Influence of In on the surface morphology of HVPE grown GaN

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Abstract

In this paper, a study is presented on the effect of In on the surface morphology of GaN grown by HVPE. Experiments are performed with N2 and H2 as the carrier gasses, both with and without In present in the reactor. The adding of In increases the morphological quality of the grown layers; this effect is most strongly observed for N2 as the carrier gas. It is found that adding In reduces the growth rate and also increases the steepness of the growth hillocks on the surface. The step velocity, which is calculated from hillock slopes and the growth rate, decreases upon adding In. Without In, trails are visible across the surface where steps are distorted by passing a dislocation outcrop. With In present this pinning is still present, however, the trails do not form. Two possible explanations for this phenomenon are an increased surface diffusion due to a mono- or bi-layer of In on the surface and the slower step motion when In is present.

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1. Introduction

In many systems of semiconductor growth the use of isoelectronic doping is shown to improve the quality of the layers. Especially the use of In and InAs for GaAs and InP is well known for improving the crystalline quality of the layer [1]. Ideally, the isoelectronic doping improves the morphology and does not get incorporated into the crystal lattice, i.e. it behaves as an ideal surfactant. For GaN, such an effect of improving quality has been shown for the addition of In during the growth by both metal-organic chemical vapour deposition (MOCVD) and molecular beam epitaxy (MBE) [2–6].

In MBE the addition of In to the system results in more uniform growth [2], and in the improvement of the morphological and optical properties of the grown GaN layer. It is stated that In acts as a surfactant, modifying the surface kinetics and increasing the Ga mean free path at the surface, allowing 2D growth. Indium is an interesting material to be used as a surfactant. The weaker In–N bond as compared with the Ga–N bond is the main driving force for surface segregation of In and little In will be incorporated: no alloying will take place. The same effects have been observed in MOCVD growth. Experiments with In as surfactant for MOCVD growth of GaN at 950°C showed that In was incorporated at a level less than 0.001% [7]. Further, the surface morphology as well as the optical properties improve [3–5]. Like in MBE, this is attributed to In modifying the growth kinetics [4, 6]. In addition, the dislocation density reduces and the formation of deep energy levels is suppressed [8, 9]. Both in MBE and MOCVD the addition of In to the growth system leads to better quality layers. In a theoretical paper [6], this is explained by the formation of an In mono- or bi-layer at the surface. This layer facilitates the diffusion of N over the surface and leads to better quality material. These calculations were performed for a substrate temperature of 827°C, which is a lower temperature than used for MOCVD growth. However, in Ref. [3] experimental
evidence of In acting as a surfactant is shown for the higher temperature of 1100 °C.

On the effect of isoenergetic doping of GaN with In in

the HVPE growth of GaN, to our best knowledge no publications are available. The growth of pure InN by HVPE has been tried. Because of the high dissociation pressure of InN only growth at low temperatures is possible. Depending on the choice of precursors (InCl or InCl₃), the growth temperature for pure InN varies from 530 to 750 °C [10–13]. In order to grow alloys of InGaN, the growth temperature also needs to be low. This does not promote obtaining good quality layers [14], moreover, still only very little In can be incorporated. Besides the temperature also the carrier gas is important, growth of InN is faster in an inert carrier gas, like N₂ or He [12].

Since in both MOCVD and MBE In is found to act as a surfactant, it might also play this role in the HVPE growth of GaN. Because the growth temperature is high, no or very little In is expected to be incorporated into the layer. However, the positive effects of In on the quality of GaN grown by MOCVD and MBE could still be present for growth by HVPE. The In, which is assumed to be present at the surface, may change the growth kinetics and the roughness of the grown layers may decrease. This would be especially interesting for high growth rates in which roughening of the surface is more pronounced and thus poses a problem.

2. Experimental details

In our experiments, we used a home-built, horizontal HVPE reactor equipped with a rotating disc susceptor [15]. Pieces of a 2 in GaN/sapphire wafer are used as a template for HPVE growth. All templates used for the experiments described are cut from the same wafer, which is prepared by the gallium treatment step (GTS) method [16]. In general, MOCVD templates obtained with this method allow the growth of thick (300 μm) GaN layers without cracks by HVPE [17]. Growth experiments are performed at normal temperatures (1000–1100 °C); the carrier gas is either N₂ or H₂ (2800 sccm). The other gases used are NH₃ (1000 sccm) mixed with N₂ (60 sccm) and HCl (50 sccm) mixed with N₂ (200 sccm). The boat used to place the gallium for growth has two compartments (see Fig. 1). The bottom of one of the compartments is always completely covered by Ga, the other one can be filled with In. The width of the boat is constant over the entire length (22.2 mm), the lengths of the compartments with In and Ga are 19.2 and 72.7 mm, respectively. This leads to a ratio between the In and Ga surface areas of 4:15. Before growth, the In is cleaned by etching in an aqueous HCl solution.

