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Growth of high-quality Al$_x$Ga$_{1-x}$As ($x = 0.05–0.65$) by low-pressure metalorganic vapour phase epitaxy using dimethylethylamine-alane

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Abstract

High-quality Al$_x$Ga$_{1-x}$As ($x = 0.05–0.65$) has been grown by low-pressure metalorganic vapour phase epitaxy (MOVPE) using dimethylethylamine-alane (DMEAAl) as aluminium precursor. No temperature dependence is found for the growth rate or for the aluminium incorporation between $T = 575^\circ$C and $T = 725^\circ$C. The aluminium incorporation is linearly dependent on the fraction of DMEAAl in the gas phase. Photoluminescence (PL) measurements show a very low carbon incorporation, which is independent of the aluminium fraction and the growth temperature. Because of this low carbon content, the epilayers show $n$-type conductivity up to aluminium fractions of 0.65 and high carrier mobilities. Excitonic PL peaks show narrow linewidths that are comparable with the best values reported in the literature. This indicates that the impurity content is low and that compositional uniformity throughout the layer is very good. A multi quantum well with good PL properties has also been grown.

1. Introduction

There is a great interest in replacing the conventional aluminium precursor trimethylaluminium (TMAI) by alternative precursors in metalorganic vapour phase epitaxy (MOVPE) of Al$_x$Ga$_{1-x}$As. The use of TMAI in this process, especially in combination with trimethylgallium (TMGa), results in Al$_x$Ga$_{1-x}$As epilayers that contain significant concentrations of carbon [1]. This carbon contamination arises from the incomplete elimination of methyl groups from the mono-methylaluminium species during the growth. With respect to this point, some improvements can be made when triethylaluminium (TEAAl) is used [2]. However, TEAAl suffers from low volatility, which necessitates heating of source and reactor lines. This can lead to premature decomposition of TEAAl and, in turn, causes problems with uniformity of thickness and composition of the AlGaAs. An additional drawback of the use of TMAI in MOVPE growth of Al$_x$Ga$_{1-x}$As is its reaction with traces of oxygen leading to the formation of volatile alkoxides [3,4]. These alkoxides will incorporate in the Al$_x$Ga$_{1-x}$As epilayers and act as deep levels which decrease the photoluminescence intensity [5].

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Recent publications [6—8] demonstrated the successful use of the alternative aluminium precursor trimethylamine-alane (TMAAI), i.e. AlH3 · ((CH3)3N), for the MOVPE growth of AlxGa1−xAs. Because of the absence of a direct carbon—aluminium bond, it was expected that the growth with this precursor leads to a decrease of carbon incorporation as compared with using TMAI and TMGa. However, for both atmospheric and reduced-pressure MOVPE, no reduction of the carbon concentration was found using this precursor with TMGa. In case of the combination of triethylgallium (TEGa) and TMAAI, a significant reduction in carbon incorporation was reported [9]. Although these results with TMAAI are promising, the major drawback of this precursor is its high melting point (77—78°C). Being a solid at ambient temperature, it can cause the same problems with dosimetry as are encountered with trimethylindium (TMIn) [10,11]. Recently, Olsthoorn et al. [12] and Wilkie et al. [13] described the properties of AlxGa1−xAs grown with a related aluminium precursor: dimethylethylamine-alane (DMEAAI), i.e. AlH3 · (CH3)2(C2H5)N. This aluminium precursor has the same advantages as TMAAI over TMAI, but lacks the problem with dosimetry because it is liquid at room temperature [14]. PL measurements showed a very low intensity of the carbon acceptor emission along with high overall PL intensities and very narrow excitonic peaks [12]. Additionally, a recent publication demonstrates that the reaction products of DMEAAI with oxygen or water are non-volatile and are not likely to be incorporated [15].

In this paper we report the aluminium and carbon incorporation as a function of the gas phase concentration and growth temperature of MOVPE-grown AlxGa1−xAs with DMEAAI as the aluminium precursor. Finally, a multi-quantum well (MQW) structure is grown to investigate the quality of the AlxGa1−xAs/GaAs interface.

