# Metal Organic Chemical Vapor Deposition Growth of GaN and GaMnN Multifunctional Nanostructures

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## Abstract

Quantum dots (QDs) have been shown to improve the efficiency and optical properties of opto- electronic devices compared to two dimensional quantum wells in the active region. The formation of self-assembled GaN nanostructures on aluminum nitride (AlN) grown on sapphire substrates by Metal Organic Chemical Vapor deposition (MOCVD) was explored. This paper reports on the effect of *in-situ* activation in nitrogen atmosphere on MOCVD grown GaN nanostructures. The effect of introducing manganese in these nanostructures was also studied. Optically active nanostructures were successfully obtained. A blue shift is observed in the photoluminescence data with a decrease in nanostructure size.

## Introduction

GaN and its alloys with InN and AlN have been used for optoelectronic devices with blue and green wavelengths [1, 2]. High dislocation densities are present in group III - nitride heterostructures which render it necessary to localize the carriers for light generation and prevent nonradiative transitions. Therefore, reducing the dislocation density, increasing the amount of localization sites for carriers, or both may contribute to improved efficiency of light emitting devices. One way to achieve this is incorporating zero dimensional quantum dots (QDs) instead of the two dimensional quantum wells as QDs provide three-dimensional (3D) carrier confinement [3].

Stranski-Krastanow (SK) -like growth mode is not supported for the lattice mismatch between GaN and AlN (~2.5%). According to the theoretical model developed by Daruka et al. [4] a 3D growth by a ripening process that creates large islands is predicted for GaN/AlN heterostructures based on kinetics and thermodynamics [5]. However, under extreme growth conditions GaN nanostructures have been shown to have SK-like mode formations on SiC substrates using Molecular Beam Epitaxy (MBE) and MOCVD [6, 7]. This paper presents the nucleation studies of GaN nanostructures on AlN grown on sapphire substrates by MOCVD. Further, an activation step is introduced to the GaN/AlN hetero-system to support the formation

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of 3D islands revealing a SK-like growth mode. Optically active GaN nanostructures were successfully obtained. Mn was incorporated into the GaN nanostructures to explore the growth conditions for ferromagnetic nanostructures. It has been shown in recent years that MOCVD offers the option to control the incorporation of transition metal (TM) ions such as Mn on lattice sites which can result in room temperature ferromagnetism [8, 9]. Hence, the potential of the GaN/AlN hetero-system for the fabrication of multifunctional nanostructures needs to be explored as such a system keeps the potential of enhanced optical, electrical, and magnetic properties.

## Experiment

The formation of nanoscale GaN islands grown on AlN was studied as a function of growth temperature, growth rate, V/III ratio, and the amount of material deposited. The nucleation studies were performed in a highly modified commercial GaN MOCVD tool with a vertical injection system with a short jar confined inlet designed to minimize precursor pre-reactions. Trimethylgallium and trimethylaluminum were used as group III sources. Ammonia was used as a group V source, and bis-cyclopentyldienyl manganese was used as the manganese source. In some samples silane was introduced as an anti-surfactant.

In order to achieve high quality AlN buffer layers, a two step growth process was employed in which a low temperature AlN interlayer was grown at 600°C followed by a high temperature AlN layer grown at 1090°C. A 1x1 μm$^2$ AFM scan revealed the surface roughness of the AlN buffer layer to be less than 6 Å as shown in Figure 1.

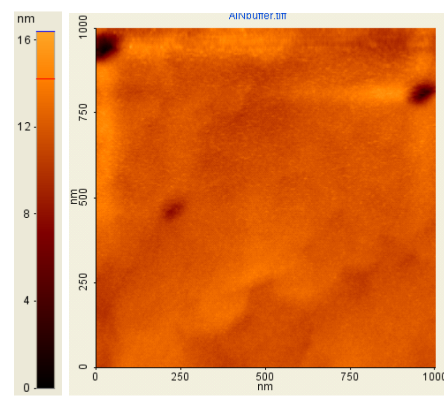

**Figure 1.** AFM image of AlN buffer layer.

A series of systematic nanostructure growth experiments were performed with temperatures between 800 and 1100°C. In order to determine the optimum molar flows for the growth a wide range of V/III ratios were explored to cover the range from standard growth conditions of high quality GaN epilayers to extremely low V/III ratios that are known to delay the transition from 2D to 3D growth.

Since the formation of GaN nanostructures is supported by a gallium bilayer [10], the influence of an anti-surfactant on the formation of nanostructures in MOCVD growth conditions was studied. Silane with 5 μmoles/min was introduced prior to GaN deposition to increase the available nucleation sites that leads to 3D formation of GaN [11, 12].

