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Reduction of threading dislocation density in $Al_{0.12}Ga_{0.88}N$ epilayers by a multistep technique

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Abstract

Although suitable for the reduction of the threading dislocation density in GaN layers the widely used two-step MOCVD method does not work as efficiently for AlGaN. This is due to slow surface diffusion of the Al species. In the present paper, the previously reported in situ multistep method for MOCVD growth of high-quality GaN films is adopted for the growth of $Al_{0.12}Ga_{0.88}N$ films on *c*-plane sapphire. The developed method for AlGaN growth is virtually GaN free in the sense that no continuous film of GaN is needed near the substrate interface. Crack-free layers of $Al_{0.12}Ga_{0.88}N$ with a thickness of about 2 μm are grown by the method. A sparse distribution of 3D GaN nucleation islands and stimulation of threading dislocation reactions enable a reduction of the threading dislocation density down to $5 \times 10^8\,cm^{-2}$ in the $Al_{0.12}Ga_{0.88}N$ films. The threading dislocation density is evaluated by etch-pit density measurements. High-resolution X-ray diffraction and transmission electron microscopy are used to study the crystallinity of the $Al_{0.12}Ga_{0.88}N$ layers. Reflectometry is utilized to analyze film growth in situ. The surface morphology of GaN nucleation layers and $Al_{0.12}Ga_{0.88}N$ epilayers is characterized by atomic force microscopy.

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Keywords: A1. Nucleation; A1. Threading dislocations; A3. MOCVD; B1. AlGaN

1. Introduction

Group III-nitride semiconductors are considered as promising materials for light-emitting devices operating in the UV and blue wavelength regions. Development of the two-step MOCVD growth method [1] for GaN has enabled the fabrication of thick GaN layers with a crystalline quality sufficient for commercial LEDs and lasers. The two-step process utilizes a thin nucleation layer (NL) at the substrate interface. The layer is grown at a lower temperature (LT) as a result of which it crystallizes in a disordered and partly amorphous phase. As process temperature is ramped up, the NL recrystallizes and GaN islands are formed. During this material redistribution process the surface morphology of the disordered LT GaN film significantly roughens, as material concentrates into islands with a predominantly hexagonal crystalline structure [2,3]. After high temperature (HT) exposure and the associated recrystallization process the NL contains a large density of Shockley and Frank partial dislocations [3]. On top of the highly faulted HT NL the large islands contain only few screw or mixed type threading dislocations (TDs). Most TDs in the GaN film are generated during the HT growth stage of the two-step process as the large GaN islands overgrow the HT NL and coalesce. TDs are formed at the coalescence boundaries of adjacent islands, henceforth referred to as nucleation islands (NIs), to accommodate for their relative crystalline misorientation [3]. When film growth restarts at HT these islands acting as nucleation centers start to grow in size. The 3D island growth continues until the NIs coalesce resulting in a continuous GaN film and a smooth film surface.

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Several attempts have been made in order to adopt the use of a LT NL for the growth of AlGaN as well [4,5]. Using Al already in the LT film is preferable. This would enable the growth of a wide band gap layer at the substrate interface helping the design of optoelectronic devices operating at UV and deep UV wavelengths. However, this type of crystal growth for AlGaN has several difficulties. The slow surface diffusion of the Al species in the MOCVD processes for group III nitrides results in a very high density of small NIs after recrystallization of an Al containing LT NL [4]. Additionally, island growth of HT AlGaN is more difficult to obtain. Consequently, island coalescence occurs very rapidly when HT AlGaN growth is started and the high density of coalescence boundaries results in TD densities of around $10^{10}\,cm^{-2}$ [6]. On the other hand, if a GaN buffer layer is utilized to improve the AlGaN quality the lattice mismatch between GaN and AlGaN results in cracking of the AlGaN epilayers [6].

Several growth techniques have been developed to decrease the TD density in GaN and AlGaN films. These techniques include pendeoepitaxy and various epitaxial lateral overgrowth (ELOG) methods [7–9]. Although the TD density can be decreased by these methods they are very time consuming, as ex situ sample manipulation is required. We have previously developed a multistep in situ technique to significantly decrease the TD density in MOCVD-grown GaN epilayers on sapphire [10–12]. The method consists of several consecutive LT deposition and recrystallization steps suppressing TDs by two distinct mechanisms. Firstly the density of GaN NIs on sapphire can be decreased by the method resulting in fewer coalescence boundaries in between the islands. Secondly the smaller NI density enables a prolonged island growth period before coalescence. This results in efficient inclination of TDs. Inclined TDs are able to react with each other by annihilation and fusion. These types of reactions reduce the TD density [13].

In this paper, we report on the adoption of the in situ multistep method to the growth of AlGaN epilayers on *c*-plane sapphire. The new MOCVD process for AlGaN is used to grow 2 μm thick crack-free $Al_{0.12}Ga_{0.88}N$ epilayers with a TD density of down to $5\times10^{8}\,cm^{-2}$. In the developed method AlGaN is grown on a discontinuous GaN NL enabling the penetration of the Al species closer to the substrate interface.

