

Characterisation of III–V Multilayers Grown by Low-pressure Metal Organic Vapour-phase Epitaxy*

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Abstract

Undoped and doped layers of gallium arsenide and aluminium gallium arsenide have been grown on gallium arsenide by low-pressure metal organic vapour-phase epitaxy (MOVPE). Delta doping and growth on silicon substrates have also been attempted. Of particular interest in the present study has been the influence of growth parameters, such as growth temperature, group III mole fraction and dopant flow, on the electrical and physical properties of gallium arsenide layers. An increase in growth temperature leads to increased doping efficiency in the case of silicon, whereas the opposite is true in the case of zinc. Deep level transient spectroscopy (DTLS) studies on undoped GaAs layers showed two levels, the expected EL₂ level and a carbon-related level. The determination of optimum growth conditions has allowed good quality GaAs and AlGaAs epitaxial layers to be produced for a range of applications.

1. Introduction

Growth of epitaxial layers of compound semiconductors is of considerable interest due to the existence of a wide range of applications for these materials as starting substrates for the fabrication of electronic and optoelectronic devices. Although liquid-phase epitaxy (LPE) and vapour-phase epitaxy (VPE) have been the techniques of choice for producing thick epitaxial layers, the complexity and small scale of multilayer structures required for advanced devices has led to the development of techniques such as molecular beam epitaxy (MBE) and metal organic vapour-phase epitaxy (MOVPE). Both of these techniques have been widely used for growing epitaxial layers of III–V compound semiconductors. Due partly to problems associated with the growth of phosphorus-based compounds using MBE and also ultrahigh vacuum technology, MOVPE is widely used in industry for the large-scale production of epitaxial layers of III–V semiconductors.

In MOVPE, at least one of the constituents to be incorporated into the epitaxial layers is obtained as vapour from a metal organic source (Manasevit 1968). Group III materials and some dopants (e.g. zinc) are usually obtained this way, whereas group V species are supplied as hydrides such as arsine and phosphine (and the dopant silicon as silane) although, increasingly, metal organic sources are replacing hydrides due to the less toxic nature of the former.

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In this paper we present the results obtained from the systematic growth of layers on gallium arsenide carried out using the ANU MOVPE reactor. Wider studies and initial results are also briefly reviewed.

2. Experimental Details

A commercial MR Semicon MOVPE reactor was used for the growth of the epitaxial layers in the present study. The reactor is of horizontal type with a rf-heated, SiC-coated susceptor as a wafer carrier. The carrier gas is ultrahigh purity hydrogen and growth is carried out at low pressure (76 Torr). Low-pressure growth inhibits parasitic reactions, and the incorporation of carbon is believed to be lower. Trimethylgallium (TMG) was used as the metal organic (MO) source and arsine as a hydride source. For AlGaAs growth, trimethylaluminium (TMA) was used as the source material. Silane diluted with hydrogen (100 ppm silane in hydrogen) and dimethylzinc (DMZ) diluted with hydrogen (1000 ppm DMZ in hydrogen) were used as n-type and p-type dopant sources respectively. Starting substrates were obtained commercially as epi-ready (n^+ or semi-insulating) (100) GaAs (2° off axis). Growth was also attempted on (100) n-type Si (2° off) substrates.

Layers were characterised by a variety of techniques such as Hall effect, C-V profiling, deep level transient spectroscopy (DTLS), double crystal X-ray diffraction, photoluminescence and Rutherford backscattering spectrometry with channelling (RBS-C). Some of the results from these characterisations, particularly for the growth of GaAs on GaAs, will be reported here.

3. Results and Discussion

(3a) Undoped GaAs

Epitaxial layers of GaAs were grown at different growth temperatures in the range 575–700°C. This range is within the desired mass-transport-limited growth regime. Here the growth rate is mainly controlled by the diffusion of TMG through the boundary layer over the susceptor (Stringfellow 1978), hence the TMG flow controls the growth rate if arsine overpressure is maintained (arsine/TMG > 1). Although the growth rate is nearly constant in this temperature range for a fixed group III partial pressure (flow rate), the morphology and purity of the layers, and their electrical and optical properties, are dependent on the growth temperature. In this study it was found that a growth temperature of 650°C is optimum for the growth of good quality GaAs epitaxial layers. For AlGaAs the optimum growth temperature is 750°C. However, for the growth of GaAs on Si a two-step process is used, involving a low-temperature (400–450°C) nucleating step (100–200 Å) and a high temperature (650°C) step to grow 1–2 μm GaAs. The composition of AlGaAs layers was determined by double crystal X-ray diffraction. RBS-C studies of GaAs on Si showed that χ_{min} is about 6%, suggesting good crystallinity quality of these layers.