The surface morphology, size, and density of the nanostructures were analyzed using *ex- situ* experimental Atomic Force Microscopy (AFM) in a PSIA XE 100 in both contact and non-contact mode. Raman spectroscopy measurements were performed to determine the crystalline quality using a Renishaw micro-Raman system with a 488 nm excitation source. The optical property of the nanostructures was analyzed by Photoluminescence (PL) measurements using a 325nm HeCd laser with a PIXIS100 CCD camera.

## Results and Discussions

The temperature, V/III ratio, and the amount of material deposited were varied to investigate the dimensions and density of the GaN nanostructures grown on AlN epitaxial layers on sapphire substrates. The strong impact of the growth temperature on the nanostructures' density and dimensions was confirmed by varying growth temperatures between 800°C and 1100°C. It was determined that 810˚C is the favorable growth temperature as it resulted in comparatively smaller nanostructures with a high density. This relatively low temperature reduces both the kinetic energy of the atoms at the surface and the diffusion length, thereby supporting a 3D growth mode [5]. In this process the atoms are localized at the sites where they arrive at the surface instead of migrating to the edges of extended islands.

The V/III ratio is very important in nanostructure growth. Therefore, a wide range from 4.5-3500 was explored to determine the optimum conditions. Low V/III ratios favor 3D growth as it creates a metal rich condition that enhances the mobility of Ga atoms and enhances nucleation. Relatively low temperatures and extremely low V/III ratios are needed to form GaN nanostructures as shown in GaN QD growth on SiC [7, 13]. Further, the deposition time was determined to control the size of the nanostructures and the amount of material deposited. Deposition time was kept as low as possible to enable a GaN deposition between two and 20 monolayers (MLs). The critical thickness for the transition from 2D to 3D growth is reported to fit in this range according to studies on SiC [7, 14]. Silane was added to enhance nucleation in these experiments. AFM measurements resulted in nanostructures with lateral dimensions of 50 nm, height of 5 nm, and density of $3 \times 10^9$ cm$^{-2}$ for a V/III ratio of 20 and growth temperature of 810°C.

A further reduction in the nanostructure dimensions and an increase in their density were achieved using V/III ratios of less than 4.5. However, preliminary nucleation studies revealed that a thermal activation step after the deposition at ~810°C was necessary to promote the formation of nanostructures [15]. A temperature ramp was immediately applied in the reactor under a nitrogen atmosphere after GaN deposition for the activation step. A clear transition to 3D growth mode was observed for temperatures up to 970°C (Figure 2). This is because the temperature ramp increases the energy of the GaN atoms, which coalesce to from islands with smaller dimensions and larger height. AFM scans revealed nanostructures with a lateral dimension of 40 nm and height of approximately 4 nm with island densities of $1 \times 10^{10}$ cm$^{-2}$. Temperature ramps above 1000°C result in an increase in lateral dimensions which can be attributed to the ripening of the islands. A similar technique for the formation of nanostructures by an *in-situ* activation step has been demonstrated for CdSe/ZnSe QDs [16]. The strong impact of the activation temperature on the nanostructures' density and dimensions was further confirmed by performing *ex-situ* annealing in a RTA in a nitrogen atmosphere.

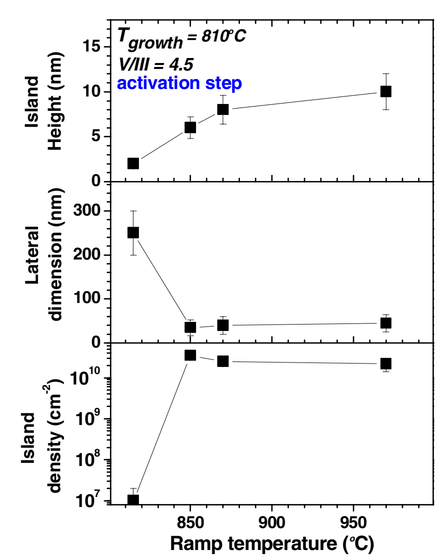


**Figure 2.** Density and dimensions of GaN/AlN nanostructures grown at 810°C and a V/III ratio of 4.5 as a function of the maximum temperature applied for the activation step

The physical properties of the nanostructures were studied in more detail by AFM and Raman spectroscopy. The nanostructure morphology and their density as obtained by AFM revealed an SK–like growth mode. The first critical thickness was observed at two MLs where the 2D growth (layer-by-layer growth) migrates into a 3D growth process. Thus, the thickness of the wetting layer is determined to be 2MLs. The density of the nanostructure increases beyond two MLs, while the size remains fairly constant. However, above eight MLs, the island density decreases and the lateral dimensions of the nanostructures increases, indicating the onset of a ripening process (Figure 3) [15, 17].

