

# Variations in mechanisms of selective area growth of GaN on nano-patterned substrates by MOVPE

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The growth behaviour of GaN selective area growth (SAG) by MOVPE on two types of nano-patterned GaN substrates has been investigated. Samples were characterized by SEM, AFM and TEM. Results indicate that well formed nano-pyramids with base size of ~150 nm, and sharp tips are readily grown through mask patterns defined by electron beam lithography (EBL). A growth rate of nearly zero on the  $\{10\bar{1}1\}$  nano-facets, effectively self-limiting growth (SLG), has been observed under a wide range of growth conditions using a conventional growth

mode. In contrast, pulsed growth is able to change the SLG behaviour, and thereby control the size of pyramids, even to coalesce the pyramids to form flat, smooth GaN films. SLG-like behaviour of GaN SAG on patterns defined by nano-imprint lithography (NIL) is also observed and enabled nano-pyramids to form. However, GaN SAG on NIL patterns shows accelerated growth in some pores at the early stage of the growth. This accelerated growth is attributed to the possible presence of screw-type dislocations in the pore.

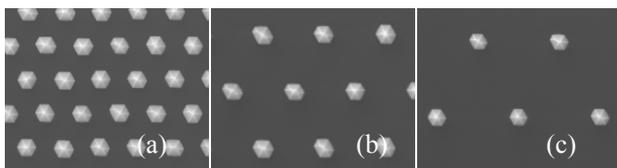
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**1 Introduction** Selective area growth (SAG) of GaN by MOVPE has been demonstrated at the micro-scale [1–3]. In this regime, the morphology of GaN grown through arrays of patterned pores can be controlled by growth conditions such as growth temperature, reactor pressure, V/III ratio [1, 2] and doping [3]. It is common that hexagonal pyramids with  $\{10\bar{1}1\}$  facets can easily form in the pores due to the slow growth rate on the facets [1, 2]. More and more interest has shifted to nano-structure growth on nano-patterned templates due to their potential applications. In this nano-scale regime, extreme growth anisotropy in the vertical to lateral growth rate ( $>1000$ ) can be achieved by the control of growth conditions and growth sequences leading to the formation of novel structures like GaN nanocolumns [4]. For example, the Vapour-Liquid-Solid (VLS) growth method using molten metal as catalyst has been well developed and the growth mechanisms have been well explained [5]. A growth method that avoids catalysts has also been developed, and uniform nanocolumns

are successfully grown using patterned substrates. However, the growth mechanisms are not well understood.

In the case of very small area windows in the growth mask, the morphology of the GaN growth fronts frequently acquire a pyramidal shape defined by the  $\{10\bar{1}1\}$  facets before emerging above the top of the growth mask. Nanocolumn growth can be achieved if pulsed growth conditions are applied at a critical point when the growth front is still below the mask surface [4]. It has been suggested that, by considering the growth sequence, the mechanism for this may be related to that of VLS growth [4].

Applications of nano-enabled GaN growth can be envisaged where a large lateral to vertical growth rate ratio on the nano-scale is required in order to obtain a continuous thin GaN layer above the growth mask. In this study, we aim to achieve well formed nano-pyramids above the growth mask, control their size and subsequent coalescence into continuous, smooth films by MOVPE. Differences in the growth mechanisms related to the nano-



**Figure 1** SEM images of GaN nano-pyramids grown on EBL patterns with the same pore size but three different pitch sizes: (a) 500 nm, (b) 750 nm and (c) 1000 nm.

pyramids growth, size and control of their coalescence are reported for nano-patterns, fabricated by electron beam lithography (EBL) and nano-imprint lithography (NIL), indicating process or growth mask geometry dependent behaviour.

