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Effect of Magnesium and Silicon on the lateral overgrowth of GaN patterned substrates by Metal Organic Vapor Phase Epitaxy

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Metalorganic vapor phase epitaxy was used to achieve selective regrowth of undoped, Mg- and Si-doped GaN on a silicon nitride patterned mask, capping a GaN epitaxial layer deposited on (0001) sapphire substrate. Hexagonal openings in the mask defined into 10 µm diameter circles separated by 5µm were used as a pattern for the present study. Uniform undoped and Mg-doped GaN hexagonal pyramids, delimited by C (0001) and R $\{1\bar{1}01\}$ facets, were achieved with a good selectivity. Si-doped GaN hexagonal pyramids delimited by vertical $\{1\bar{1}00\}$ facets and (0001) top facet were obtained for a high SiH_4 flow rate in the vapor phase. We found that the GaN growth rates V_R and V_C, measured in the R $\langle 1\bar{1}01\rangle$ and C $\langle 0001\rangle$ directions respectively, were drastically affected by the Mg and Si incorporation. By adjusting the Mg partial pressure in the growth chamber, the V_R/V_C ratio can be increased. Hence, the delimiting top C facet do not vanish as usually observed in undoped GaN selective regrowth but conversely expands. On the other hand, under proper growth conditions, 20µm-high Si-doped GaN columns were obtained.

1 Introduction

The successful development of short wavelength light emitting diodes and the more recent realization of nitride semiconductor lasers have stimulated great interest in the application of these materials for blue and ultraviolet optoelectronic devices [1]. Due to their large lattice mismatches with sapphire or 6H-SiC, nitrides epitaxial layers contain a large density of extended defects (10^9-10^{10} dislocations·cm^{-2}) despite the use of a two-step growth method [2] [3] [4]. It has been demonstrated that a three dimensional (3D) growth mode leads to the reduction of the defects densities in the 10^8 cm^{-2} range [5] [6]. Recently, a significant reduction in the dislocation densities in GaN films was achieved via lateral mask overgrowth [7] [8]. Because of the growth rate anisotropies, the selective growth of GaN using hexagonal mask openings has led to the formation of GaN hexagonal pyramids delimited by six $\{1\bar{1}01\}$ facets. Generally, the growth rate (V_C) of the C (0001) facets is higher than that of the R $\{1\bar{1}01\}$ facets. Therefore the coalescence of these hexagonal pyramids is very difficult. We have recently used two growth techniques, MOVPE and Halide Vapour Phase Epitaxy (HVPE), respectively, in order to achieve selective growth of GaN and lateral overgrowth until coalescence of the islands [9]. Assessment by X-ray diffraction has showna FWHM in ω scan of 50 arsec on the flat part of an HVPE overlayer . Recently, Kapolnek *et al.* [10] reported that a maximum epitaxial lateral mask overgrowth can be obtained at high temperature and ammonia flow. Magnesium was widely used to obtain p-type conductivity in nitride epilayers. We have previously reported that the introduction of Mg in the vapor phase reduces the growth rate of GaN in the $\langle 0001\rangle$ direction (perpendicular to (0001) plane of sapphire) grown directly on GaN nucleation layer on sapphire substrate [11]. In this paper, we report the effect of magnesium and silicon on the GaN lateral overgrowth on patterned substrates by Metal Organic Vapor Phase Epitaxy.