The electrical properties of unintentionally doped GaAs layers are controlled by the V/III ratio employed during growth. Results reported in the literature (Ito *et al.* 1973; Dapkus *et al.* 1981) have shown that p-type and n-type layers of unintentionally doped GaAs can be grown by varying the V/III ratio. The

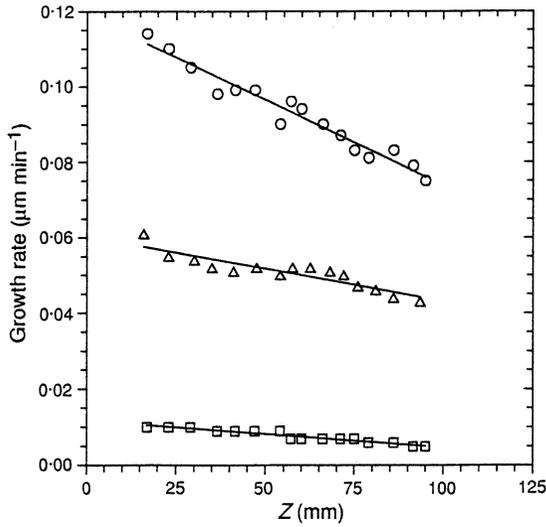


Fig. 1. Growth rate of GaAs as a function of longitudinal distance along the susceptor for different group III flows (mol min^{-1}) at a carrier flow of 7.5 slm. (□) 6.83×10^{-6} , (△) 2.63×10^{-5} , (○) 4.66×10^{-5} .

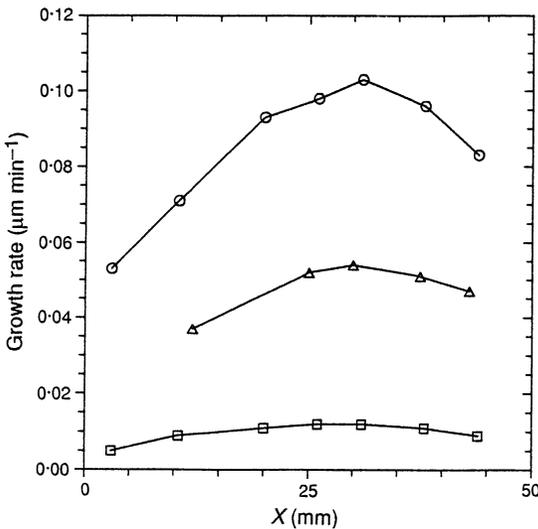


Fig. 2. Growth rate of GaAs as a function of lateral distance across the susceptor for different group III flows (mol min^{-1}) at a carrier flow of 7.5 slm. (□) 6.83×10^{-6} , (△) 2.63×10^{-5} , (○) 4.66×10^{-5} .

transition point at which p- to n-type conversion takes place is dependent on the reactor geometry, cell pressure, growth temperature, etc. In this study a V/III ratio of 33 was employed, which resulted in highly resistive GaAs layers which were slightly n-type with carrier concentrations of $\sim 3 \times 10^{14} \text{ cm}^{-3}$.

The growth pressure also influences the quality of the layers, although most of the early work on MOVPE growth of III-V layers was carried out at atmospheric pressure. Recently, low-pressure growth has been employed routinely, since parasitic reactions can be eliminated under these conditions, leading to lower incorporation of impurities such as carbon during growth. In our study we used a growth pressure of 76 Torr.

The growth rate is also dependent on both the position of the substrate on the susceptor and the carrier flow rate. We have used a number of carrier flows ranging from 2 slm (standard litre per minute) to 10 slm and found the best uniformity over a 5 cm wafer at 7.5 slm. The growth rate variation as a function of the longitudinal position of the substrate on the susceptor is shown in Fig. 1. Clearly, the growth rate decreases with an increase in the distance from the cell entrance region, suggesting depletion of reactants (group III mole fraction) along the cell. The growth rate is a function of the lateral distance across wafers for three different mole fractions of group III is shown in Fig. 2. From Figs 1 and 2 it can be seen that lower growth rates give improved longitudinal and lateral uniformity of layers for substrates placed at the same position on the susceptor.