2. Experimental procedure

The studied $Al_{0.12}Ga_{0.88}N$ films were grown in a vertical flow $3\times2''$ close-coupled showerhead MOCVD reactor. Ammonia was used as the precursor for nitrogen and TMAl and TMGa were used as precursors for aluminum and gallium, respectively. Hydrogen was used as carrier gas throughout every growth run. The substrates were 2″ epi-ready *c*-plane sapphire wafers. Before deposition, the substrates went through in situ annealing at 1070 °C for 300 s in a hydrogen atmosphere. Subsequent surface nitridation was carried out at 530 °C for 300 s with an ammonia flow of 2000 sccm.

The novel multistep method was used to grow a sparse distribution of GaN NIs as described in Ref. [12]. These islands were subsequently overgrown with HT GaN and HT $Al_{0.12}Ga_{0.88}N$. The growth of HT GaN was terminated prior to the formation of a continuous GaN film as described in more detail in the next section. The growth pressures for LT GaN, HT GaN and HT $Al_{0.12}Ga_{0.88}N$ were 500, 200 and 50 Torr, respectively. Varying the ammonia flow rate between 70 and 220 mmol/min for the HT GaN growth varied the V/III ratio between 450 and 1500. The TMAl and TMGa flow rates during $Al_{0.12}Ga_{0.88}N$ growth were kept constant at 11 and 95 μmol/min, respectively. Etch-pit density (EPD) measurements were used to determine the TD density of the $Al_{0.12}Ga_{0.88}N$ layers. High-resolution X-ray diffraction (HR-XRD) was used to support the EPD measurements. The surface morphology of GaN NL samples was evaluated by atomic force microscopy (AFM). The TD content inside the GaN NIs and the $Al_{0.12}Ga_{0.88}N$ epilayers was determined by transmission electron microscopy (TEM).

3. General description of the multistep AlGaN method

The new multistep method for AlGaN growth takes advantage of the good surface diffusivity of the Ga species on a nitrogen-terminated surface [14]. This enables us to grow GaN NIs with a small density by several consecutive process cycles where LT GaN is deposited on top of recrystallized GaN islands [12]. Fig. 1 illustrates the surface reflectivity of a sample during a multistep AlGaN process where four process cycles were used for the growth of GaN NIs. The reflectivity was measured in situ in normal incidence geometry at a wavelength of 638 nm. The growth of HT GaN was started after the growth of GaN NIs at

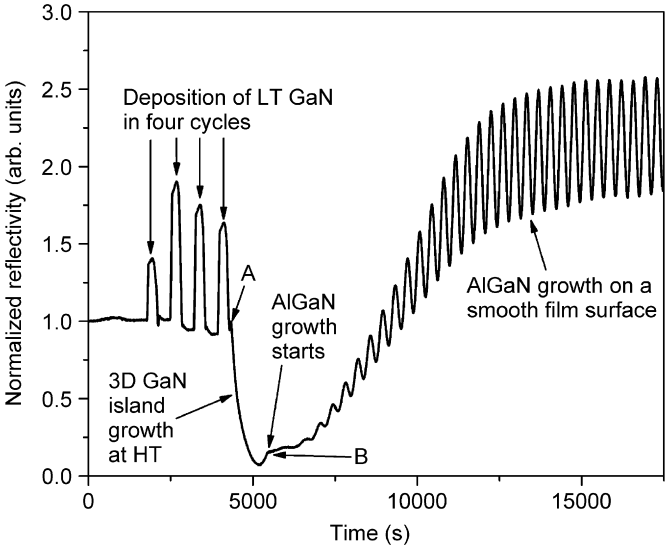

Fig. 1. In situ reflectivity data from the multistep AlGaN process. Critical points in the process are labeled in the graph.

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point A in Fig. 1. The rapid decrease in surface reflectivity between points A and B in the transient is caused by surface roughening due to the 3D growth of GaN NIs. The surface morphology of the sample at point B is presented in the AFM data of Fig. 2. This data were obtained from a separate sample, which was rapidly cooled down to room temperature in a hydrogen–ammonia atmosphere after reaching point B of the multistep process. It can be observed that at this point of the process the 3D growth of GaN has reached a stage where the NIs have not yet coalesced and they form a discontinuous GaN film. When the HT AlGaN growth starts (point B in Fig. 1) the reflectivity transient begins to oscillate with small but increasing amplitude. This suggests that AlGaN grows relatively uniformly over the GaN NIs and in the pits in between the NIs. The situation is different to the one observed in HT GaN growth where complete island coalescence would result in a big increase in surface reflectivity before the beginning of strong interference effects and oscillations [15]. Finally, the surface reflectivity starts to increase asymptotically after point B as the surface of the AlGaN film becomes smoother.