2 Experimental

For this study, a home-made Metalorganic Vapor Phase Epitaxy (MOVPE), vertical reactor operating at atmospheric pressure, was used to achieve the selective growth of GaN. The features for undoped, Si or Mg-doped GaN were studied. The growth process started by growing a 1.5 µm thick GaN layer at 1080°C on a GaN nucleation layer deposited at 600°C on a (0001) sapphire substrate. Trimethylgallium (TMGa), bis-methylcyclopendienyl-magnesium ($(MeCp)_2Mg$), silane (SiH_4) and ammonia were chosen as Ga, Mg, Si and N precursors respectively. A Si_xN_y mask layer (thickness≅2nm as checked by cross section transmission electron microscope observations) was subsequently deposited on the GaN film by introducing ammonia and silane together in the growth chamber. The flow rates of SiH_4 (100ppm in H_2) and NH_3 were 50sccm/min and 2slm/min, respectively. A mixture of N_2 and H_2 (2:2 slm) was used as the carrier gas. The exact stoichiometry of the Si_xN_y film has not been measured, but it was successfully used as a selective mask despite its weak thickness. Hexagonal openings in the mask defined into 10 µm diameter circles separated by 5µm, were then achieved by photolithography and dry etching techniques. The selective growth of undoped and Mg-doped GaN was performed on such patterned samples with conditions similar to those used for standard GaN growth except for the TMGa flow rates. These ones were established at smaller values than that used for undoped GaN (typically 16 µMole/min). This is necessary to avoid excessively high growth rates resulting from a very efficient collect of Ga atoms impinging on the masked surface. It should be stressed out that no nucleation was observed on Si_xN_y mask. Growth rates were measured either *in situ* by laser reflectrometry [11] or *ex-situ* by scanning electron microscope measurements (SEM) on cross sections.

3 Selective growth of undoped GaN

A SEM micrograph of the undoped GaN selectively grown on such patterned masks with increasing duration is shown in figure 1. Figure 1 (a), (b), (c) and (d) correspond to GaN pyramids grown with growth times of 5, 10, 20 and 30min, respectively. After 20 min of growth (figure 1 (c)), hexagonal pyramids, delimited by C (0001) and R ($1\bar{1}01$) facets, were achieved with a good selectivity. Figure 2 shows the plot of growth time t versus the lengths $W_B(t)$, $W_T(t)$ and H(t) as defined in figure 3. A straightforward kinematical model involving only the two delimiting planes mentioned above yields the following expressions:

$$H(t) = tV_C \tag{1}$$

$$W_B(t) = W_{B0} + \frac{2V_R t}{\sin(\theta_R)} \tag{2}$$

$$W_T(t) = W_{B0} + 2t\left(\frac{V_R - V_C\cos(\theta_R)}{\sin(\theta_R)}\right) \tag{3}$$

Where V_C, V_R and θ_R are the growth rates in the R and C directions and the angle between C and R planes. Equations 1 and 3 hold until a growth time t_0 at which the top facet vanishes ($W_T(t_0)=0$). For t greater than t_0, H should vary at a slower rate given by $V_R/\cos(\theta_R)$. From linear regression through experimental points (lines labelled 1 to 3 in Figure 2) we have obtained the following results: V_C = 13 µm/h, V_R = 2.1 µm/h, W_{B0} = 7.6 µm and θ_R = 62.1°. The value obtained for θ_R is in excellent agreement with that expected from the lattice parameters of GaN (61.97°). V_C is extremely high compared to the 1 µm/h growth rate measured for standard epitaxy on (0001) substrate using the same vapour phase composition. Since impinging Ga molecular species are only incorporate at the GaN surface in the openings, Ga species diffuses on the surface of dielectric until reach the openings. As a result, the ratio V_R/V_C is only about 0.15.

For growth times exceeding t_0, the pyramids now delimited by ($1\bar{1}01$) planes only expand laterally until they get in contact with the neighbouring ones. We observe then that the top C facets reappear, indicating a significant modification in the growth kinetics, most likely a decrease of V_C since the concentration effect is suppressed, the Si_xN_y mask being fully covered by the GaN overgrowth. In our work, the growth temperature and the TMGa partial pressure were not essential parameters to increase the growth rate of the ($1\bar{1}01$) facets. Hence, the control of lateral overgrowth of undoped GaN hexagonal pyramids is still difficult.