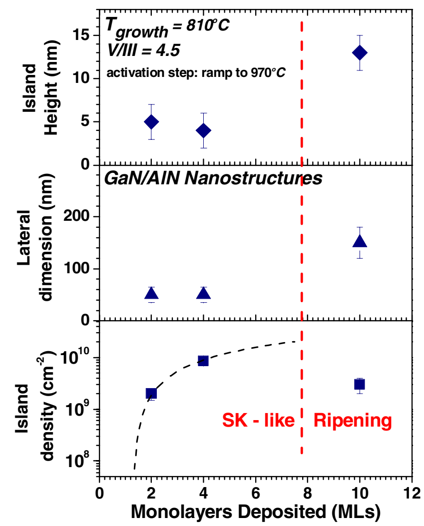


**Figure 3.** GaN / AlN nanostructure density and dimensions as a function of MLs deposited. Nanostructures begin to form at two MLs

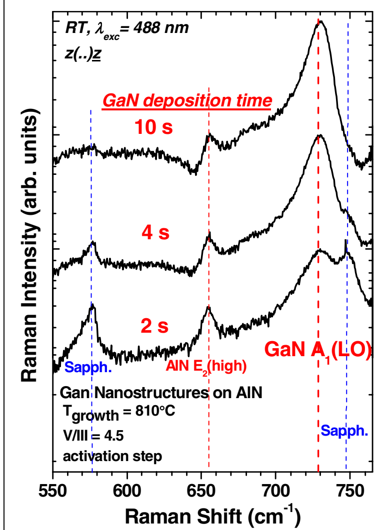


**Figure 4.** Raman spectra of GaN nanostructures for different GaN deposition times. The intensity of the GaN modes increases with the deposition time

The Micro-Raman spectroscopy data obtained from these nanostructures grown with a V/III ratio of 4.5 and a temperature of 810°C followed by an activation step at 970°C is shown in Figure 4. The presence of the GaN $A_1$(LO) mode confirms the high crystalline quality of the nanostructures despite the extremely low V/III ratio and low growth temperature. Furthermore, the intensity of the GaN related Raman mode increases with deposition time (i.e., monolayer deposition), while the intensity of the observed AlN and sapphire related modes decreases.

PL measurements were conducted on GaN nanostructures which were capped with a thin AlN layer of approximately 50 nm. As seen in Figure 5, optically active nanostructures were obtained. The lattice mismatch between the AlN template and GaN islands, results in strained islands that increase the piezoelectric fields along the c-axis. The measured transition energies of the QDs is determined to be an interplay between the quantum size effect and the giant

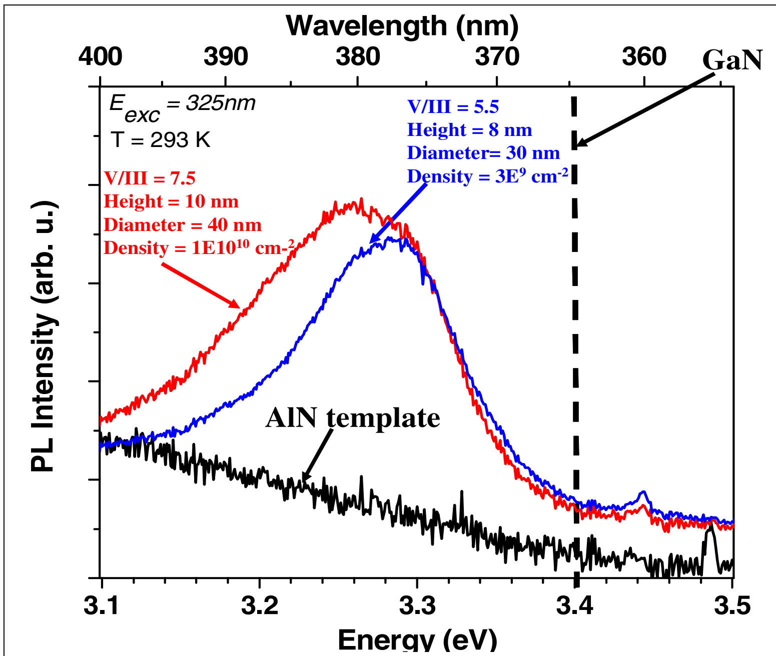


**Figure 5.** PL measurement data for GaN nanostructures. A blue shift in seen with a decrease in the nanostructure size.

piezoelectric field along the c-axis as outlined by e.g., Daudin et. al. [18]. As shown in figure 5, the GaN nanostructures show also a dependence of the PL transition energy on the dot size (height). A piezoelectric field strength of a few MV/cm (~2MV/cm) was estimated according to the respective island height and PL transition energies. In addition, the intensity of the PL is dependent on the density of the nanostructures. A higher PL intensity is obtained with a higher density of nanostructures.