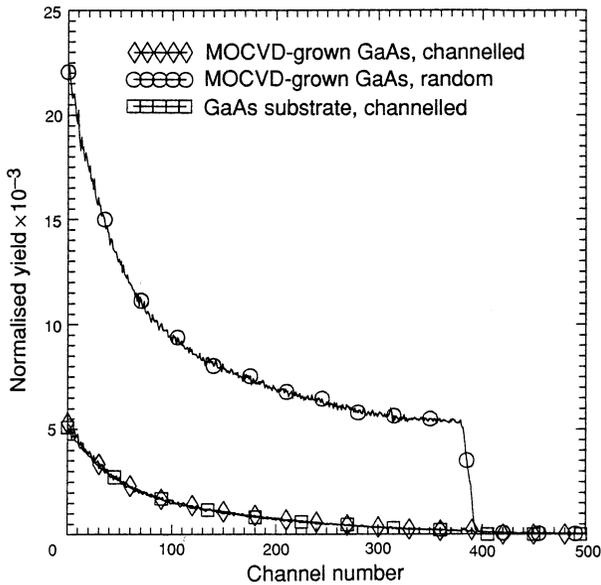


Fig. 3. RBS-C spectra of GaAs substrate (\square), epitaxial layer (\diamond) and random (\circ).

Electrical properties of the undoped GaAs layers grown at 650°C and at 76 Torr with a V/III ratio of 33 are shown in Table 1. These values are close to the best found in the literature (Stringfellow 1989). In order to verify the crystalline quality of the epitaxial layers, RBS-C studies were carried out; typical channelled spectra of an epitaxial layer, substrate and a random spectrum are shown in Fig. 3. These studies show that the χ_{\min} values of the epitaxial layers are comparable with that of the substrate. Photoluminescence (PL) studies were

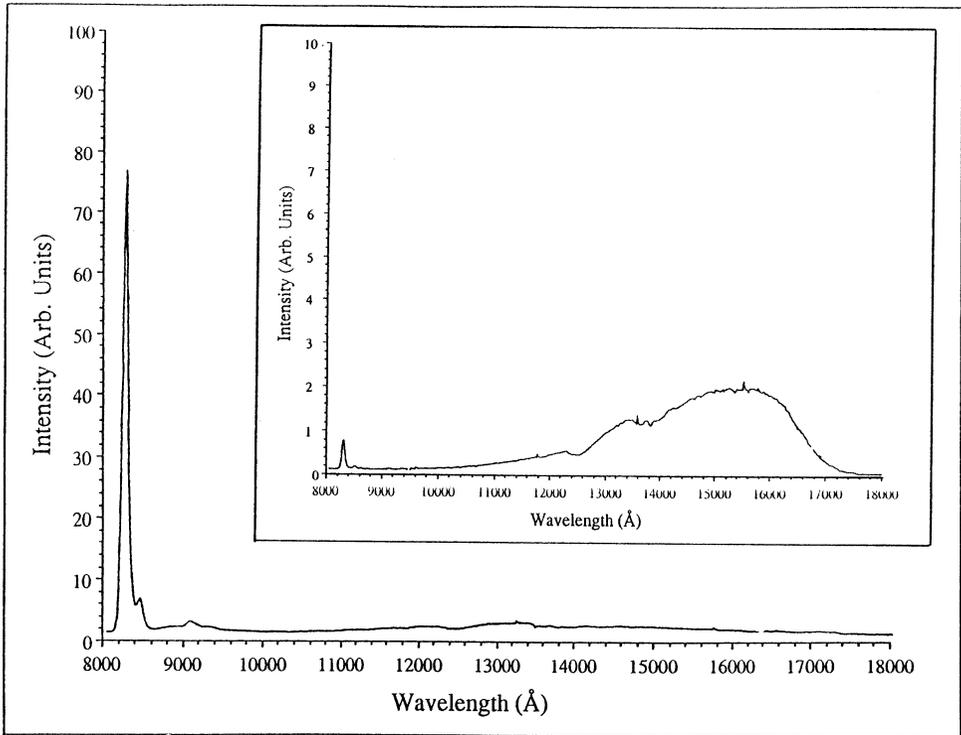


Fig. 4. Photoluminescence spectrum of an epitaxial layer of GaAs. Insert is a PL spectrum of the substrate.

also made on the undoped epitaxial layers of GaAs and a PL spectrum is shown in Fig. 4. For the sake of comparison, a PL spectrum of the substrate is also shown (inset) in this figure. The sharpness of the excitonic emission peak from the epitaxial layer suggests that the quality of such layers is good. Finally, deep level transient spectroscopy (DLTS) studies were made on an undoped epitaxial layer of GaAs. The DLTS spectrum in Fig. 5 shows two distinct peaks. The one at the high-temperature side of the spectrum is due to the EL_2 level and the other peak is possibly a carbon-related level. The concentration of the EL_2 defect, which is attributed to antisite defects (Stringfellow 1989) is of the order of $1 \times 10^{13} \text{ cm}^{-3}$.