4 Selective growth of Mg-doped GaN

We have previously reported that the introduction of Mg in the vapor phase reduces the growth rate of GaN in the ⟨0001⟩ direction grown directly on GaN nucleation layer on sapphire substrate. The evolution of the GaN pyramids morphology with the Mg incorporation for different [Mg]/[Ga] mole ratio is shown in figure 4. Figure 4 (a), (b), (c) and (d) correspond to GaN pyramids grown with [Mg]/[Ga] mole ratios of 0 (undoped GaN pyramids), 0.08, 0.11 and 0.14, respectively. The common conditions were: growth time 30 min, growth temperature 1080°C, TMGa flow 16 µMole/min, N_2, H_2 and NH_3 flows 2sl/min for each. We have recently reported that $(MeCp)_2Mg$ and ammonia react strongly forming particles [12], therefore we have chosen to maintain a constant flow of $(MeCp)_2Mg$ and varying the TMGa amount. This insures that the concentration of Mg available at the surface of the growing islands is identical from sample to sample. As the growth is linearly controlled by the TMGa supply, the growth rates were then normalized for comparison. The figure 4 clearly evidences that the presence of Mg has enhanced the ratio V_R/V_C. Therefore the top (0001) facets widen. Moreover, the selectivity of the growth was not affected by the presence of $(MeCp)_2Mg$.

Figure 5 shows the variation of the growth rates normalized to the TMGa molar flux, in both ⟨0001⟩ ($V^N{}_C$) and <$10\bar{1}1$> ($V^N{}_R$) directions, as functions of the [Mg]/[Ga] ratio in the vapor phase. We have found that the $V^N{}_C$ decreases rapidly from ~0.8 to ~0.1 µm/h/µMole, while the $V^N{}_R$ increases slightly from ~0.16 to ~0.4 µm/h/µMole when the mole ratio [Mg]/[Ga] varies from 0 to 0.17. As a result, the lateral to vertical growth rate ratio (V_R/V_C) increases considerably from 0.21 to 4.

5 Selective growth of Si-doped GaN

In order to get a better understanding of the mechanism of the evolution of the {$1\bar{1}01$} facets, we have tried to grow selectively Si-doped GaN pyramids. The selective growth of Si-doped GaN was achieved using the growth conditions defined by: growth time 30 min, growth temperature 1080°C, TMGa flow 40 µMole/min, N_2, H_2 and NH_3flows 2sl/min for each. The flow rate of SiH_4 was varied from 0.88 nMole/min to 0.223 µMole/min. As an indication, the lower flow rate of SiH_4 used here i.e. 0.88nmole/min, leads to electron concentration of ~$5x10^{18}cm^{-3}$ for classical Si-doped GaN growth. For a low SiH_4 flow rate in the vapor phase (0.88nmole/min), uniform Si-doped GaN hexagonal pyramids, delimited by C (0001) and R {$1\bar{1}01$} facets were achieved with a good selectivity. However, for high SiH_4flow rate (0.2µmole/min), the selectivity becomes poor. The prismatic forms disappear and are replaced by columnar forms delimited by vertical {$1\bar{1}00$} facets. These columns can reach 20µm high (figure 6). This morphology is the result of a very high growth rate in the C ⟨0001⟩ directions. It should be noticed that the Si-doped GaN columns grown selectively were defined into circles whose diameter was smaller than that of the openings in the mask (=10µm). This indicates a considerable decrease of the lateral growth when a high Si concentration is introduced in the vapor phase. Therefore, the Si incorporation has remarkably influenced the growth rate anisotropy.

6 Conclusion

Atmospheric pressure MOVPE has been performed to study the effect of magnesium and silicon on the lateral overgrowth of GaN pyramid structures grown selectively using a Si_xN_y mask. A considerable lateral epitaxial overgrowth was obtained by introducing Mg. On other hand, in this study we have observed that the vertical growth rate (V_C) can be easily increased by introducing a high Si concentration in the vapor phase.

