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A nucleation study of group III-nitride multifunctional nanostructures

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Abstract

A Stranski–Krastanow (SK)-like growth mode is shown for GaN nanostructures on AlN template layers grown by metalorganic chemical vapor deposition on sapphire substrates. A wide temperature range from 800 to 1100 °C and V/III ratios ranging from 4.5 to 3500 were explored to determine the optimal growth conditions. Silicon was used as an anti-surfactant to enhance the nucleation. Further, an activation step was introduced to the GaN/AlN heterosystem to support the formation of 3D islands revealing a SK-like growth mode. Initial nucleation studies on GaMnN grown on AlN epilayers were performed to achieve multifunctional nanostructures, combining the advantages of quantum dots and diluted magnetic semiconductors. It is shown that manganese incorporation enhances the nucleation of GaN nanostructures. Further studies reveal that no additional activation step is necessary for nanostructures containing manganese.

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1. Introduction

Quantum dots (QDs) provide three-dimensional (3D) carrier confinement which results in discrete energy levels and in enhanced overlap of carrier wave functions giving an increased optical gain [1]. Nitride-based semiconductors have received much interest due to their applications in short-wavelength optoelectronic devices [2,3]. However, the efficiency of these devices is reduced by the presence of dislocations in the active layer. An active layer incorporating QDs offers a solution to this problem as the diffusion of carriers to non-radiative recombination centers, introduced by defects, is suppressed due to the localization in the QDs.

In addition, III-nitrides have also drawn attention because of their potential for spintronic applications, since the incorporation of transition metals (TM) such as Mn may result in room temperature ferromagnetism [4]. It has been shown that metalorganic chemical vapor deposition (MOCVD) offers the option to control the incorporation of TM ions on lattice sites which is desired for diluted magnetic semiconductors [5]. Thus, the potential of the GaN/AlN heterosystem for the fabrication of multifunctional nanostructures, which has both enhanced optical and electrical properties, needs to be explored.

A theoretical model developed by Daruka et al. [6] suggests that the formation of nanostructures in a Stranski–Krastanow (SK)-like growth mode is not supported for the lattice mismatch between GaN and AlN (~2.5%). A 3D growth by a ripening process creating islands with infinite size is predicted for GaN/AlN heterostructures based on kinetics and thermodynamics [7]. However, GaN nanostructures were recently shown to have SK-like mode formations on SiC substrates using

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molecular beam epitaxy (MBE) and MOCVD [8,9]. This paper presents the first nucleation studies of GaN nanostructures on AlN templates grown on sapphire substrates by MOCVD. Further, an activation step is introduced to the GaN/AlN heterosystem to support the formation of 3D islands revealing a SK-like growth mode. To explore the growth conditions of ferromagnetic nanostructures, the effect of Mn incorporation in GaN QD formation was studied.

2. Experiment

The formation of nanoscale GaN islands grown on AlN template layers deposited on sapphire substrates are 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 of the samples silane was introduced as an anti-surfactant.

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 1050 °C. A 10 μm atomic force microscopy (AFM) scan revealed the surface roughness of the AlN buffer layer to be 10 Å. XRD studies on AlN epilayers show that two kinds of dislocations are present, namely edge and screw dislocation. The first is observed along the *a*-axis while the later along the *c*-axis [10]. To counter this Indium was introduced to improve the surface morphology of the buffer layer. The dislocations from the buffer layer were not significant as the GaN islands obtained show SK-like growth.

A series of systemic runs were done with a temperature variation of 800–1100 °C for growth of the nanostructures. Different V/III ratios ranging from 4.5 to 3500 were used to determine the optimum molar flows for the growth. The physical characteristics of the nanostructures were controlled by the deposition time.

The growth layer time is only a few seconds as a result of the hardware limitations of the MOCVD tool, and the only way to further control the typically fast growth rate of GaN is by lowering the growth temperature. Since the decomposition efficiency of ammonia increases with temperature, a decrease of the temperature below 800 °C was not considered. V/III ratios were chosen 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 3D to 2D growth.