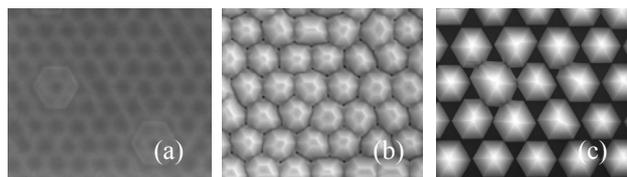
**2 Experiments** A SiO<sub>2</sub> mask was nano-patterned by NIL and EBL technologies, on GaN templates grown on c-plane sapphire substrates. The NIL process produced hexagonal arrays of oval shaped nano-pores with an average diameter of ~200 nm on a 450 nm pitch [6]. The SiO<sub>2</sub> mask was 100 nm thick and the pattern fill factor was ~50%. The pattern array was produced on a 2-inch wafer, but growth was conducted on 1×1 cm pieces cut from this wafer. The nano-patterns produced by EBL are also hexagonal arrays of pores in a 40 nm thick SiO<sub>2</sub> mask. The pore size was 150 nm and there were three pitch sizes of 500, 750 and 1000 nm. The different pitches were used in order to study the relative roles of adatom surface diffusion and gas phase diffusion in nano-pyramid growth and their coalescence. Uniform 100×100 μm pattern arrays with the three pitch sizes were fabricated within 1mm×1mm area. This design ensured that the morphology observed is only related to the sizes of the pattern, eliminating influence from growth non-uniformity. The pattern fill factors for the three different pitches are 9.0%, 4.0% and 2.3 % respectively. It is worthwhile noting that the pattern fill factor of EBL patterns is about one order of magnitude lower than that of NIL patterns.

GaN growth was conducted in an AIX 200/4HT RF-S MOVPE reactor. Both a conventional growth mode, i.e. when gallium and nitrogen precursors are switched into the growth chamber simultaneously, and pulsed growth mode [7] were applied. Under the conventional growth mode, a wide range of growth conditions were used in the experiments: growth temperature in the range of 900–1150 °C, reactor pressure in the range of 50–200 mbar, V/III ratio in the range of 500–10000, and growth time for nominal planar growth in the range of 10 to 700 nm. For pulsed growth, the influence of the time point for switching to pulsed growth mode on the surface morphology was investigated. H<sub>2</sub> was used as carrier gas in all the growth experiments. Samples were characterised using SEM, AFM and TEM.

### 3 Results and discussion

#### 3.1 GaN pyramids growth and coalescence on EBL patterns

SEM images of nano-pyramids grown on



**Figure 2** SEM images show the pyramids have increased in size for the 1000 nm pitch (c), have started to coalesce for the 750 nm pitch (b), and have formed a smooth film for the 500 nm pitch (a).

EBL patterns are shown in Fig. 1. The growth temperature, reactor pressure and V/III ratio for this sample were 1070 °C, 200 mbar and 4000. Regular hexagonal GaN pyramids with {10 $\bar{1}$ 1} facets were formed. The pyramidal base is ~150 nm, and is determined by the pore size. The size of the pyramids grown on patterns with the three different pitches is identical, not changing with pattern fill factor at all.

Following this observation, we have applied a wide range of growth conditions as aforementioned in the growth experiments. We found that the pyramid morphology stays the same in Fig. 1; not only independent of fill factor, but also independent of the range of growth conditions used. Therefore we describe the formation of nano-pyramids defined by {10 $\bar{1}$ 1} oriented facets as self-limiting growth (SLG).

SEM images identical to those shown in Fig. 1 for a sample with only 10 nm nominal planar growth indicated that the GaN growth was enhanced by the SiO<sub>2</sub> mask when the growth front was below the mask. Yet, once the nano-pyramids are formed, the growth rate of the {10 $\bar{1}$ 1} facets of the pyramids is near zero. Therefore, any fill-factor-dependent growth enhancement in ELO-GaN growth previously seen on stripe patterns [2] is no longer observable in these nano-pyramids since, once the nano-pyramids are fully formed, SLG dominates.