2. Experimental procedure

The experiments were carried out in a horizontal low-pressure MOVPE reactor at 20 mbar. All epilayers were grown with a V/III ratio ranging from 133 to 185, at temperatures between 575 and 725°C, and with a total gas flow of 7 SLM (i.e. a mean gas velocity of 228 cm/s). The growth was performed using arsine (AsH3), TEGa, TMGa and DMEAAI. Hydrogen, purified by a Pd diffusion cell, was used as a carrier gas. All epilayers were grown without buffer layers on (100) 2° or 4° off oriented towards (110) substrates.

Electrical properties were measured with the Hall—Van der Pauw technique at room temperature and with capacitance—voltage (C—V) measurements using a conventional C—V profiler. During growth the pressure of the DMEAAI was monitored with an ultrasonic gas concentration analyser. At 25°C and at an operating pressure of 1000 mbar, a pressure of 1.75 mbar for DMEAAI was measured, whereas at 500 mbar operating pressure this pressure was 3.35 mbar. These values are comparable with previous published results [13].

The PL measurements were performed at 4.3 K with the sample in helium exchange gas. Optical excitation was provided by the 2.41 eV (514.5 nm) line from an Ar+ laser with densities ranging from 2.6 × 10−4 to 2.6 W/cm² at a spot size of 3.8 × 10−2 cm². The luminescence was dispersed by a 0.6 m double monochromator and detected by a cooled photomultiplier tube with a GaAs photocathode.

The aluminium fractions x of the AlxGa1−xAs samples with direct bandgaps were calculated using Casey’s relationship [16]:

$$E_g(\text{Al}_x\text{Ga}_{1-x}\text{As}) = E_g(\text{GaAs}) + 1.247x,$$

where the bandgap ($E_g$) of AlxGa1−xAs was derived by the addition of the exciton binding energy as a function of x [17] to the energy of the free exciton peak. The aluminium fractions of the samples with indirect bandgaps were calculated according to Guzzi et al. [18]:

$$E_{(\text{D}^{0},\text{X})}(x) = 1.957 + 0.25x,$$

where $E_{(\text{D}^{0},\text{X})}$ represents the PL energy of the donor-bound exciton.
3. Results and discussion

3.1. Al incorporation as function of the input mole fraction DMEAAI

All the grown epilayers possessed mirror-like surfaces, independent of the input mole fraction DMEAAI, the gallium precursor, the growth temperature or the solid composition.

The aluminium incorporation in the Al$_{x}$Ga$_{1-x}$As epilayer is investigated as a function of gas phase composition at three different growth temperatures (625, 650 and 725°C), while the group III partial pressure and V/III ratio were kept constant. Most growth experiments were carried out using TEGa, since this is expected to be the most promising combination [12,13].

In Fig. 1, the solid composition of the Al$_{x}$Ga$_{1-x}$As epilayers is plotted versus the fraction of DMEAAI of the group III partial pressure ($X_{\text{gas phase}}$) for the three different growth temperatures. At all temperatures the same linear dependence between $X_{\text{gas phase}}$ and the solid composition is observed, with a slope of unity if $X_{\text{gas phase}} > 0.3$. This linear dependence simplifies the adjustment of the solid composition. For $X_{\text{gas phase}} < 0.3$ the slope is 0.5, which can be explained by a higher saturation rate of the hydrogen pick up gas because of the low flow rates required.

As the partial pressures of the group III compounds are near zero at the interface and as the diffusion coefficients of the two growth species will be about equal, a 1:1 relation between the fractions of aluminium in the gas phase and the solid phase is expected. Along with results presented in the next section on the temperature dependence of the aluminium incorporation and the growth rate, we conclude that the Al$_{x}$Ga$_{1-x}$As growth with TEGa and DMEAAI is diffusion-limited. This behaviour is due to the low decomposition temperatures of TEGa and DMEAAI. At the used growth temperatures both precursors are fully decomposed and, consequently, diffusion of growth species through the gas phase will determine the incorporation ratio.

In Fig. 1 the results are plotted of experiments with DMEAAI in combination with TMGa at $T_e = 625^\circ$C. This combination shows a similar behaviour of aluminium incorporation as the growth with TEGa and DMEAAI. However, the relative PL intensity of the carbon-related peak compared with that of the exciton peak is 10 times lower for samples grown with TEGa instead of TMGa under the same conditions. This strongly reduced carbon incorporation directed our research towards growth with TEGa.

