate all

the TMG, resulting in a constant growth rate with increasing temperature. Above 630°C , the gradual decrease in growth rate is considered to be caused by the desorption of gallium atoms or partially cracked TMG.

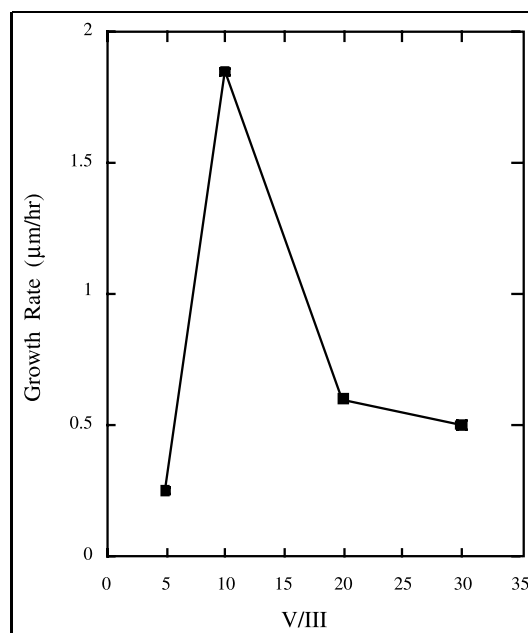


Fig. 4. Effect of V/III ratio on growth rates ($T = 630^{\circ}\text{C}$, The group III gas pressure was held constant).

Figure 4 represents the effect of V/III ratio on the growth rate at a substrate temperature of 630°C . In this experiment, the pressure of group III gas was kept constant with increasing AsH_3 pressure. The growth rate increased rapidly reaching the maximum value at V/III ratio of 10 and decreased with further increase in V/III ratio. The sharp increase in growth rate with V/III ratio may suggest that the preadsorption of arsenic or AsH_3 radicals is required for decomposition of TMG and subse-

quent formation of GaAs epitaxial layer. However, the adsorption of TMG seems to be hindered by co-adsorption of AsH_3 or arsine radicals resulting in the decrease of growth rate at a higher V/III ratio due to site competition.

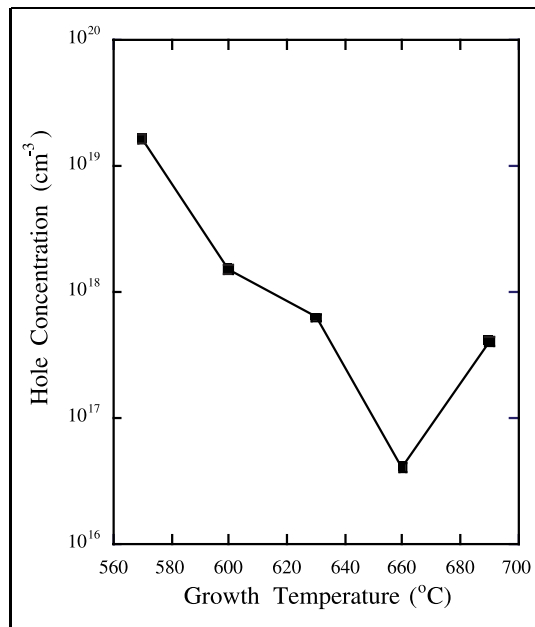


Fig. 5. Dependence of hole concentrations in the film on the substrate temperature.

The free carrier concentration and Hall mobility were obtained from van der Pauw measurements. The thicknesses of the grown layers were measured by SEM and they were typically $0.5 \sim 3 \mu\text{m}$. The free carrier concentration was not corrected for any depletion layers but the deviation from the correct value is not significant in the range of carrier concentrations examined in this study [9]. Figs. 5 and 6 show the changes of hole concentrations as a function of growth temperature and V/III ratios with arsine pressure constant, re-

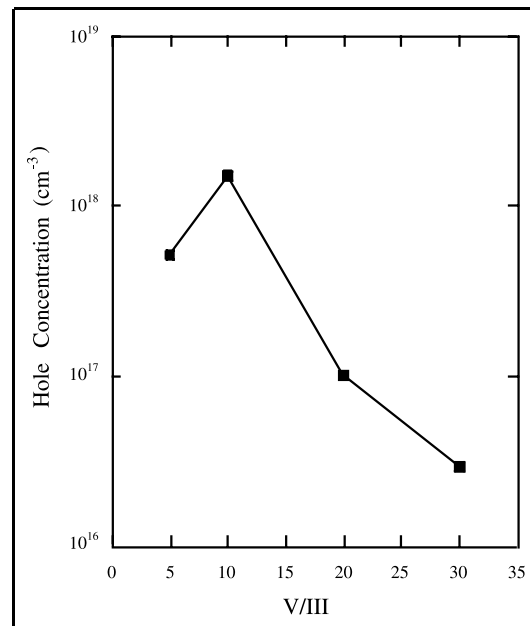


Fig. 6. Dependence of hole concentrations in the film on the V/III ratio ($T = 650^\circ\text{C}$, The group V gas pressure was kept constant).

