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A study of Indium incorporation efficiency in InGaN grown by MOVPE

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Abstract

InGaN/GaN heterostructures have been deposited by MOVPE onto (0 0 0 1) sapphire substrates. It has been noted that the Indium incorporation efficiency depends on different growth parameters, namely the growth rate, reaction kinetics and partial pressure of H_2 in the reaction cell. In this work the InGaN composition has been investigated by different techniques and the incorporation efficiency of indium is then correlated with substrate temperature, substrate rotation, H_2 partial pressure and input flows of TMG and TMI.

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1. Introduction

Nitride semiconductors are nowadays widely applied in opto-electronic and micro-electronic device fabrication. InGaN alloys are in particular needed for fabrication of green-blue LEDs, either with simple p/n junction or with quantum well structures [1,2]. It must be noted that the larger the In molar fraction the smaller the bandgap energy. Correspondingly, the emission wavelength of the ternary alloys varies from UV in the case of very low In content ($<3\%$) to green when the In fraction is $>20\%$. Despite the rapid advances of preparation technology, which has driven the marketing of many nitride-based devices, many growth aspects are still not entirely known and deserve further investigation: for example, it is very important to define which growth parameters are more suitable for controlling the final In/Ga ratio in the epilayers. Therefore, in this study the In fraction of the ternary alloy was varied by imposing different growth parameters. A series of InGaN samples were grown under different total gas flow, substrate rotation, substrate temperature, different carrier gas (N_2 or N_2+H_2 mixture), and ratio between TMG and TMI. The principal results are as follows: (i) the hydrogen partial

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pressure in the reactor has a strong influence on the In incorporation, i.e. the higher the H_2 partial pressure the lower the In molar fraction in the solid; (ii) the higher substrate rotation leads to higher growth rate and, consequently, to an higher In molar fraction incorporated in the layer; (iii) the In incorporation is more effective at lower growth temperature; (iv) growing under higher TMG flow and constant TMI flow (nominally more Ga available in the gas phase) results in a higher In incorporation; therefore, surprisingly, the higher Ga/In ratio in the gas phase produces layers with smaller Ga/In. Some of the above-mentioned results are not entirely new as other authors have previously reported similar findings corresponding to individual parameters [3–8], however, to our knowledge, this is a complete assessment of the InGaN epilayers, that takes into account all growth parameters. As it will be clear from the discussion of experimental data, it can be said that the In incorporation ultimately depends on growth rate, reaction kinetics and partial pressure of H_2.

2. Experimental procedure

The InGaN epilayers presented in this work were grown in an atmospheric pressure cold-wall vertical MOVPE reactor with shower configuration. Standard ammonia, TMG and TMI precursors were employed, while N_2 was always used as main carrier gas. However, H_2 was also introduced into the reactor through two channels: first, it was always used as carrier gas for the alkyls and, second, in controlled amounts via an additional make-up line. This allowed for an investigation about the role of the overall H_2 partial pressure in controlling the In incorporation. The TMG precursor was delivered to the reactor via a double-dilution line, which allows to change the Ga molar fraction while maintaining constant the hydrogen flow injected into the growth chamber. The TMI was instead introduced via a standard single-dilution line, where a given hydrogen flow enters into the bubbler and drags a quantity of TMI dependent on the temperature and the bubbler pressure controlled, respectively, by a thermostatic bath and an on-line pressure controller. Obviously with this system the TMI molar fraction delivered to the growth chamber is always proportional to the hydrogen flow.

The 2″ sapphire substrates were rotated about their axis at rates varying between 120 and 750 rpm whereas the deposition temperature of the InGaN film was changed between 800°C and 840°C.

The standard heterostructure included a 80–100 nm thick GaN buffer grown at 510°C, a 600 nm thick GaN layer deposited at 1080°C (typical V/III ratio was about 7000) on the top of which the ternary alloy was deposited under the variable conditions reported above. The epilayers were characterised by PL at 12 K using an He–Cd laser (line at 325 nm) for sample excitation. The emitted radiation was collected and focused by quartz lenses through the input slit of a 1 m monochromator and then detected by a bi-alkali photomultiplier and standard chopper/lock-in detection chain. The In composition was further studied by X-ray diffraction (standard $\theta/2\theta$ diffractometer) assuming that the lattice parameter varies linearly with the In fraction according to Vegard's law. The results of PL and X-ray characterisation showed that the ternary InGaN alloy exhibits a marked bowing effect, in agreement with previous reports [9,10].