The surface morphology, size, and density of the nanostructures were analyzed using AFM in a PSIA XE 100 AFM 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.

3. Results and discussion

The temperature, V/III ratio, and GaN coverage (amount of deposited material) were varied to control the formation of GaN nanostructures 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 and 1100 °C. The smallest island dimensions and highest island densities occurred around 810 °C. 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 [7]. The reduced height of the islands with increasing temperature is in agreement with the assumption that the growth process is kinetically controlled: the atoms get localized at the sites where they arrive at the surface instead of migrating to the edges of extended islands.

The V/III ratio is a very important factor in nanostructure growth. A wide range from 4.5 to 3500 was explored to determine the optimum conditions. Low V/III ratios favor 3D growth as it creates a metal-rich condition that 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 [9,11]. Further, the deposition time was determined to control the height of the nanostructures and the amount of material deposited. The growth rate was determined to be approximately 1 ML/s. Deposition time was kept as low as possible to enable a GaN deposition between 2 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 [9,12].

Since the formation of GaN nanostructures is supported by a gallium bilayer [13], the influence of an anti-surfactant on the formation of nanostructures in MOCVD growth conditions was studied. Therefore, silane was introduced as an anti-surfactant prior to GaN deposition. It is assumed that silane changes the surface free energy, thereby increasing the nucleation sites for GaN and thus supporting the formation of nanostructures [14,15]. In this study, extremely low V/III ratios (below 20) were applied to support the nucleation of nanostructures.

AFM scans show nanostructures having typical lateral dimensions of 50 nm and height of 5 nm with a density of $3\times10^{9}\,cm^{-2}$ for a V/III ratio of 20 and growth temperature of 810 °C (see Fig. 1(a)). A further reduction in the nanostructure dimensions and an increase in their density were achieved using even lower V/III ratios $<$ 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. A temperature ramp was immediately applied in the reactor under a nitrogen atmosphere after GaN deposition for the

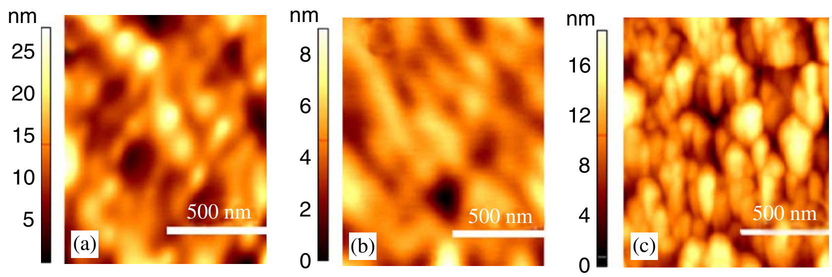

Fig. 1. (a) GaN/AlN nanostructures obtained at a V/III ratio of 20 with silane incorporation. (b) 2D growth at a V/III ratio of 4.5 without silane. (c) Sample grown under the same conditions as in (b), but with an activation step including a temperature ramp up to 970 °C applied after the GaN deposition. The activation step enhances 3D growth.