The growth species GaCl and InCl are formed in situ by passing HCl over the Ga-boat at 850 °C (see Fig. 1). The HCl first passes over the liquid Ga surface and then over the liquid In surface. Experiments were performed to see if the order of In and Ga had any influence on the growth. No effect on the growth rate was found. This shows that the amount of GaCl that is transported into the reactor does not depend on the order of In and Ga in the boat. The configuration of first passing the HCl over Ga and then over In is the easiest experimental option.

To investigate the effect of In with N₂ and H₂ as the carrier gas, four growth runs are performed: two without In as a reference, and two with In. The HCl flow through the boat is kept constant for all four experiments. The growth time is 1 h. An overview of the experiments is shown in Table 1.

After growth the surfaces of the samples are studied with differential interference contrast microscopy (DICM), two-beam interferometry [18,19] and atomic force microscopy (AFM; tapping mode).

3. Results and discussions

3.1. Growth rate

The growth rates for the different growth runs are reported in Table 1. The letters A, B, C, and D will be used to refer to the growth conditions. The highest growth rate is found for growth with N₂ as the carrier gas (sample A). When In is added to the growth system the growth rate decreases (sample B). A similar effect is seen for H₂ as the main carrier gas: again the growth rate decreases when In is added (samples C and D). The decrease in growth rate does not depend on whether the HCl flow first passes the Ga and then the In or the other way around. The same amount of GaCl, which is the species that determines the growth rate of GaN, is transported into the reactor for both cases. We have also seen that the HCl flow is not saturated with Ga after passing the boat, as the growth rate increases when the surface area of the Ga is increased. This means that InCl can be formed with the HCl that remains [10,14] and In is transported into the reactor. This also means that the same amount of GaCl enters the reactor irrespective of whether In is present or not. Apparently In influences the growth mechanism.

As both In and Ga are present in the gas phase, it can be assumed that both species will be present at the surface as well. It can be expected that the In atoms will only be incorporated into the bulk material at very low levels, because of the weaker In–N bond as compared to the Ga–N bond. However, the reduced growth rate in the experiments where In is added indicates its presence at the surface. There it will probably block positions where

![Fig. 1. Ga-boat with both In and Ga; the HCl gas first flows across the liquid Ga and then over the liquid In. The surface ratio of In and Ga is 4:15.](image-url)
Ga could be built into the material. This reduces the incorporation rate of Ga and thus the growth rate [4]. This suggestion will be confirmed in the morphology section where the surface morphology of the grown layers is discussed.

The lower growth rate for growth under H$_2$ as compared to N$_2$ carrier gas is in contrast with what was found before in our reactor [20]. From this previous study, it follows that the growth rate is very much dependent on the position in the reactor and on the presence of convection and buoyancy. The most important factor in determining the growth rate is not chemistry, but the interplay between hydrodynamics and diffusion. From the conclusions drawn in Ref. [20], it therefore follows that the deposition rate is strongly dependent on reactor geometry. Since the geometry used in the current experiments is different from the previous study [20], the results cannot be directly compared. Apparently, in the present configuration the highest growth rate is obtained for growth under N$_2$ instead of H$_2$ as was the case for the previous configuration [20].

### 3.2. Surface morphology

Although it is expected that the added In is not incorporated, it still has an effect on the growth rate as was shown before. It also affects the surface morphology, as is shown by optical DICM micrographs in Fig. 2. With N$_2$ as the carrier gas small hillocks are formed in a hexagonal pattern. When In is added the structures become larger and more irregular. In both cases, the largest hillocks are located above cracks which have been healed during growth. These cracks are readily imaged by focusing the DICM microscope downwards into the layers.

The hillocks are also visible for growth with H$_2$ as the carrier gas and In added (Fig. 2d). However, these hillocks have a slightly ragged appearance. Without In, the surface morphology is very different. The pattern at the surface represents growth on a slightly misoriented substrate [21] (Fig. 2c). This misorientation (one-tenth of a degree at maximum) is due to spread in the production of the sapphire wafers. At larger magnification macroscopic steps are visible in between the (almost) vertical lines (see Fig. 3c).

