A study of In incorporation in InGaN layers grown by atmospheric pressure MOVPE

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Abstract

InGaN/GaN heterostructures have been deposited by MOVPE onto (0001) sapphire substrates. It has been noted that the Indium incorporation efficiency depends on different growth parameters, always amenable to growth rate, reaction kinetics and partial pressure of H_2 in the reaction cell. In this work the composition of InGaN alloys, studied by photoluminescence and X−ray diffraction, is correlated with substrate temperature, substrate rotation, H_2 partial pressure and input flows of TMG and TMI.

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. The larger the In molar fraction the smaller the bandgap, which passes from UV emission in the case of very low In content (< 3%) to green emission when the In fraction is > 20 %. It is important to define which growth parameters are more effective in controlling the final In/Ga ratio in the epilayers. Therefore, in this study the In fraction in the crystal, determined by photoluminescence (PL) and X−ray diffraction, is varied by imposing different growth parameters. Namely, we grew the samples under different total gas flow, H_2 flow, substrate rotation, substrate temperature and ratio between TMG and TMI and we observed the following results: i) higher substrate rotation corresponds to higher growth rate and higher In molar fraction; ii) growing under different 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, iii) the hydrogen partial 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, iv) the In incorporation is more effective at lower growth temperature. These results are not entirely new as other authors reported similar findings corresponding to the individual parameters[1−4], however, to our knowledge this is a complete assessment of the InGaN epilayers, that takes into account all growth parameters. As it will be apparent from the discussion below, it can be said that the In incorporation ultimately depends on growth rate, reaction kinetics and partial pressure of H_2.

Experimental

The InGaN epilayers presented in this work were grown in a atmospheric pressure vertical MOVPE reactor having a "shower head" configuration. Standard ammonia, TMG and TMI precursors were employed, while N_2 was always taken as main carrier gas. However, H_2 was also voluntarily introduced into the reactor through two channels: first, 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 2" sapphire substrates were rotated about their axis at rates varying between 120 and 750 rpm whereas the deposition temperature of the ternary alloy was changed between 800 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 on the top of which the ternary alloy was deposited under the conditions reported above. The epilayers were characterized 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 θ/2θ diffractometer) assuming that the lattice parameter varies linearly with the In fraction according to Vegard's law. The results of PL and x−ray characterization show that the ternary InGaN alloy exhibits a marked bowing effect [5] (bowing parameter ~ 3.07, according to our estimates [6]).

Results and discussion

The addition of hydrogen to the gaseous precursors was seen to have a drastic effect on the In incorporation efficiency. This is evidenced in Figure 1 where we plotted the In fraction incorporated in the alloy as a function of the total H_2 flow. These samples were grown under identical conditions with regard to temperature, flowdynamics (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 clearly shows that the higher the H_2 flow the smaller the In incorporation efficiency, in agreement with what reported in ref. [1,4]. The reason for such behavior is not entirely clear: perhaps the addition of H_2 to the growth environment can slow down the reaction between NH_3 and TMI due to the fact that H_2 is a reaction byproduct. This is suggested by the thermodynamic calculations of Koukitu et al. [2]. However, there can also be the possibility for In atoms to form hydride compounds [4].

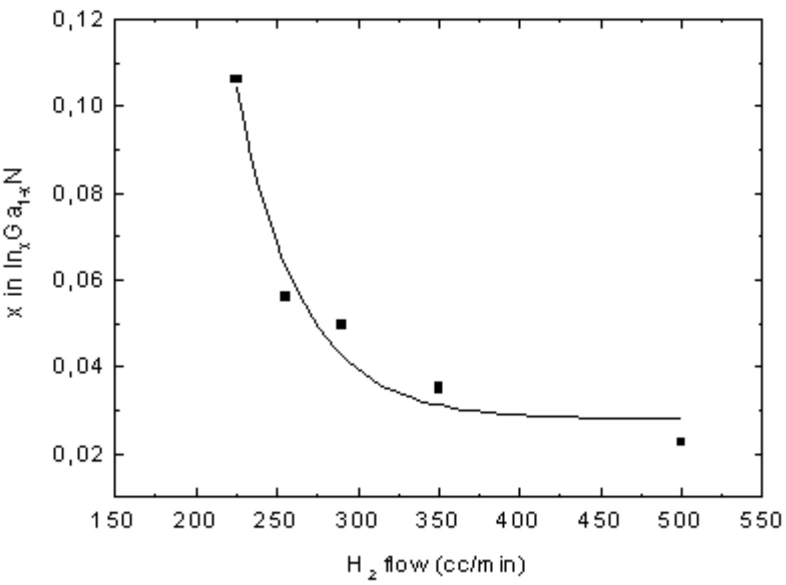

Fig. 1: In content in In_x Ga_{1-x} N alloy vs H_2 flow introduced in the reactor through a make up line. The experimental points are fitted by an exponential decay function.