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FIGURES

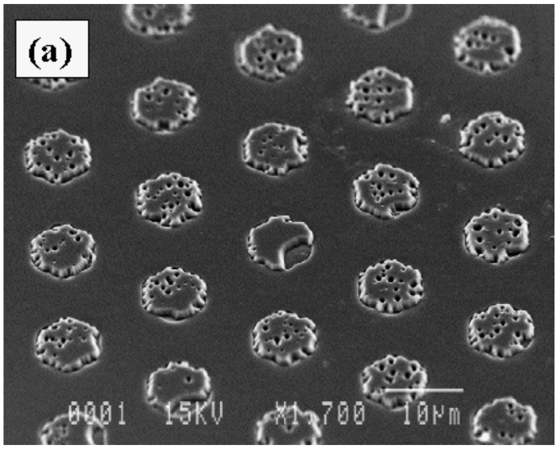

Figure 1a. SEM photograph of GaN localized islands on the patterned Si_xN_y mask with growth times of 5min. The growth temperature was 1080°C with 16µMole/min TMGa flow.

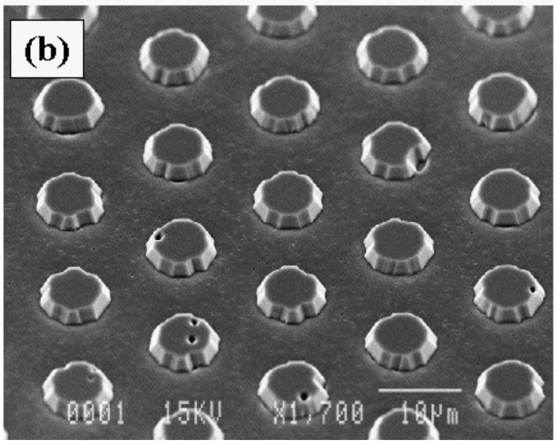

Figure 1b. SEM photograph of GaN localized islands on the patterned Si_xN_y mask with growth times of 10min.

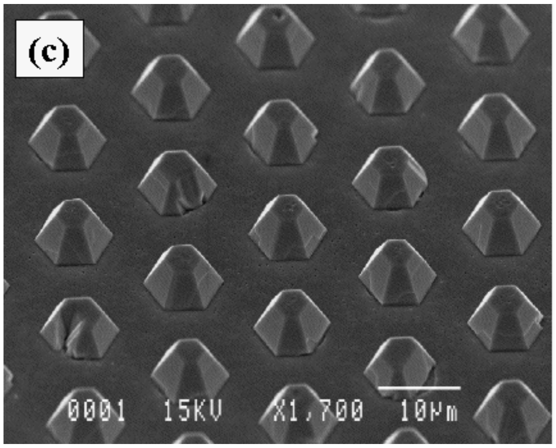

Figure 1c. SEM photograph of GaN localized islands on the patterned Si_xN_y mask with growth times of 20min. At this stage, the GaN pyramids are delimited by six facets $\{1\bar{1}01\}$ and a top C(0001) facet.

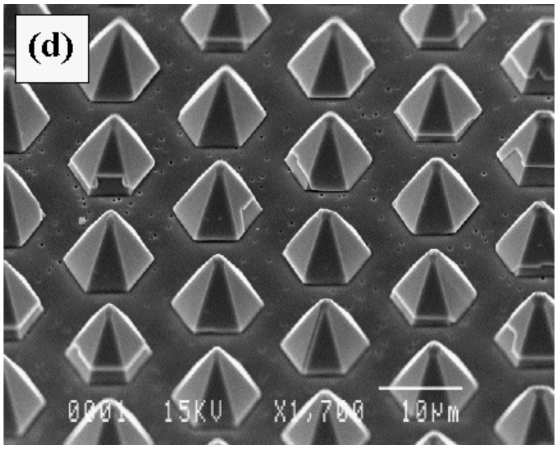

Figure 1d. SEM photograph of GaN localized islands on the patterned Si_xN_y mask with growth times of 30min. After a such growth time, the top C(0001) facet is vanished.