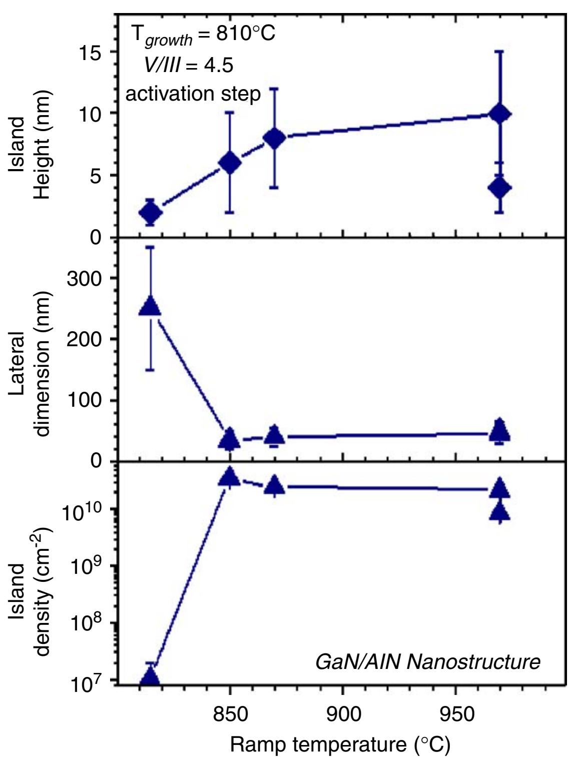

Fig. 2. Two-step growth process: GaN/AlN nanostructure density and dimensions as a function of the maximum temperature applied for the activation step.

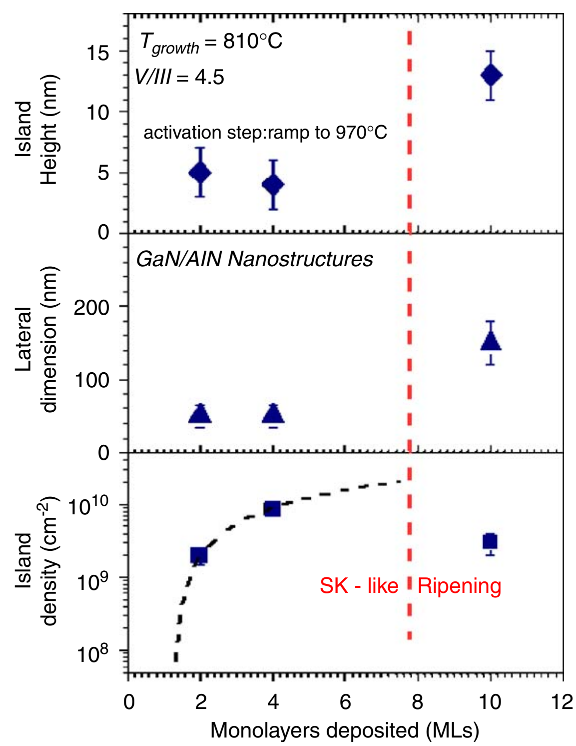

Fig. 3. GaN/AlN nanostructure density and dimensions as a function of the monolayers deposited. Two critical thicknesses are observed at approximately 2 and ~8 MLs.

activation step. A clear transition to 3D growth mode was observed for temperature ramps up to 970 °C. AFM scans show nanostructures with a lateral dimension of 40 nm and height of approximately 4 nm with island densities of $1 \times 10^{10}\,cm^{-2}$ (see Fig. 1 and Fig. 2). The nanostructures had a lateral dimension of 100 nm indicating a ripening of the islands for temperature ramps up to 1000 °C and above. A similar technique for the formation of nanostructures by an in situ activation step has been demonstrated for CdSe/ZnSe QDs [16].

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 (Fig. 3). The first critical thickness was observed at 2 MLs where the 2D growth (layer-by-layer growth) migrates into a 3D growth process. The density of the nanostructure increases beyond 2 MLs, while the size remains fairly constant. However, above 8 MLs of coverage, the island density increases and the lateral dimensions of the nanostructures increases, indicating the onset of a ripening process [17]. Thus, ~8 MLs is the second critical thickness of observed SK-like growth mode.

The enhanced Raman interaction cross-section in QDs was exploited to detect the lattice dynamics of the nanostructures by Micro-Raman spectroscopy (Fig. 4). The presence of the GaN A_1(LO) mode confirms the high crystalline quality of the nanostructures despite the