We observed that the substrate rotation has a remarkable influence on the growth rate of the layer. This is a well known flowdynamic effect (basically the rotating substrate acts as a fan which "sucks" axially the fluid and expels it tangentially) which finally improves the mass transport from gas phase. Therefore, higher rotation rates correspond to higher growth rates and, consequently, to an increase of the In incorporation as shown in Figure 2. The two InGaN samples of Fig. 2 were deposited under the same conditions except the rotation speed that was in one case 120 rpm and in the other 675 rpm. The higher speed resulted in a 18% higher growth rate, while the In molar fraction passed from 0.15 to 0.16.

In Figure 3 we have plotted the indium incorporation efficiency (defined as $[X_{In}/X_{Ga}]_{solid}/[X_{In}/X_{Ga}]_{vapor}$) as a function of the reactor temperature for three different epilayers. Here we considered the incorporation efficiency since the TMG and TMI input flows were also varied together with the temperature. However, it is important to note that the temperature is the dominant parameter as the sample with the lowest $[X_{In}/X_{Ga}]$ in the gas phase exhibits the highest $[X_{In}/X_{Ga}]$ in the epilayer, just because it was grown at the lowest temperature. The latter observation brings 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 TMI/TMG molar ratio in the gas phase is the easiest way to achieve the desired composition in the solid.

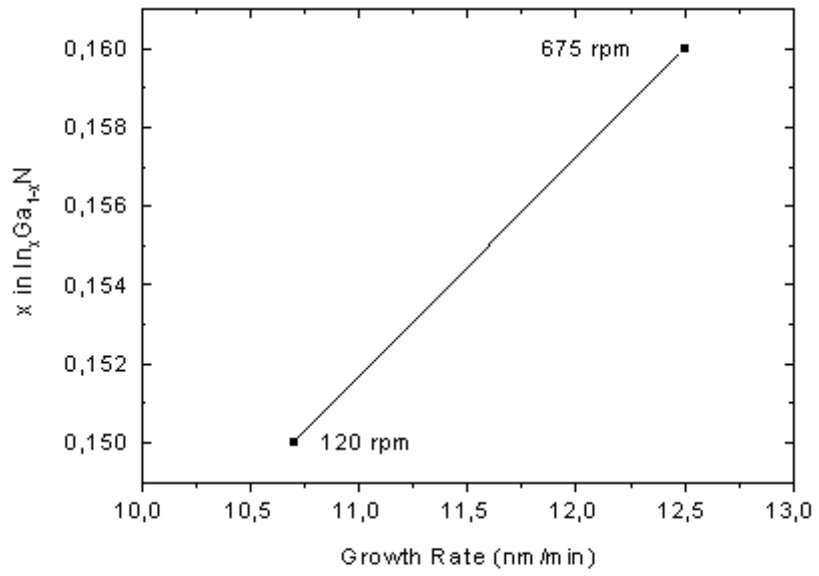

Fig. 2: Effect of the growth rate (determined by substrate rotation) on In incorporation in the alloy