We found that the growth rate of the Al$_{x}$Ga$_{1-x}$As epilayers is independent of the gas phase composition at a constant group III concentration, which shows a negligible influence of parasitic gas phase reactions, in contrast with results in Refs. [13,19].

3.2. Al incorporation as a function of the growth temperature

In Fig. 2 it is shown that the aluminium incorporation with TEGa and DMEAAI is almost constant over the growth temperature range of 575 to 725°C; $X_{\text{gas phase}}$ was 0.367 and the V/III ratio was 184 for these samples. The minor variations are within the uncertainty limits of the mass flow controllers. This independence of the growth rate
and the solid composition is again an indication that the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ growth with these precursors is limited by gas phase diffusion. Because of its insensitivity of the aluminium incorporation on the temperature, this diffusion-limited growth is advantageous for the fabrication of devices. Therefore, temperature variations across the susceptor, which are in practice always present in MOVPE reactors, do not lead to differences in aluminium composition or to variations in layer thickness.

3.3. Electrical characterization

Electrical measurements showed n-type conductivity for all $\text{Al}_x\text{Ga}_{1-x}\text{As}$ epilayers, even those with aluminium fractions of 0.65. In contrast, for the growth of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ with TMGa and TMAI, the layer changes from n- to p-type with increasing aluminium content. The n-type conduction in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers with low x values is caused by silicon impurities in the TMAI. The change in conduction type upon increasing x is caused by an increasing incorporation of carbon which originates from the TMAI. The absence of the direct carbon–aluminium bond in DMEAAI prevents this enhanced carbon incorporation.

A second remarkable property of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers is that the carrier concentrations obtained with C–V measurements show only little deviation from those obtained with Hall measurements. This indicates a low content of deep levels in the material because these levels are included in C–V, but not in Hall measurements.

DMEAAI contains silicon as the major contaminant in about the same concentrations as the conventionally used TMAI (<0.03 ppm), which explains the n-type conductivity of the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers. In Table 1 the carrier concentrations and mobilities are given for $\text{Al}_x\text{Ga}_{1-x}\text{As}$ layers with $x = 0.22$ grown at different temperatures. With increasing growth temperature, the carrier concentration increases as is expected for silicon doping [20]. The sample grown at 575°C shows a low mobility, indicating a high compensation ratio caused by enhanced carbon incorporation; this is confirmed by PL measurements (see Section 3.4). At $T_G = 625°C$ the highest mobility is recorded, indicating a good electrical quality and a relatively low compensation ratio. The remaining compensation can be caused by the incorporation of silicon at an As site or by other p-type impurities. The first is the case at the two highest temperatures, because at higher growth temperatures more silicon is incorporated at both lattice sites, thereby reducing the mobility.

In Table 2 the electrical results of epilayers with different aluminium fractions grown at a temperature of 725°C are presented. At all alu-

Table 1

<table>
<thead>
<tr>
<th>$T_{\text{growth}}$ (°C)</th>
<th>$n$ (cm$^{-3}$)</th>
<th>$\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>575</td>
<td>$2.3 \times 10^{15}$</td>
<td>1405</td>
</tr>
<tr>
<td>600</td>
<td>$1.7 \times 10^{15}$</td>
<td>3596</td>
</tr>
<tr>
<td>625</td>
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<td>4028</td>
</tr>
<tr>
<td>650</td>
<td>$1.7 \times 10^{16}$</td>
<td>3077</td>
</tr>
<tr>
<td>725</td>
<td>$2.6 \times 10^{16}$</td>
<td>3255</td>
</tr>
</tbody>
</table>