3. Results and discussion

In order to discuss the mechanisms that govern the Indium incorporation in $In_xGa_{1-x}N$ it is useful to introduce the Indium incorporation efficiency η, defined as:

$$\left(\frac{M_{In}}{M_{Ga}}\right)_{Alloy} = \eta \left(\frac{M_{In}}{M_{Ga}}\right)_{Gas\ \ phase},$$

where M_{In} and M_{Ga} are the molar fraction of indium and gallium in the gas phase or in the solid. The reported values for η are commonly low, of the order of 0.02–0.3 [8,11,14], so that it is usual to provide a very large M_{In}/M_{Ga} fraction in the gas phase (as large as 1–1.5) to obtain a solid alloy with an In fraction as low as 0.04–0.10.

Let us first consider the dependence of In incorporation on the vapour phase composition.

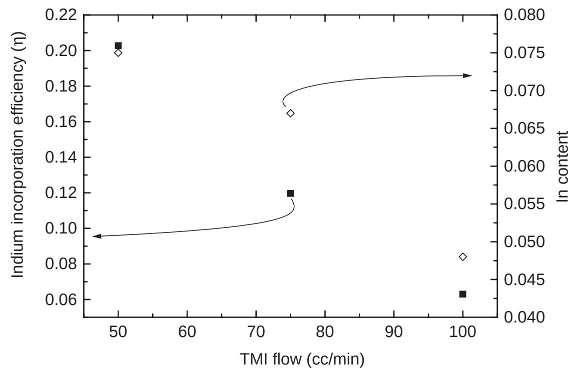

Fig. 1. In incorporation efficiency and In content in $In_xGa_{(1-x)}N$ alloy for three samples grown under identical conditions except for the TMI flow (the carrier gas for TMI is hydrogen). Growth temperature was 840°C and substrate rotation 750 rpm. No additional hydrogen flow was injected through the make up lines.

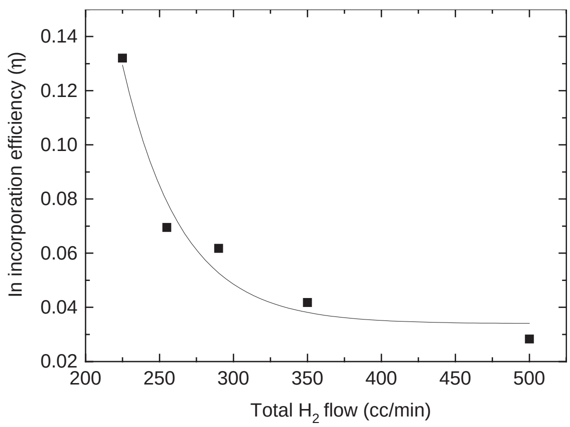

Fig. 2. In incorporation efficiency vs. additional H_2 flow introduced in the reactor. All the parameters (including the total gas flow) besides H_2 flow were kept constant. The experimental points are fitted by an exponential function.

Fig. 1 shows the indium incorporation efficiency and the In content of three InGaN layers grown at the same temperature (840°C), with constant TMG, ammonia and N_2 flows but different TMI flows. Surprisingly, the sample grown under the lowest TMI flow is found to produce the largest In content in the alloy. As with our metal-organic bubbler configuration the increase in the TMI flow means to simultaneously increase also the hydrogen in the growth chamber, the behaviour of Fig. 1 suggests that the addition of even a small amount of hydrogen in the gas phase drastically affects the In incorporation in the alloy. To further clarify this aspect, a series of samples was grown under identical conditions with regard to temperature, flow-dynamics (same total gas flow, including $NH_3+N_2+H_2$), TMG and TMI partial pressure in the reactor. Only the partial pressure of H_2 was varied from run to run, by changing the H_2 flow through the makeup lines. The result is reported in Fig. 2, where η is plotted as a function of the total H_2 flow. The result clearly shows that the higher the H_2 flow the smaller the In incorporation efficiency, in agreement with what reported in Refs. [3,6]. The reason for such a behaviour is still not entirely clear: the thermodynamic calculations of Koukitu et al. [4] suggests that the addition of H_2 to the growth environment can slow down the reaction between NH_3 and TMI, since H_2 is a by-product of the growth reaction $In(g) + NH_3(g) \rightleftharpoons InN(s) + \frac{3}{2}H_2(g)$, and adding H_2 to gas phase shifts the equilibrium towards left.