Coalesced surfaces formed by SLG could be expected to be of very high crystal quality and therefore suitable on which to grow device quality epitaxy. Doing so requires a growth mode that overcomes the SLG process. Pulsed growth has been shown to enhance the lateral growth of the {11 $\bar{2}$ 0} facets of stripe-patterned micron-scale formed by epitaxial lateral overgrowth [7]. This growth mode was applied in an attempt to expand laterally the GaN nanostructures of this study. SEM images of a sample grown using the pulsed growth mode from the outset are shown in Fig. 2. Both the on and off duration of the NH<sub>3</sub> were 10 seconds, and the growth was terminated after 20 periods of pulsing. It can be seen that the pulsed growth causes the nano-pyramids to widen with a c-plane facet forming on their tops. After 20 pulses, the nano-pyramids grown with a 1000 nm pitch are widened to ~500. The nano-pyramids formed on a 750 nm pitch are just starting to coalesce, whereas those on a 500 nm pitch have fully coalesced to form a flat, smooth epitaxial film. The pattern still observable in the SEM image is due to the

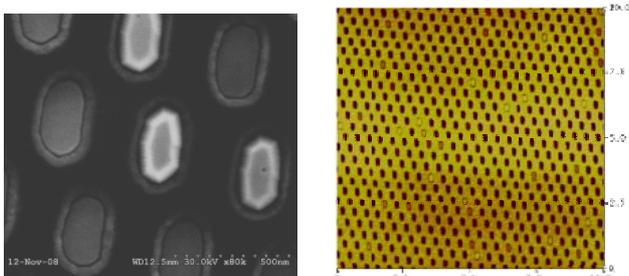
transparency of the coalesced film to the electron beam. This clearly demonstrates that pulsed growth is not a self-limiting process and can be used in conjunction with the SLG growth mode to control the lateral extent, even the coalescence of the nano-pyramids into continuous films.

The impact on the growth morphology of varying the time at which the growth process is changed from conventional to pulsed growth mode has also been investigated. At one end of extremes was to switch without any GaN nucleation (the sample with SEM images showing in Fig. 2 was grown like this), and at the other end of the extreme is to switch when the pyramids were fully formed. It was found that in order to coalesce the nano-pyramids it is most effective to start with pulsed growth from beginning, and the least effective to start from fully formed pyramids.

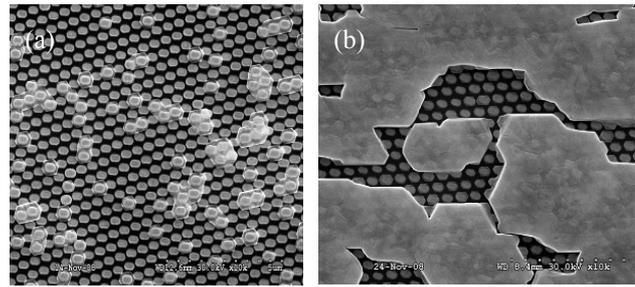
**3.2 GaN pyramids growth and coalescence on NIL patterns** GaN growth in NIL patterns shows accelerated growth under both conventional and pulsed growth modes in some pores at a very early stage in nanostructure formation, as shown in Fig. 3.

Under the conditions used, a film of only ~10 nm would have grown on an un-patterned c-plane GaN template. However, in some of the NIL-generated pores the GaN nanostructure has grown at least as high as the top of the growth mask (~100 nm). The fast-growing nanostructures have a truncated hexagonal pyramidal shape. This is the first report of such an ELO-GaN growth process at the nano-scale. Analysis of large area SEM and AFM images has revealed the density of pores in which accelerated growth occurs is  $4.7 \times 10^7 / \text{cm}^2$ . This number is similar to the pure screw threading dislocation density in the GaN growth template used.

Following the growth of a 10 nm nucleation layer, the growth mode was switched to a pulsed growth sequence comprising 10 pulses. The taller GaN pillars expand laterally during the pulsed growth and nano-scale epitaxially overgrown GaN (NELO-GaN) platelets form. Meanwhile GaN nanostructures continue to grow upwards at a slower rate in the pores where accelerated growth has not occurred, as shown Fig. 4(a). The lateral expansion of the platelets is relatively quick and shorter nanostructures are overgrown, possibly without contacting them. The density of rapidly growing nanostructures is now  $2.2 \times 10^8 / \text{cm}^2$ , a number approximately half of the expected density of threading dis-