Table 2

<table>
<thead>
<tr>
<th>$x$</th>
<th>$n$ (cm$^{-3}$)</th>
<th>$\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
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<tbody>
<tr>
<td>0.05</td>
<td>$3.4 \times 10^{15}$</td>
<td>6946</td>
</tr>
<tr>
<td>0.11</td>
<td>$6.4 \times 10^{15}$</td>
<td>3736</td>
</tr>
<tr>
<td>0.21</td>
<td>$1.6 \times 10^{16}$</td>
<td>3255</td>
</tr>
<tr>
<td>0.45</td>
<td>$4.3 \times 10^{16}$</td>
<td>2180</td>
</tr>
<tr>
<td>0.64</td>
<td>$2.2 \times 10^{16}$</td>
<td>2280</td>
</tr>
</tbody>
</table>
The excitonic peak heights and the acceptor-related peak heights did not vary much between the samples (the one grown at 575°C showed a ratio of 0.4). We did not find a further significant influence of the growth temperature on carbon incorporation.

To minimize the broadening of the exciton peak by ionized impurities, this part of the spectrum was also recorded at an excitation density of \(2.6 \times 10^{-2}\) W/cm², as shown in the inset of Fig. 3. The linewidth (FWHM) of this bound exciton peak is then 2.8 meV. The alloy broadening in a perfectly random alloy was calculated to be 1.1 meV at an aluminium fraction of 0.22 by Singh and Bajaj [21]. This means that an additional 1.7 meV broadening in the exciton peak is caused by both ionized and non-ionized impurities, and by local variations in the composition. It is assumed that the additional 1.7 meV broadening is caused only by variations in alloy composition (which is not very likely), then by Eq. (1) the maximum compositional deviation \(\Delta x\) may be calculated. Thus the 1.7 meV broadening represents a deviation of less than 0.0014 in the absolute value of the aluminium fraction, both laterally (over the area of the laser spot size) and, more significantly, throughout the 2 \(\mu m\) depth of the epilayer, since the excitons are known to diffuse easily over such a depth [22]. This extremely good compositional uniformity throughout the depth of the layer is a result of using only group III precursors which are liquids at the temperature at which they are used, and consequently give very reproducible pick-up rates during a single growth experiment.

The excitonic linewidths of the other samples reported were also very narrow. We did not find a significant influence of growth temperature on these linewidths. This means that for all these temperatures the uniformity of the aluminium fraction throughout the depth of the epilayers was excellent.

In Fig. 4 we compare our narrowest excitonic linewidths of the AlₓGa₁₋ₓAs samples with direct bandgap with the theoretical values of the FWHM for perfectly random alloys, using both classical (dashed curve) [23,24] and quantum mechanical (solid curve) [21] calculations. Further-

![Fig. 3. PL spectrum of an AlₓGa₁₋ₓAs layer (x = 0.22) grown at 625°C using DMEAAl and TEGa recorded at an excitation density of \(2.6 \times 10^{-2}\) W/cm². The relative gain used to record the carbon peak with respect to the exciton peak is shown to the left. The inset of the figure shows the exciton peak recorded at an excitation density of \(2.6 \times 10^{-2}\) W/cm².](image.png)
more, the best experimental data as found in the literature for MOVPE grown Al$_x$Ga$_{1-x}$As are shown. The linewidths measured in this study are amongst the narrowest. Remarkable is the relatively large improvement of these linewidths as compared with those of samples grown with the other alternative aluminium precursors TMAAl and DEAlH-NMe$_3$.

Fig. 5 shows the 4.3 K PL spectrum of one of the Al$_x$Ga$_{1-x}$As samples with indirect bandgap ($x = 0.60$) recorded at an excitation density of 2.6 W/cm$^2$. The highest-energy peak is attributed to a no-phonon bound-exciton emission. This no-phonon transition from the conduction-band minimum at the X point to the valence-band maximum at the $I$ point (indirect transition) has a finite matrix element for optical transitions due to momentum conservation provided by the impurity. The other peaks at lower energies are replicas, where phonons provide the momentum conservation. The phonon energies in Al$_x$Ga$_{1-x}$As are well-known [30–32], so all peaks can be attributed easily. The two lowest energy peaks are replicas where two phonons are emitted. To our knowledge, this has never been reported in the literature for indirect bandgap Al$_x$Ga$_{1-x}$As. Furthermore, no acceptor-related peaks are detected, which again indicates that the carbon contamination in these epilayers is very low. No dependence on growth temperature was found: all Al$_{0.65}$Ga$_{0.35}$As spectra were exactly equal for growth at 625, 650 and 725°C.