Another possibility is that In atoms might react with hydrogen to form hydride compounds, that results in a gas phase depletion of indium and thus lowers the amount of In available for incorporation in the crystal, as suggested in Ref. [6].

Although there is some ambiguity about the actual role played by hydrogen, these experimental results prove however that the presence of a variable amount of this gas is crucial in determining the indium incorporation in InGaN, otherwise from other ternary compounds like InGaP, where In incorporation is always found to be proportional to the In partial pressure in the vapour phase [12].

We also observed that the substrate rotation has a remarkable influence on the growth rate of the layer. This is a well-known flow-dynamic effect which finally improves the mass transport from gas phase (basically the rotating substrate acts as a fan which sucks axially the fluid and expels it tangentially). In particular, theoretical calculation for a vertical reactor with rotating substrate demonstrates [15] that the boundary layer thickness is inversely proportional to the square root of the rotation rate. The InGaN samples of Fig. 3 were deposited under the same conditions except

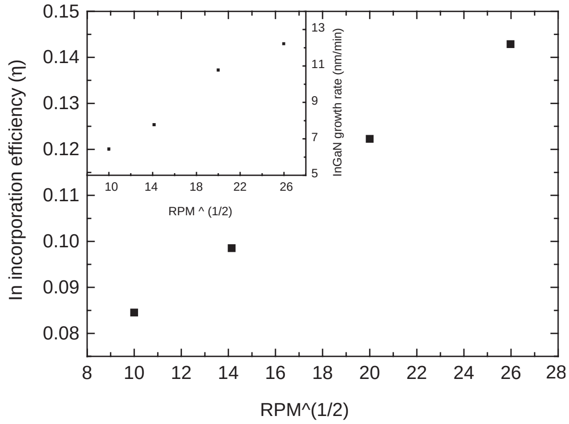

Fig. 3. Effect of the substrate rotation on In incorporation efficiency. The inset shows the dependence of the growth rate on the substrate rotation. All growth parameters except substrate rotation were kept constant for all the samples.

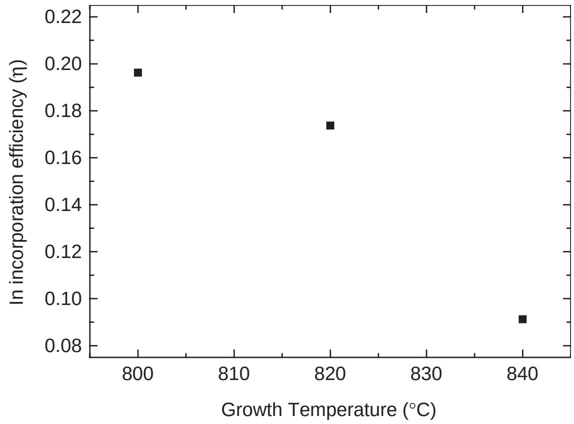

Fig. 4. In incorporation efficiency vs. growth temperature. The other growth parameters are the same for all the samples. In particular, In/Ga ratio in the gas phase was set to 0.80.

for the rotation speed that was varied between 100 and 675 rpm: in this range the dependence of Indium incorporation efficiency vs. $\text{rpm}^{1/2}$ is seen to be practically linear. In the same figure we also plotted the dependence of the InGaN growth rate on the rpm square root (see inset), which is found to behave very similar to the In incorporation. One has to conclude that higher rotation rates correspond to higher growth rates and, ultimately, to higher In incorporation efficiency. The fact that both growth rate and incorporation efficiency go as $\text{rpm}^{1/2}$ suggest that the effect is primarily connected with the reduction of the boundary layer thickness.

The substrate temperature during deposition was also found to strongly affect the growth rate and In incorporation. Fig. 4 reports the indium incorporation efficiency as a function of the reactor temperature for three different epilayers grown with the same parameters but temperature: a change in InGaN growth temperature from 840°C to 800°C permits to double the Indium incorporation efficiency.