**Figure 3** (left) SEM and (right) AFM images on a sample grown on NIL pattern after 10 nm nominal GaN growth.



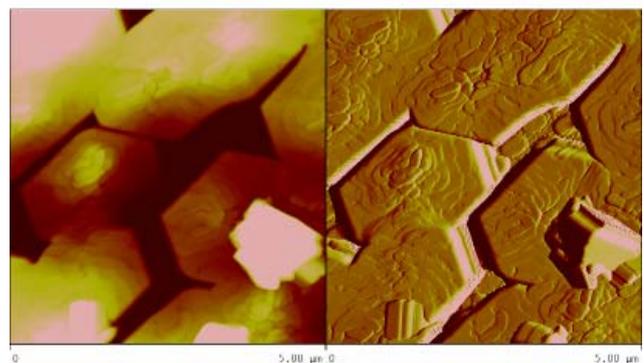
**Figure 4** SEM images on (a) a sample after 10 period of pulsing, and (b) on a sample after 40 periods of pulsing.

locations with screw components (including pure and mixed type dislocations) in the GaN template.

AFM measurements on the platelets do not show any pits and spirals; the reason for this is not clear at the moment. After a sequence of 40 growth pulses the platelets have increased in lateral size, as shown in Fig. 4(b). AFM imaging revealed one or more growth spirals on each platelet, as shown in Fig. 5. With further growth, a continuous NELO-GaN film is eventually formed by the coalescence of the platelets though TEM shows that dislocations form at the coalescence fronts due to twist and tilt between the platelets. AFM measurements also revealed large hillocks on the surface, which are believed to coincide with the spirals on the platelets.

Enhanced growth at screw-type dislocation sites on planar InGaN and InGaN/GaN quantum well surfaces has previously been observed [8]. Enhanced growth was also observed at nanopipe sites on the planar GaN surface, which is linked to screw-type dislocations [9]. At this stage, we tentatively ascribe the accelerated growth to screw-type dislocation existing in the pore, though further investigation is needed. However, the density of rapidly growing nanostructures, and growth spirals at the sites of accelerated growth are consistent with such an explanation of their origin.

Accelerated growth is not observed in micro-scale ELO-GaN growth. Neither is the non-uniform growth observed on NIL patterns readily observed on EBL patterns. A possible explanation for micro-scale ELO-GaN growth

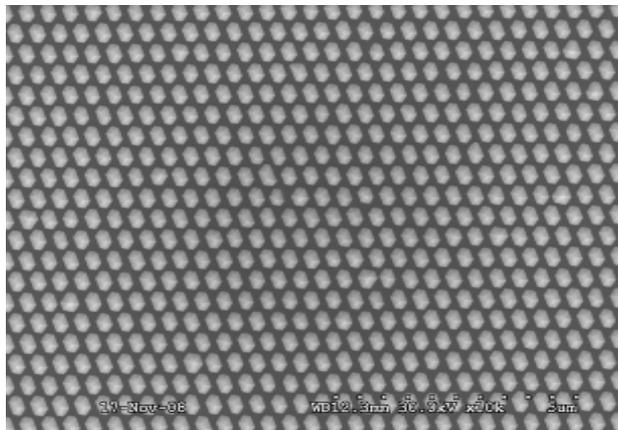


**Figure 5** AFM image on a sample with 40 periods pulsed growth, showing the growth spiral on the laterally grown platelet centres.

is that there exists screw-type dislocation(s) in each and every pore. Therefore, the growth behaviour of GaN in each individual pore is quite similar. On the other hand, the reason for the uniform growth on EBL patterns could be due to the smaller pores sizes and fill factors for the EBL patterns. Therefore, the possibility of a screw-type dislocation coinciding with a pore is quite low, though not impossible. In fact, we actually can see two hexagonal features in the coalesced film in Fig. 2(a), which we think might have the same origin.