To achieve multifunctional nanostructures initial nucleation studies on GaMnN grown on AlN epilayers were performed. Controlling the incorporation of transition metal ions in these nanostructures will enable control of their magnetic and optical properties. GaMnN nanostructures were grown by introducing Mn to GaN flows under the optimal conditions for the formation of nanostructures. The amount of Mn incorporated was calibrated by secondary ion mass spectroscopy measurements of bulk GaMnN layers [9]. Mn was varied from 0 to 2%, as beyond this composition phase segregation effects have been observed in bulk GaMnN layers [19]. Strain effects are not deemed to be significant at this level of composition as Mn and Ga are similar in size. The surface morphology was strongly affected by the presence of Mn atoms. The AFM characterization (Figure 6) revealed the lateral dimension decreased to 30 nm and a height of 2 nm from the Mn deposition. Further, island density increased to $3.0\times10^{10}$ $cm^{-2}$.

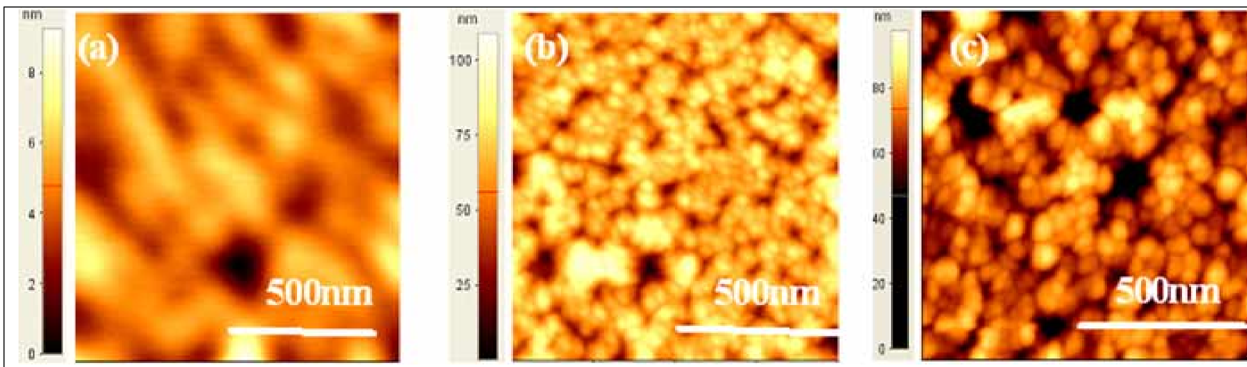


**Figure 6.** a) 0% Mn shows 2-D like behavior. (b) Mn incorporation enhances nucleation and results in 3-D growth, resulting in increased island density and reduced lateral dimension. (c) An activation step above 880°C in GaMnN nanostructures leads to ripened islands.

No annealing step was necessary to provide small nanostructures of high density — unlike for the formation of GaN nanostructures as described above. In addition, the activation temperatures for the formation of nanostructures are significantly reduced, and above 880°C ripening processes lead to increased island dimensions and smaller island densities (Figure 6c). At this time, it may be speculated that the increase in the metal concentration (decrease in the V/III ratio), the role of Mn in enhancing nucleation, or both are responsible for the observed nucleation behavior of GaMnN nanostructures.

## Conclusions

Optically active GaN nanostructures were successfully grown on AlN template layers by MOCVD that exhibit a SK-like growth mode. A low growth temperature of 810°C and a V/III ratio less than 20 were shown to promote nanostructure growth. An *in-situ* activation step involving a temperature ramp up to 970°C in a nitrogen atmosphere was successfully applied after GaN deposition to initialize a 3D growth process. Nanostructures with a lateral dimension of 40 nm and a height of approximately 4 nm with island densities of ~$10^{10}$ $cm^{-2}$ were obtained. The presence of the GaN $A_1$(LO) mode in Raman measurements confirms the high crystalline quality of the nanostructures despite the extremely low V/III ratio growth conditions at relatively low deposition temperatures. A blue shift was observed in the PL for smaller GaN nanostructures.

Initial nucleation studies on GaMnN grown on AlN template layers were performed to enable multifunctional nanostructures. Incorporation of Mn in GaN nanostructures enhanced nucleation and resulted in nanostructures with a lateral dimension of 30 nm and a height of 2 nm with increased island density of 3 x $10^{10}$ $cm^{-2}$. Unlike the GaN nanostructures, an activation step was not required to enhance nucleation in these multifunctional nanostructures.

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