(3b) Silicon-doped GaAs

Silicon-doped GaAs layers were grown on n^+ -GaAs substrates using a mixture of silane and hydrogen (100 ppm silane in hydrogen). In order to study the influence of various growth parameters on the dopant concentration, the silane flow was varied while the growth temperature and group III mole fraction were kept fixed. Electrochemical C-V profiling showed sharp doping interfaces (Fig. 8) in these samples corresponding to flow rate changes. The electron concentration is shown as a function of silane flow in Fig. 6. In order to achieve higher dopant concentrations, higher growth temperatures are needed (Bass 1979; Bottka *et al.*

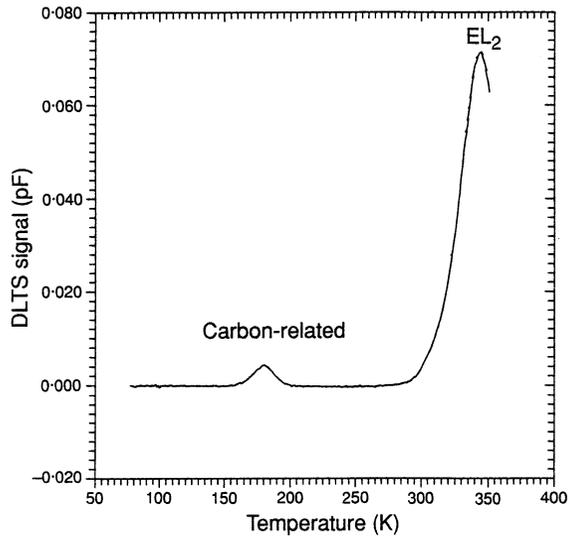


Fig. 5. A typical DLTS spectrum of an undoped GaAs epitaxial layer.

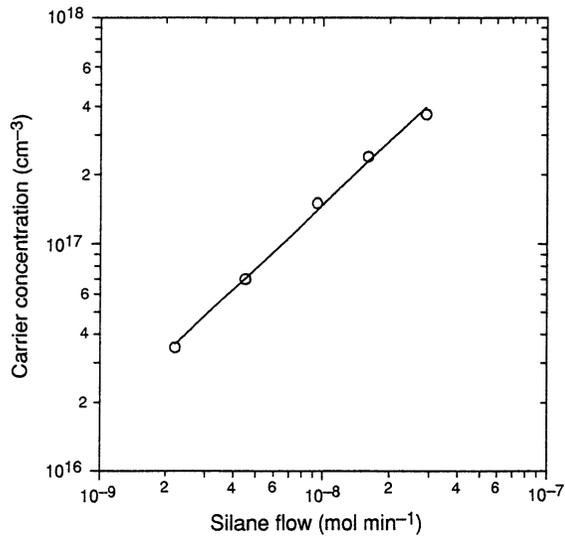


Fig. 6. Free electron concentration as a function of silane flow for a fixed group III flow (3.66×10^{-5} mol min⁻¹) at a growth temperature of 650°C.

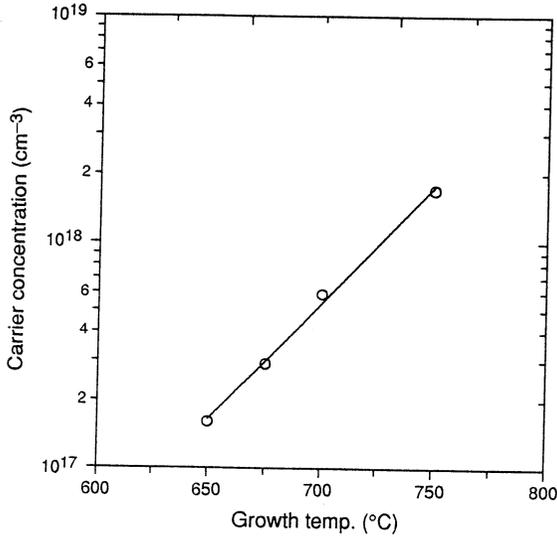


Fig. 7. Free electron concentration as a function of growth temperature for fixed group III (3.66×10^{-5} mol min⁻¹) and silane (9.4×10^{-9} mol min⁻¹) flows.