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**Table 1**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Growth rate ($\mu$m/h)</th>
<th>$\theta$ (°)</th>
<th>$\nu_{\text{step}}$ ($\mu$m/h)</th>
<th>$\nu_{\text{step}}$ ($\mu$m/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_2$</td>
<td>A 87</td>
<td>0.45</td>
<td>11.0 x 10$^3$</td>
<td>B 39</td>
</tr>
<tr>
<td>H$_2$</td>
<td>C 57</td>
<td>&lt;0.15</td>
<td>&gt;21.7 x 10$^3$</td>
<td>D 35</td>
</tr>
</tbody>
</table>

**Fig. 2.** Optical micrograph (DICM) images of the surface morphology of grown layers at large scale: (a) sample A, (b) sample B, (c) sample C, and (d) sample D. The white bar in (a) indicates 1000 $\mu$m; all images have the same scale.
As the same template was used in all growth runs, the differences in morphology are caused by differences in growth conditions. For the case of N₂ carrier gas the frequency of step generation at certain growth centres increases with adding In to the system, leading to the growth of the larger hillocks. This might be introduced by different dislocation configurations ending at the hillock summits [22]. For growth under H₂ without In the source of steps for growth is mainly due to a slight misorientation of the template. When In is added, the main source of growth steps are the hillocks. Adding In changes the growth mode for both carrier gasses.

Fig. 3 shows optical microscope images at a higher magnification. Macroscopic steps are visible at the surface, they are especially clear in Fig. 3a and d. When AFM images are made of the surfaces, the macro steps are visible for all HVPE growth runs (see Fig. 4). The terraces between the macro steps are most narrow for growth under N₂ (with and without In), and they are wider for growth under H₂. This is related to the steepness of the hillocks. The inclination of the hillock sides with respect to the substrate (θ) are measured using two-beam interferometry after Michelson [18,19]. The resulting angles are given in Table 1. The numbers confirm the conclusions from the AFM images: the steepest hillocks are formed for growth under N₂ with In added, and changing the carrier gas to H₂ or removing the In reduces the steepness of the hillocks. For growth in H₂ in absence of In, no hillocks are visible as they are overruled by misorientation steps. This implies that the steepness of the missing hillocks is less than the misorientation of the sapphire substrate from the (0 0 0 1) plane, which is less than 0.1°.

The average step velocity, \( v_{\text{step}} \), follows directly from the hillock slope (\( \theta \approx h_{\text{step}}/d \)) and the growth rate (\( R_g = h_{\text{step}}v_{\text{step}}/d \)), and is given by \( v_{\text{step}} = R_g/\theta \). Here \( d_{\text{step}} \) and \( h_{\text{step}} \) are the average spacing and height of the steps, respectively. The numbers are given in Table 1. If In is present for both carrier gasses, the step velocity decreases. Because the hillock slope increases upon In addition, which would lead to a larger growth rate, this implies that the step velocity is the main factor determining the overall growth rate, \( R_g \). As suggested in the growth rate section this can be the result of In atoms blocking Ga positions at the steps.

The heights of the macro steps as measured by AFM vary between 2 and 5 nm, indicating that they are much higher than single or half unit cell steps, which would be about 0.25 and 0.5 nm, respectively. The steps are concentrically oriented along the sides of the hillocks (samples A, B, and D), indicating that the source of the steps is located at the centre of the hillock. Since the hillocks tend to be located above healed cracks, we think that these elevations are single or multiple growth spirals related to dislocations.

AFM images at a higher magnification are shown in Fig. 5. In between the macro steps some lower steps are present. These are visible on sample D (see Fig. 5d). A detailed, contrast-enhanced AFM image with the steps more clearly visible is shown in Fig. 6. Judging from the image contrast, we think that they are unit cell or half unit cell height steps. The steps are rather difficult to distinguish.
because of some contamination which is visible as spots covering the surface. These spots of 1 nm or less in height probably result from an uncontrolled reaction during cooling off after cessation of growth at the end of the experiment. Such a shut-off effect is a common problem in the ex-situ observation of crystal surfaces by high resolution microscopic methods.

3.3. Pinning of steps by dislocations

In all AFM images of Fig. 5 dark spots are visible. These spots represent the outcrops of dislocations at the surface. The local strain fields around the dislocations cause small depressions at the surface, which are visible as dark spots.