Growth masks are known to act as dislocation filters with their effectiveness determined by the diameter and spacing of the growth windows. A sparse array of nano-scale growth windows offering the best filtering provided that the formation of new dislocation networks at the coalescence fronts can be controlled. The growth mask defined by NIL has a higher density of windows and tends to have a larger average diameter, hence the higher density of larger GaN structures formed by accelerated growth. At this stage, damage to the surface of the GaN template exposed through the growth windows cannot be discounted as a cause for accelerated growth, as forming the pores and cleaning the samples after NIL required more aggressive processes. On balance, the available evidence points toward screw dislocations and their filtering by the growth mask being the cause of the observed differences in nano-structure growth rates.

With the understanding of the self-limiting growth mechanism of GaN nano-pyramids and the unavoidable accelerated growth in pores penetrated by screw-type dislocations, we have found a method for growing arrays of uniform pyramids from NIL patterned growth masks. The growth process involves exploiting SLG so that the fast-growing nanostructures acquire a nano-pyramidal shape and size commensurate with the dimension of the windows in the growth mask. Once the defined size has been achieved, SLG prevents their further growth, while the slower growing nanostructures catch up and form nano-pyramids of the same size that are then also subject to SLG. The SEM image in Fig. 6 shows the results, indicating very



**Figure 6** SEM image of GaN nano-pyramids grown on a NIL pattern.

regular array of nano-pyramids. Further, we have been able to coalesce the denser arrays of nano-pyramids defined by NIL to form continuous epitaxial films.

**4 Conclusions** A self-limiting growth behaviour of GaN SAG on EBL and NIL patterned substrates has been observed. The size of the pyramids formed by the SLG mode is determined by the pore size of the patterns, and is not affected by the pitch of the patterns, and does not change under a wide range of growth conditions. This behaviour is attributed to the very slow growth rate of the  $\{10\bar{1}1\}$  facets and the nano-scale size of the pyramids. Pulsed growth has been shown to be able to overcome the SLG process to enable control of the pyramid size, their evolution into flat top (defined by the c-plane) truncated hexagonal structures and their evolution into continuous epitaxial films by coalescence. Accelerated growth in some pores at the early stage of the growth was observed on NIL patterns. This has been attributed to screw-type dislocations penetrating the pores to provide sites for accelerated growth. This is justified by two experimentally observed factors: the density of the pores in which accelerated occurs is very similar to the density threading dislocations with screw-type expected in GaN growth templates formed on sapphire substrates and, second, growth spirals often associated with dislocations are observed to originate from the rapidly growing GaN nanostructures but not the slowly evolving ones.

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## References

- [1] D. Kapolnek, R.D. Underwood, B.P. Keller, S. Keller, S.P. DenBaars, and U.K. Mishra, *J. Cryst. Growth* **170**, 340 (1997).
- [2] K. Hiramoto, *J. Phys.: Condens. Matter* **13**, 6961 (2001).
- [3] B. Beaumont, S. Haffous, and P. Gibart, *Appl. Phys. Lett.* **72**, 921(1998).
- [4] S.D. Hersee, X.Y. Sun, and X. Wang, *Nano Lett.* **6**, 1808 (2006).
- [5] F. Qian, Y. Li, S. Gradecak, D. Wang, C. J. Barrelet, and C.M. Lieber, *Nano Lett.* **4**, 1975 (2004).
- [6] G. Hubbard, S.J. Abbott, Q. Chen, D.W.E. Allsopp, W.N. Wang, C.R. Bowen, R. Stevens, A. Šatka, D. Haško, F. Uherek, and J. Kováč, *Physica E* **41**, 118 (2009).
- [7] C. Liu, P.A. Shields, S. Denchitcharoen, S. Stepanov, A. Gott, and W.N. Wang, *J. Cryst. Growth* **300**, 104 (2007).
- [8] S. Keller, U.K. Mishra, S. P. DenBaars, and W. Selfort, *Jpn. J. Appl. Phys.* **37**, L431 (1998).
- [9] W. Qian, G.S. Rohrer, M. Skowronski, K. Doverspike, L.B. Rowland, and D.K. Gaskill, *Appl. Phys. Lett.* **67**, 2284 (1995).