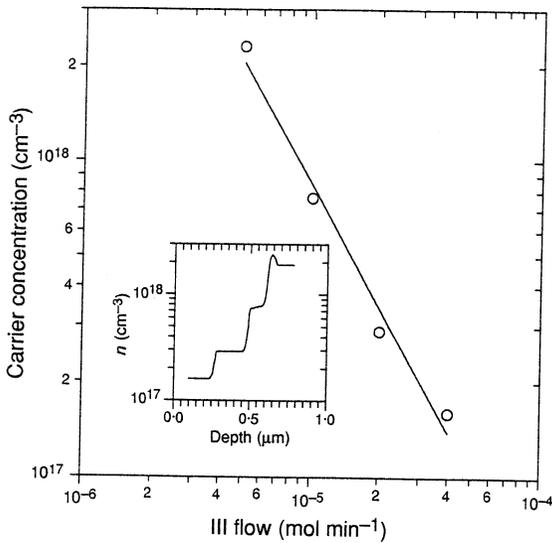


Fig. 8. Free electron concentration as a function of group III flow for a fixed silane flow (9.4×10^{-9} mol min⁻¹) at a growth temperature of 650°C. Inset shows the dopant profile as a function of depth obtained from electrochemical C-V profiler.

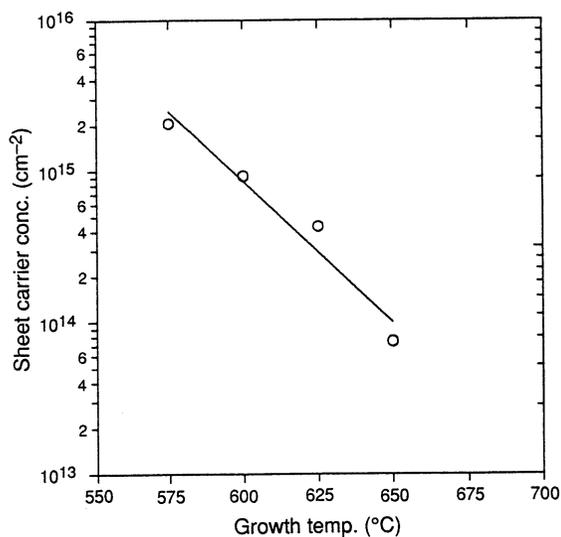


Fig. 9. Free hole concentration as a function of growth temperature for fixed DMZ (8.48×10^{-7} mol min⁻¹) and group III (2.39×10^{-5} mol min⁻¹) flows.

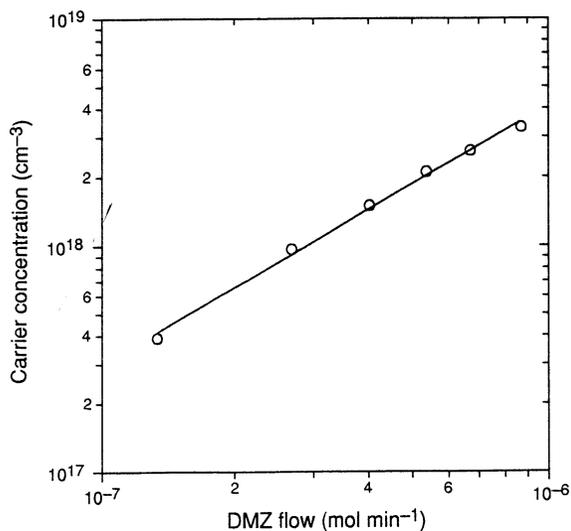
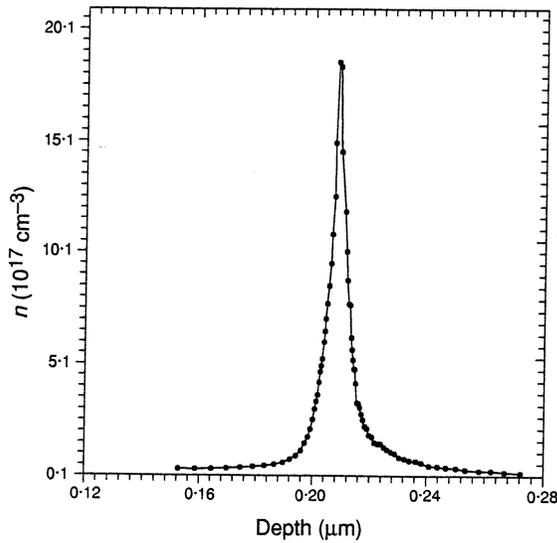


Fig. 10. Free hole concentration as a function of DMZ flow for a fixed group III flow (3.59×10^{-5} mol min⁻¹) at a growth temperature of 550°C.