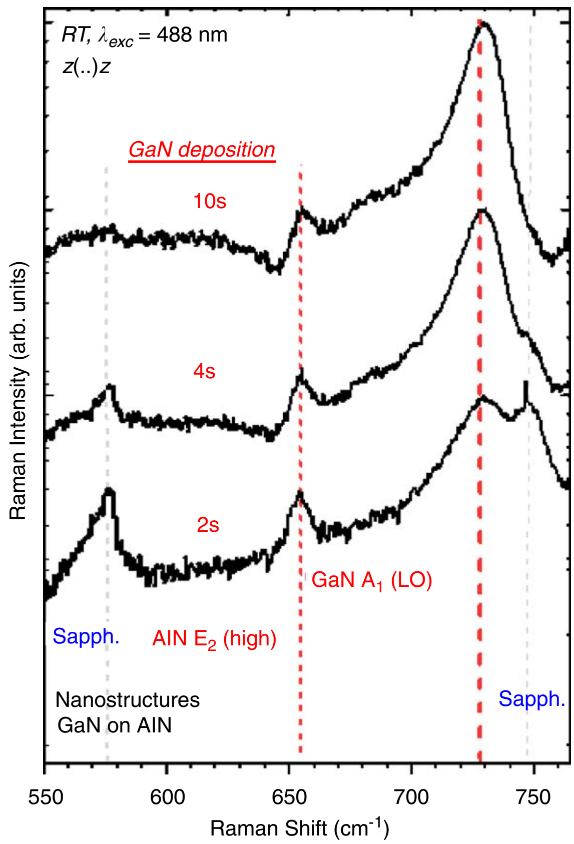

Fig. 4. Raman spectra of GaN nanostructures for different GaN deposition times. The intensity of the GaN modes increases with the deposition time.

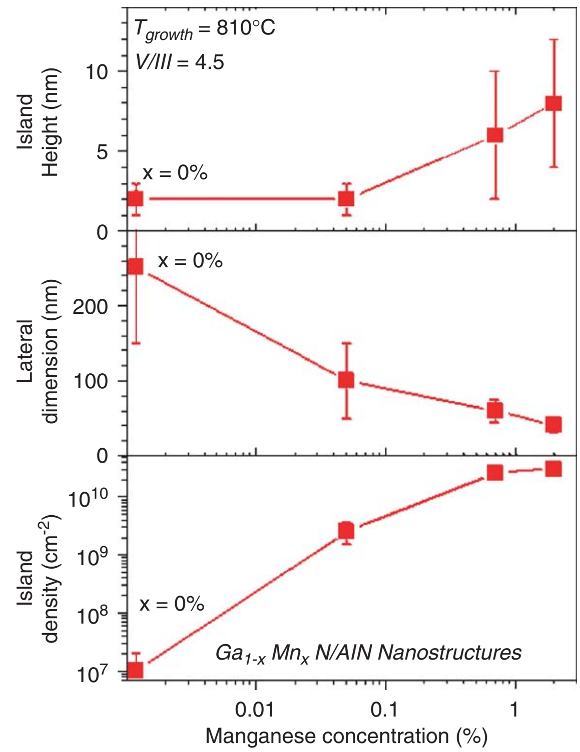

Fig. 5. GaMnN nanostructure density and dimensions as a function of Mn concentration. The presence of Mn enabled the formation of nanostructures without an activation step.

extremely low V/III ratio growth conditions at the relatively low deposition temperatures. The intensities 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 decrease.

The strong impact of the activation temperature on the nanostructures' density and dimensions were further investigated by performing ex situ annealing in a RTA in a nitrogen atmosphere. Activation temperatures varying from 820 to 970 °C were successfully applied. Above 850 °C a transition towards 3D growth was observed with AFM images showing increased island density and reduced lateral dimensions. These findings support the studies made by the in situ activation step as described above.