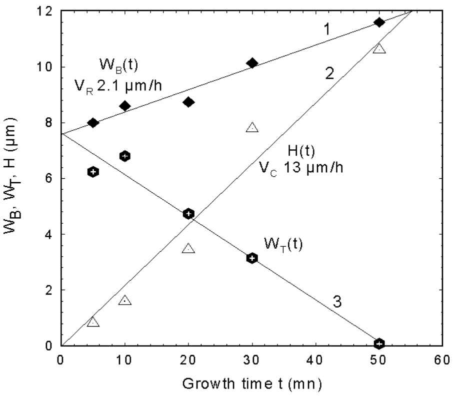

Figure 2. Measurements vs. growth time of the different characteristic dimensions of the hexagonal pyramid. Lines labeled 1 to 3 are regressions through the measured values. From these slopes, the growth rates V_C and V_R in the C and R direction were estimated to be 13 and 2.1 µm/h respectively. The growth temperature was 1080°C with 16µMole/min TMGa flow.

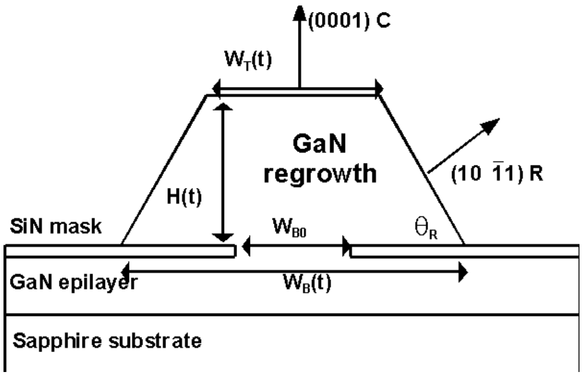

Figure 3. Cross section perpendicular to the $(11\bar{2}0)$ direction of a localized GaN truncated hexagonal pyramid shown in figure 1(c). W_T and W_B were respectively the width of the top facet and bottom base; H was the height of the pyramid. W_T, W_B and H were function of the growth duration t. θ_R was the angle between (0001) and $((10\bar{1}1)$ delimiting planes. W_{B0} was the width of the aperture in the Si_xN_y mask.

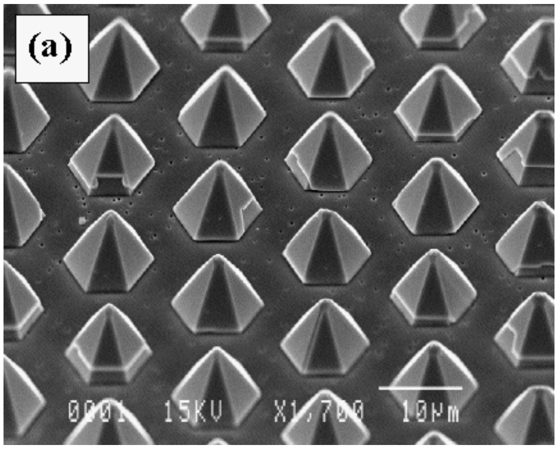

Figure 4a. SEM photograph of GaN localized islands grown on the patterned Si_xN_y mask with [Mg]/[Ga] mole ratios of 0 (undoped GaN pyramids). Except for the Mg introduction, the growth conditions (temperature 1080°C, TMGa 16 µMole) and time (30’) were identical for both samples.

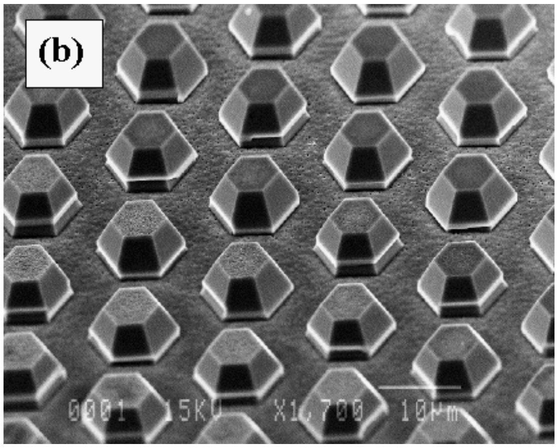

Figure 4b. SEM photograph of GaN localized islands grown on the patterned Si_xN_y mask with [Mg]/[Ga] mole ratios of 0.08.