Finally, apart from the sample grown at 575°C, all overall luminescence intensities were very high, indicating a low density of deep levels in the epilayers.

3.5. Applications of the AlGaAs growth: a multi-quantum-well

To investigate the abruptness of interfaces, a multi quantum layer was grown consisting of Al$_x$Ga$_{1-x}$As barrier layers with $x = 0.23$ and GaAs wells of different widths. In Fig. 6, the PL spectrum at 4.3 K of the multi quantum well is shown. Because the barrier layers were only 700
ration and the growth rate were independent of the growth temperature between $T = 575^\circ C$ and $T = 725^\circ C$. These two results are very advantageous, since this gas phase diffusion-limited growth eases the adjustment of the solid composition, and is an indication for the absence of parasitic gas phase reactions. The growth behaviour did not change when TEGa was replaced by TMGa; however, the carbon incorporation increased considerably.

Electrical measurements showed n-type conductivity for all epilayers, even those with high ($x = 0.65$) aluminium fractions. This, as well as the high mobilities, is a direct result of the low carbon incorporation which reduces the compensation in the layers. Layers grown at 625°C showed the best electrical quality, whereas those grown at 575°C resulted in material with a lower mobility caused by a high compensation ratio. Hall measurements showed carrier concentrations equal to those measured with $C-V$, which is an indication for a low density of deep levels.

Fig. 6. PL spectrum of the multi quantum well recorded at excitation densities of 2.6 W/cm² (AlGaAs part) and $2.6 \times 10^{-2}$ W/cm² (QW). Calculated well widths and PL linewidths (FWHMs) are indicated.

Å thick, the excitation density had to be higher to get a reasonable signal from this part of the sample. Due to this high excitation density, the AlGaAs excitonic peak is broader than those in Section 3.4. Due to diffusion of excitons from the cladding layers into the wells, the intensity of the AlGaAs exciton-peak is lower than those of uniform epilayers of Section 3.4. The thicknesses of the wells are calculated to be 25, 42 and 76 Å, respectively. The linewidths (FWHM) of the well peaks are very narrow, and for two of them even below the values for the FWHM which can be calculated for fluctuations in well thickness of 1 monolayer [33]. The fact that our linewidths are much narrower (and so the interfaces sharper) than those of quantum wells grown with TMAAl and TEGa [34] again shows the advantages of the use of liquid precursors.

4. Conclusions

Al$_x$Ga$_{1-x}$As layers have been grown with low-pressure MOVPE using DMEAAI in combination with TEGa. A linear dependence was found between the aluminium fraction in the solid state and the fraction of DMEAAI in the gasphase. Furthermore, the aluminium incorporation and the growth rate were independent of the growth temperature between $T = 575^\circ C$ and $T = 725^\circ C$. These two results are very advantageous, since this gas phase diffusion-limited growth eases the adjustment of the solid composition, and is an indication for the absence of parasitic gas phase reactions. The growth behaviour did not change when TEGa was replaced by TMGa; however, the carbon incorporation increased considerably.

Electrical measurements showed n-type conductivity for all epilayers, even those with high ($x = 0.65$) aluminium fractions. This, as well as the high mobilities, is a direct result of the low carbon incorporation which reduces the compensation in the layers. Layers grown at 625°C showed the best electrical quality, whereas those grown at 575°C resulted in material with a lower mobility caused by a high compensation ratio. Hall measurements showed carrier concentrations equal to those measured with $C-V$, which is an indication for a low density of deep levels.

PL measurements showed that the carbon incorporation is indeed very low (except for the layer grown at 575°C); they showed no variations with growth temperature or aluminium fraction. The linewidths of the bound exciton peaks are comparable with the best values reported in the literature. This implies a low concentration of unintentional impurities and an extremely good uniformity of the aluminium content throughout the depth of the layers. This is a direct result of using only liquid precursors. The overall PL intensities were very high, which is again an indication for a low density of deep levels. A multi quantum well (MQW) was grown with very narrow PL linewidths, indicative of very sharp interfaces.

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