Initial nucleation studies on GaMnN grown on AlN epilayers were performed in order to achieve multifunctional nanostructures combining the advantages of QDs and diluted magnetic semiconductors. Controlling incorporation of TM ions in these nanostructures will enable control of their magnetic and optical properties. GaMnN nanostructures were grown by introducing Mn to GaN flows under optimal conditions for the formation of nanostructures. The amount of Mn incorporated was calibrated by secondary ion mass spectroscopy measurements of bulk GaMnN layers [5]. Mn was varied from 0% to 2%, as beyond this composition phase-segregation effects have been observed in bulk GaMnN layers [18]. Strain affects 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, as shown in Fig. 5. The AFM characterization (see Fig. 6) revealed the lateral dimension decrease to 30 nm and a height of 2 nm from the Mn deposition. Further, island density increased to $3.0 \times 10^{10}\,\mathrm{cm}^{-2}$. No annealing step was necessary to provide small nanostructures of high density unlike the GaN nanostructures. In addition, the activation temperatures for the formation of nanostructures are significantly reduced, and above 880 °C ripening processes lead to islands of infinite size reflected by increased island dimensions and smaller island densities (see Fig. 6(c) and Fig. 7). At this time, it may be speculated that the increase in the metal concentration (decrease in the V/III ratio) and/or the role of Mn in enhancing nucleation are responsible for the observed nucleation behavior of GaMnN nanostructures.

4. Conclusions

GaN nanostructures were successfully grown on AlN template layers by MOCVD in a SK-like growth mode. A low 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

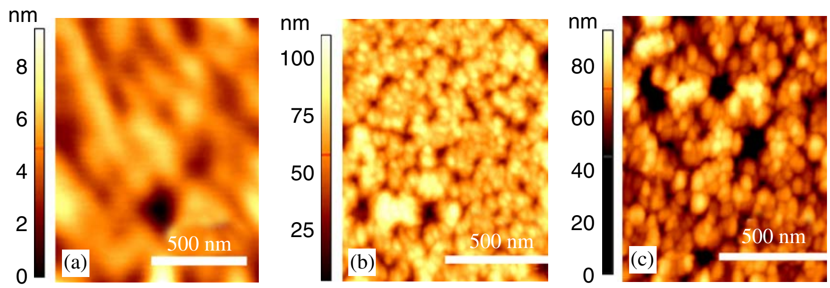

Fig. 6. (a) 0% Mn shows 2D like behavior. (b) Mn incorporation enhances nucleation and results in 3D growth, resulting in increased island density and reduced lateral dimension. (c) Activation step above 880 °C in GaMnN nanostructures leads to ripened islands.

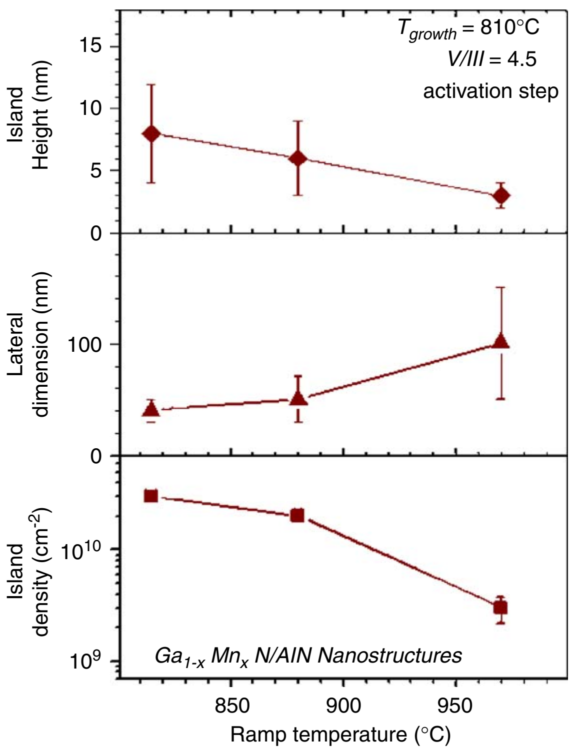

Fig. 7. GaMnN containing 2% Mn is activated at different temperatures. Activation steps with temperatures above 880 °C applied to GaMnN nanostructures lead to a ripening process providing larger islands and smaller densities.

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 $\sim 10^{10}\,cm^{-2}$ 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.

Initial nucleation studies on GaMnN grown on AlN template layers were performed to enable multifunctional nanostructures. Incorporation of Mn into 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 $3 \times 10^{10}\,cm^{-2}$. Unlike the GaN nanostructures, an activation step was not required to enhance nucleation in these multifunctional nanostructures.

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