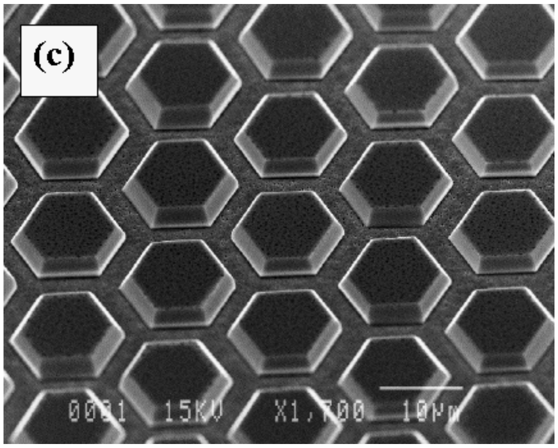

Figure 4c. SEM photograph of GaN localized islands grown on the patterned Si_xN_y mask with [Mg]/[Ga] mole ratios of 0.11.

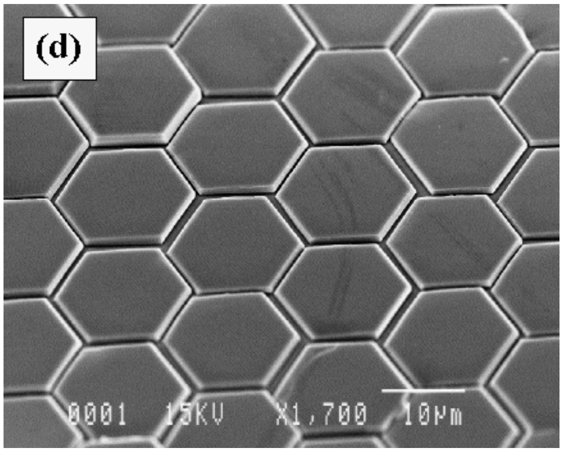

Figure 4d. SEM photograph of GaN localized islands grown on the patterned Si_xN_y mask with [Mg]/[Ga] mole ratios of 0.14. The V_R/V_C is about 4.

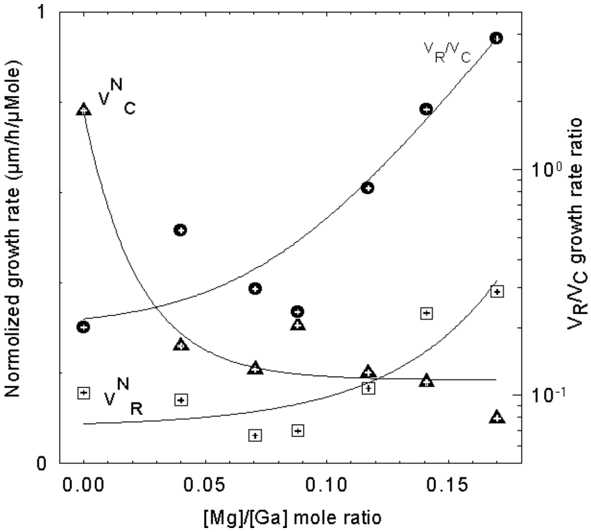

Figure 5. Growth rate vs. Magnesium to Gallium precursor mole ratio in the vapor phase deduced from measurements on SEM plan view and cross section of hexagonal pyramids as shown on figure 3. Lines were guides for eyes.

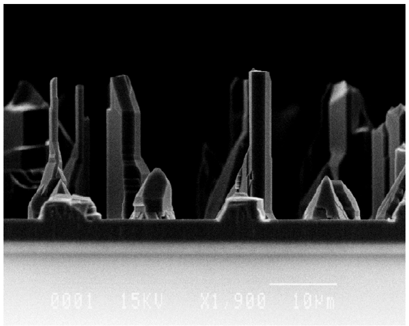

Figure 6. SEM photographs of high Si-doped GaN localized islands. The growth conditions were : SiH_4 0.20μMole, temperature 1080°C, TMGa 40μMole and growth time 30'.