Table 1. Electrical properties of undoped epitaxial layers of GaAs and $\text{Al}_{0.24}\text{Ga}_{0.76}\text{As}$

Material	Temperature (K)	Carrier concentration (cm^{-3})	Mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)
Undoped GaAs	Room temp. (290)	2.18×10^{14}	7618
	77	3.20×10^{14}	131 216
Undoped $\text{Al}_{0.24}\text{Ga}_{0.76}\text{As}$	Room temp. (290)	2.50×10^{15}	2120
	77	2.20×10^{15}	2381

**Fig. 11.** Doping concentration as a function of depth in a silicon-delta-doped GaAs layer grown at 650°C .

1984). To study the influence of growth temperature on the doping concentration, both the silane flow and the group III mole fraction were kept fixed and the growth temperature varied. An increase in carrier concentration with an increase in growth temperature can be seen in Fig. 7. This is due to the enhanced cracking of silane at higher temperatures, leading to increased doping efficiency. The influence of the group III mole fraction on the doping concentration is shown in Fig. 8. A decrease in carrier concentration with increasing group III mole fraction is observed. This observation can be explained in terms of the vacancy theory, whereby silicon, which usually occupies substitutional gallium sites in the lattice, is more likely to locate at As sites as the group III mole fraction increases. This leads to a reduction in doping efficiency.

(3c) Zinc-doped GaAs

A mixture of dimethylzinc (DMZ) and hydrogen (1000 ppm DMZ in hydrogen) is used as a dopant source for the growth of p-type layers of GaAs. The influence

of growth temperature and DMZ flow on the carrier concentration was studied. As shown in Fig. 9, an increase in the growth temperature leads to a reduction in the hole concentration. The reduction in carrier concentration with increasing growth temperature is attributed to the high elemental vapour pressure of zinc, which leads to evaporation from the growing surface (Bass and Oliver 1976). Although the morphology of undoped GaAs layers is poor at a growth temperature of 550°C, zinc-doped GaAs layers grown at 550°C showed good morphology. This is believed to be due to the enhanced cracking efficiency of arsine in the presence of zinc alkyls (Glew 1984). The carrier (hole) concentration as a function of DMZ flow is shown in Fig. 10 for a fixed group III mole fraction at a growth temperature of 550°C. An increase in DMZ flow leads to an increase in the free hole concentration in the epitaxial layers.

The above studies have led to the production of device-quality GaAs layers. Similar studies of AlGaAs have resulted in the ability to produce high quality GaAs/AlGaAs multilayer and low-dimensional structures for a range of applications. Electrical properties of $\text{Al}_{0.24}\text{Ga}_{0.76}\text{As}$ epitaxial layers grown at 750°C are shown in Table 1. Recently, the optimisation of growth parameters has allowed a significant research effort in the growth of GaAs on Si and also in the ultra-abrupt (δ) doping of GaAs with Si. Figure 11 shows the dopant profile of a silicon- δ -doped GaAs epitaxial layer. δ -doped layers with Full Width Half Maximum (FWHM) of the order of 50 Å were successfully grown. Detailed results of these studies will be reported elsewhere (Li *et al.* 1993).

4. Conclusions

Good quality epitaxial layers of undoped, silicon-doped and zinc-doped GaAs have been grown by optimising growth parameters. An increase in growth temperature is found to increase the doping efficiency of silicon, whereas in the case of zinc a reduction in doping was observed. The group III mole fraction is found to substantially influence the doping efficiency of dopants. Rutherford backscattering spectrometry with channelling (RBS-C) studies showed excellent crystallinity of these layers. Deep level transient spectroscopy and photoluminescence studies showed that the GaAs layers are of device quality with reduced levels of the EL_2 defect. Good quality AlGaAs and GaAs layers have also been produced on Si. These and recent studies of ultra-abrupt (δ) doping of Si will be reported elsewhere.

Acknowledgments

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