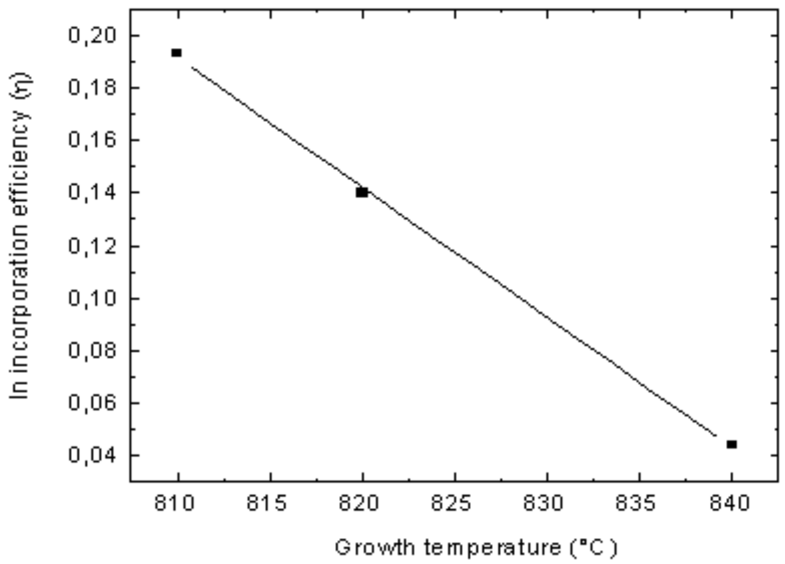

Fig. 3: In incorporation efficiency η vs. growth temperature.

However, our experimental results demonstrate that this approach is absolutely not straightforward. For example, Figure 4 shows two pairs of samples grown under the same parameters but the TMG molar fraction in the vapor phase. It is surprising that, corresponding to larger TMG flows, a larger In fraction is found in the epitaxial film. The reason for this experimental fact can only lie in a change of growth rate. Let us consider the upper pair, grown at 800 °C, with 8.81 µmol/min of In and with total 140 sccm H_2 flow into the chamber: sample 78 was grown using 4.6 µmol/min of Ga whereas sample 80 was grown under 10.5 µmol/min of Ga. The final In fraction in the epilayers was 0.13 and 0.17, respectively.

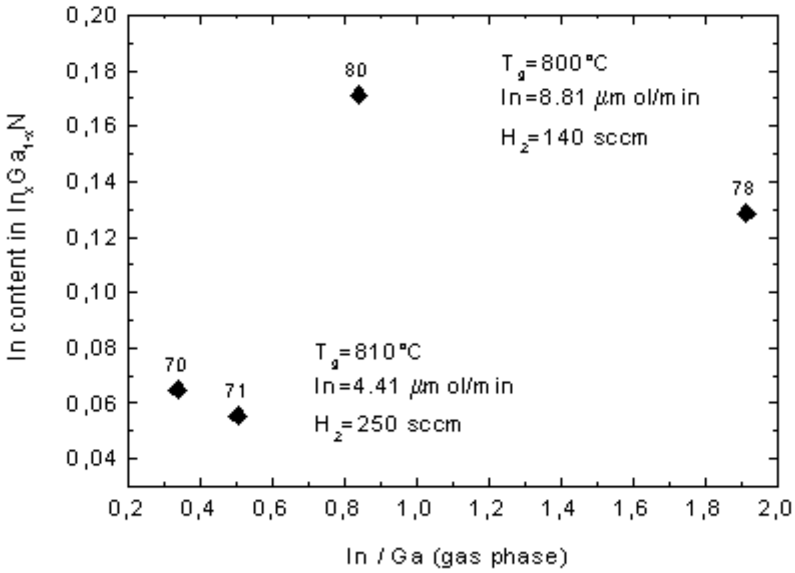

Fig. 4: In incorporation vs molar ratio In/Ga in the gas phase.

The same fact is observed for the lower pair which is grown at 810 °C, with 4.41 μmol/min of In and with total 250 sccm H_2 flow. Here, sample 71 grown under 8.7 μmol/min of Ga resulted in a In molar fraction of 0.055 in the solid and sample 70 with 13.1 μmol/min of Ga in the vapor phase exhibited a solid with In content of 0.065. This proves that, contrarily to what may be expected, the addition of a larger amount of Ga into the gas phase leads to a lower amount of Ga in the crystal. A probable explanation for this evidence is based on the lower desorption of In corresponding to the higher growth rate produced by the larger Ga availability.

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 growth rate (rotation speed), the substrate temperature, the gas phase composition have a strong influence on the final epilayer composition. These parameters were found to be strictly interconnected so that changing one of them may produce results opposite to expectations. For example, the addition of a larger amount of Ga into the gas phase leads to a lower amount of Ga in the crystal. Therefore, one has to take into account the In segregation phenomena and many growth parameters in order to put the In incorporation under control.

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