There is one very typical feature in Fig. 4. Perpendicular to the macro steps, dark lines are visible on the surfaces grown without In present in the reactor. In Fig. 5 it becomes clear that these lines are connected with the outcrops of dislocations. The lines represent distortions at the surface caused by pinning of especially the lower steps at threading dislocations. A schematic representation of this process is given in Fig. 7. The dislocation retards the movement of the step at one point. The step passes, however, a distortion remains and the step is no longer straight. During continued propagation, the step slowly straightens [23] and the trail of the dislocation disappears as can be seen from the fading contrast of the line further from its point of origin.

The situation differs if two dislocations are closer together than twice the radius of a critical two-dimensional nucleus for growth, which is determined by supersaturation and step free energy [24]. Unfortunately, both parameters are unknown for the present HVPE system. When a step hits the two dislocations it will be blocked and is unable to continue propagation in between the dislocations. The step parts outside the segment between the dislocations still continue to propagate, as is schematically drawn in Fig. 8a. They make an enveloping movement around the dislocation pair and reunite again. As a result, a lower triangular area is formed behind the dislocation pair as is shown in Fig. 8.

When In is added, the pinning of the steps is not prevented (see Fig. 5d), but all traces of step distortion are quickly removed. A first hypothesis for this phenomenon is that In accumulates at the dislocation outcrops and hinders the growth at and behind that location. However, this is just opposite to what is observed as no traces are visible when In is present. A second explanation could be an

Fig. 4. The 20 × 20 μm AFM images. The macro steps up to 5 nm in height, are clearly visible for all four samples, these steps are closest together for growth under N2: (a) sample A, (b) sample B, (c) sample C, and (d) sample D. From white to black the height difference is 20 nm.
increase in free step energy upon adding In. This makes sharp corners in the steps energetically less favourable and the step will straighten faster. The result is that no (or very little) traces will be visible after pinning of steps by dislocations. However, the hillocks grown in the presence of In are steeper than the ones grown without In, which indicates that, assuming spiral growth, the free step energy decreases when In is added [22].

Fig. 5. The 5 × 5μm AFM images. The dark spots represent outcrops of threading dislocations: (a) sample A, (b) sample B, (c) sample C, and (d) sample D. From white to black the height difference is 10 nm.

Fig. 6. Detail of the 5 × 5μm AFM image of sample D after contrast amplification; some lower steps in between the macro steps are visible.

Fig. 7. Schematic representation of the formation of trails behind dislocations: steps are pinned by the dislocation and become heavily distorted after passing the defect; this distortion straightens slowly after passing and the result is a trail behind the dislocation.
A more likely explanation is related to the efficient surface diffusion. An increase of surface diffusion was suggested upon adding In to the system in MBE and MOCVD [6]. This effect may also be present in HVPE growth. It increases the mean free path of the ad-atoms at the surface, resulting in a larger possibility of encountering a kink site in the step [22], which enhances the growth of the perturbed step regions lagging behind. This faster surface transport of species will not prevent the pinning of steps; however, traces of distorted steps will be more quickly removed once a step has passed the dislocation. Another effect related to the surface diffusion is the lower velocity of steps with In present. This means that the integration of growth units into the steps is slower and the surface diffusion is better able to keep up with the growth, which makes the distortions to be removed faster.

The continuous retardation of the step propagation by the dislocations for all four growth conditions leads to the bunching of the lower steps, as imaged by AFM. This process leads to many irregularities in the step pattern, which again results in the macro steps visible by optical microscopy.

4. Conclusions

The effect of In on the growth of GaN by HVPE is studied. It was found that the effect is larger for N₂ than H₂ as the carrier gas.

Adding In reduces the growth rate for both carrier gasses. From the measured hillock slopes and growth rates it is found that the step velocity decreases upon adding In. It is suggested that during growth the In atoms at the surface block sites where Ga incorporation could take place.

Besides reducing the growth rate also the surface morphology is changed. For all four growth conditions macro steps with a height of 2–5 nm are visible on the surface. These macro steps result from bunching of individual steps due to local retardation of step propagation by dislocations. For growth without In this pinning of the steps leads to fading trails behind the dislocations. If In is added to the system these trails are no longer visible even though the pinning of the steps is still present. An increased surface diffusion and slower step propagation are suggested to explain this effect.

Acknowledgements

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References