All experimental results showed above bring about the question of the most appropriate procedure for controlling the In molar fraction in InGaN alloys. One could think that an appropriate setting of the $M_{\text{In}}/M_{\text{Ga}}$ molar ratio in the gas phase is the easiest way to achieve the desired composition in the solid. However, our results demonstrate that this approach is absolutely not straightforward. Actually, Table 1 shows two different pairs of samples grown under the same parameters except for the TMG molar fraction in the gas phase. Surprisingly, for both pairs, the larger In fraction is found in the epitaxial film grown under larger TMG flow. Let us consider the pair grown at 800°C, with 8.81×10^{-6} mol/min of In and with total 140 sccm H_2 flow into the reactor: sample 78 was grown using 4.6×10^{-6} mol/min of Ga whereas sample 80 was grown under 10.5×10^{-6} mol/min of Ga. The final $M_{\text{In}}/M_{\text{Ga}}$ fraction in the epilayers was 0.149 and 0.204, respectively. The same fact is observed for the pair grown at 810°C, with 4.41×10^{-6} mol/min of In and with total 250 sccm H_2 flow. Here, sample 71 grown under 8.7×10^{-6} mol/min of Ga presented a $M_{\text{In}}/M_{\text{Ga}}$ of 0.058 in the solid and sample 70 with 13.1×10^{-6} mol/min of Ga in the vapor phase exhibited a solid with $M_{\text{In}}/M_{\text{Ga}} = 0.070$.

This proves that, contrarily to what one could have expected, the addition of a larger amount of Ga into the gas phase leads to a lower amount of Ga in the crystal, i.e. to a much higher efficiency of In incorporation. We explained this experimental observation by considering the strong tendency of Indium to desorb [13]. The larger

Table 1
Comparison between two pairs of InGaN layers; to each pair correspond identical growth parameters except for the TMG flow

Sample no.	Growth temperature(°C)	H_2 flow (sccm)	TMI ($\times 10^{-6}$ mol/min)	TMG ($\times 10^{-6}$ mol/min)	M_{In}/M_{Ga} gas phase	M_{In}/M_{Ga} alloy
71	810	250	4.41	8.7	0.507	0.058
70	810	250	4.41	13.1	0.336	0.070
78	800	140	8.41	4.6	1.828	0.149
80	800	140	8.41	10.5	0.801	0.204

amount of Ga in the growth chamber, may indeed hinder the In desorption since the upper layer face is exposed to the atmosphere for a shorter time (higher Ga coverage rate, i.e. growth rate).

Lowering the growth temperature is another way to reduce the In desorption rate as the In adatoms have less energy available to break the weak bonds at the surface. This is consistent to what was shown in Fig. 4 where the lowest substrate temperature gives the highest In incorporation efficiency. It should also be mentioned that other authors suggested, on the basis of thermodynamic calculations, that at elevated temperatures homogeneous nucleation of In clusters in the gas phase may be favoured [14]. These small particles could be transported out of the reactor by the carrier gas, with the consequent In impoverishment of the nutrient phase. According to these authors the lower reactor temperature tends to decrease the occurrence of clustering thus increasing the overall incorporation efficiency of the process.

Based on the set of results presented above, we came to the conclusion that once the MOVPE growth parameters have been optimised in view of good layer morphology, planarity and thickness uniformity, it is convenient to control the In fraction in the solid film just by acting on the flow of added H_2. The advantage is that one can control the In molar fraction in the solid over a wide range (see Fig. 2) simply by changing the H_2 flow of ± 50 sccm, i.e. without significantly changing the flowdynamic conditions. We have prepared in this way quantum wells and multi-quantum wells with excellent optical properties. These quantum structures are being investigated with TEM in order to assess the sharpness and quality of the interfaces, which will be the object of a forthcoming publication.

4. Conclusions

The effect of several growth parameters on In incorporation in InGaN alloys was studied. Namely, the presence of H_2 in the growth reactor, the substrate rotation speed, the deposition temperature, the gas phase composition were seen to have a strong influence on the final epilayer composition. Some of these parameters are strictly interconnected so that changing one of them may produce results opposite to expectations. Therefore, one has to precisely and simultaneously control several growth parameters in order to keep the In incorporation under control. The present results however suggest that the indium incorporation efficiency ultimately depends on the ability of the growth system to efficiently provide In adatoms and to limit the In desorption. The first instance requires an effective mass transport, for example by increasing the substrate rotation rate or decreasing the partial pressure of hydrogen, which has deleterious effects on the speed of alloy formation reaction and may "steal" In atoms via spurious reactions. The question of desorption may be faced either decreasing the growth temperature (compatibly with precursors cracking and generation of extended crystallographic defects) or using larger amount of Ga in the gas phase (i.e. higher growth rates). We also suggested that InGaN heterostructures with layers of variable In content can be obtained by varying the additional flow of H_2.

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