spectively. The PL spectrum which is shown in Fig. 7 indicates that carbon is the main source for p -type impurity in the GaAs epilayers. As shown in Fig. 5, all of the samples grown in the range of temperatures investigated in this study were p -type materials mainly due to carbon incorporation showing the hole concentrations typically of $10^{16} \sim 10^{19} \text{ cm}^{-3}$. The hole concentration decreases as substrate temperature increases below 660°C , which suggests that carbon containing species may drastically desorb from the growth surface with increasing growth temperature. Above 660°C , the hole concentration increases again mainly due to the incorporation of carbon atoms in the

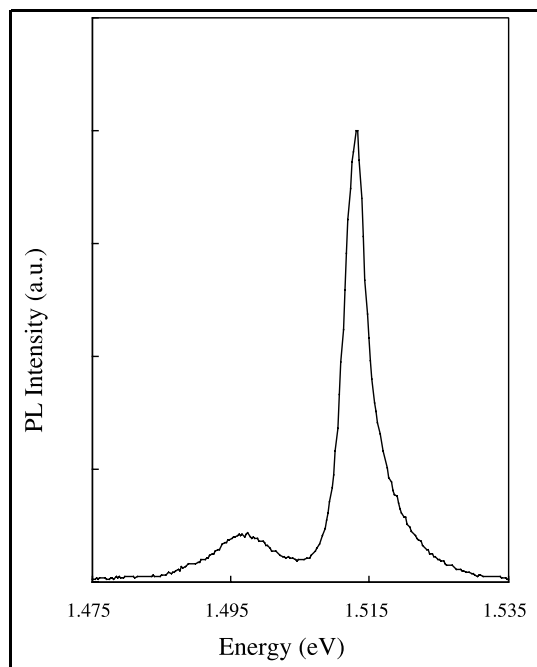


Fig. 7. Photoluminescence spectrum at $T = 19$ K of a GaAs epilayer ($T = 630^\circ\text{C}$, $V/\text{III} = 10$, and $P = 2 \times 10^{-5}$ Torr).

epilayer. The reason could be that at high substrate temperature arsenic atoms desorb from the surface, creating arsenic vacancies and allowing carbon to occupy arsenic sites. Fig. 6 shows that the hole concentration slightly increases for low value of V/III ratio, but it is observed to decrease with further increase in V/III ratio. This result indicates that the impurity content of the layers depends distinctly on the partial pressure of TMG. Similar results were obtained and it was speculated that the presence of the partially cracked radicals on the growth surface can inhibit hydrocarbon pyrolysis since a surface can play a key role in inhibiting hydrocarbon pyrolysis due

to highly populated atomic hydrogens at the surface [2]. As shown in Figs. 5 and 6, the hole concentrations are dramatically decreased by more than two orders of magnitude compared to values reported from other CBE or MOMBE works which employed precracked AsH_3 or solid arsenics as source materials [10], [11]. Furthermore, secondary ion mass spectrometry (SIMS) analysis for carbon impurity in the epilayer also agreed well with the hole concentrations obtained by electrical measurement. Therefore our experimental observation indicates that the significant drop in hole concentration is partly due to the hydrogen atoms dissociated from AsH_3 on the surface, which then aid the removal of hydrocarbon radicals.

Figure 7 shows a photoluminescence (PL) spectrum which was obtained on a film at 19 K using the 488nm line of an argon laser with an incident power density of $10\text{mW}/\text{cm}^2$. The neutral acceptor bound exciton (A^0, X) transition is clearly seen at 1.5138 eV. The shoulders at higher energy (1.516 eV) and at lower energy (1.512 eV) are attributed to free exciton (X) and defect bound exciton transition, respectively. The broad peak near 1.498 eV seems to be closely related to the transition from neutral donor to acceptor (D^0, C^0) and free electron to acceptor (e, C^0) transition at 1.490 eV and 1.494 eV, respectively. This PL spectrum which is typically observed from a GaAs sample with a low hole concentration demonstrates that carbon is responsible for the main source for p -type doping in the epilayers. Some of epitaxial films were observed to have

low Hall mobilities of 100 to 300 cm²/V·sec [12]. The carbon and silicon related transition peaks were shown in PL spectra taken from some epilayers having low hole mobilities. This indicates some degree of compensation which may be caused by carbon and silicon impurities depending on the growth conditions.

IV. CONCLUSIONS

We have investigated the effects of unprecracked AsH₃ and trimethylgallium on the CBE growth of GaAs epilayers. First, three distinct temperature-dependent regions of growth rates were observed with increasing growth temperature from 570 to 690°C representing that three different growth processes are involved. The growth rates were also strongly dependent on V/III ratio in the range from 5 to 30, which indicates that the preadsorption of arsenic or arsine radicals is necessary for TMG decomposition on the surface. On the other hand, at high pressures of AsH₃ the growth rate was found to decrease due to the competition between TMG and AsH₃ for adsorption sites on the surface. Secondly, the carbon impurity contents in the epilayers were observed to depend strongly on the growth temperature, V/III ratio, and pressure of TMG. All of the samples were *p*-type materials with a hole concentration typically of 10¹⁶ ~ 10¹⁹ cm⁻³ mainly due to carbon incorporation. These values are

significantly lower than those reported in conventional CBE studies which employ TMG and precracked AsH₃ as source materials. This result also indicates that the significant decrease in the hole concentration results from an efficient removal of carbon containing species by hydrogen atoms dissociated from AsH₃ on the surface.

ACKNOWLEDGMENTS

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