As we have demonstrated in our previous work [12] the NI density can be significantly decreased when the NL is deposited during several LT growth steps. Due to the smaller NI density we are able to use a prolonged coalescence period before the individual NIs merge. This period can be used to promote the inclination of TDs inside GaN NIs by suitably controlling the shape of the islands [10]. In practice, this is done by using a low V/III ratio during the HT GaN growth. The TEM image of Fig. 3 shows the threading dislocation content in a GaN NI and explicitly illustrates the TD inclination. This island was grown in a process with four LT deposition steps to produce a NI density of $2 \times 10^7\,cm^{-2}$. The NIs were subsequently overgrown by HT GaN for 700 s. A low V/III ratio of 650 was used during the HT stage of the process to promote vertical growth of the NIs and the resulting TD inclination.

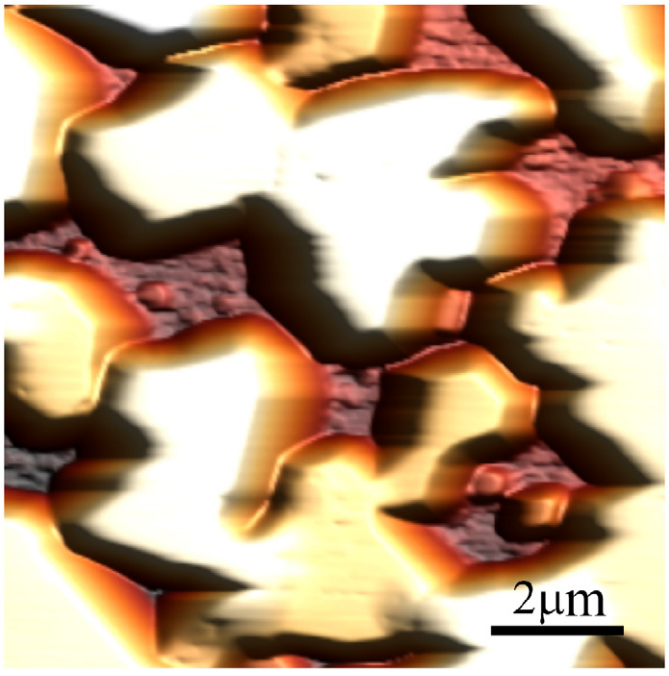

Fig. 2. AFM data illustrating the surface morphology of the GaN NL in the multistep AlGaN process prior to the beginning of AlGaN growth. The scale of the image is $10 \times 10\,\mu m$.

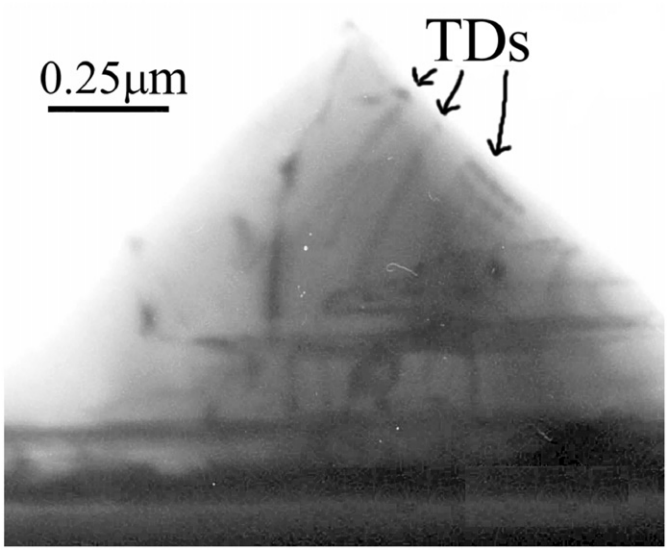

Fig. 3. Cross sectional TEM data presenting the TD content in a GaN NI. The NI was grown with a small V/III ratio of 450 to stimulate TD inclination towards the high index facets of the island.

4. Results and discussion

The multistep method for AlGaN growth was used to optimize the growth of crack-free $Al_{0.12}Ga_{0.88}N$ layers with a thickness of 2 μm. Two LT deposition cycles were used to grow the GaN NL with a small NI density of $6 \times 10^7\,cm^{-2}$. Subsequently nominally 300 nm of HT GaN was grown over the GaN NIs to increase their size. The growth of $Al_{0.12}Ga_{0.88}N$ was started when the GaN NIs approached coalescence as described above (see Fig. 2).

To demonstrate the effect of the new multistep method on the TD density of AlGaN layers several $Al_{0.12}Ga_{0.88}N$ films were grown. For these samples the V/III ratio was varied during the HT GaN growth stage. The samples illustrated in the AFM data of Fig. 4 went through wet chemical etching [12] before the AFM measurement in order to bring out TDs as etch-pits. For the sample in Fig. 4(a) (sample A) a V/III ratio of 1500 was used during the HT GaN growth stage. For the sample in Fig. 4(b) (sample B) the V/III ratio was decreased to 450 to promote the vertical growth of the NIs and the resulting TD inclination. The calculated EPD for samples A and B was $2.8 \times 10^9\,cm^{-2}$ and $5 \times 10^8\,cm^{-2}$, respectively. These samples also exhibited smooth surface morphologies, which could be further improved by a reduction in the H_2 flow rate. Previously ex situ techniques like ELOG or pendeoepitaxy have been required to obtain

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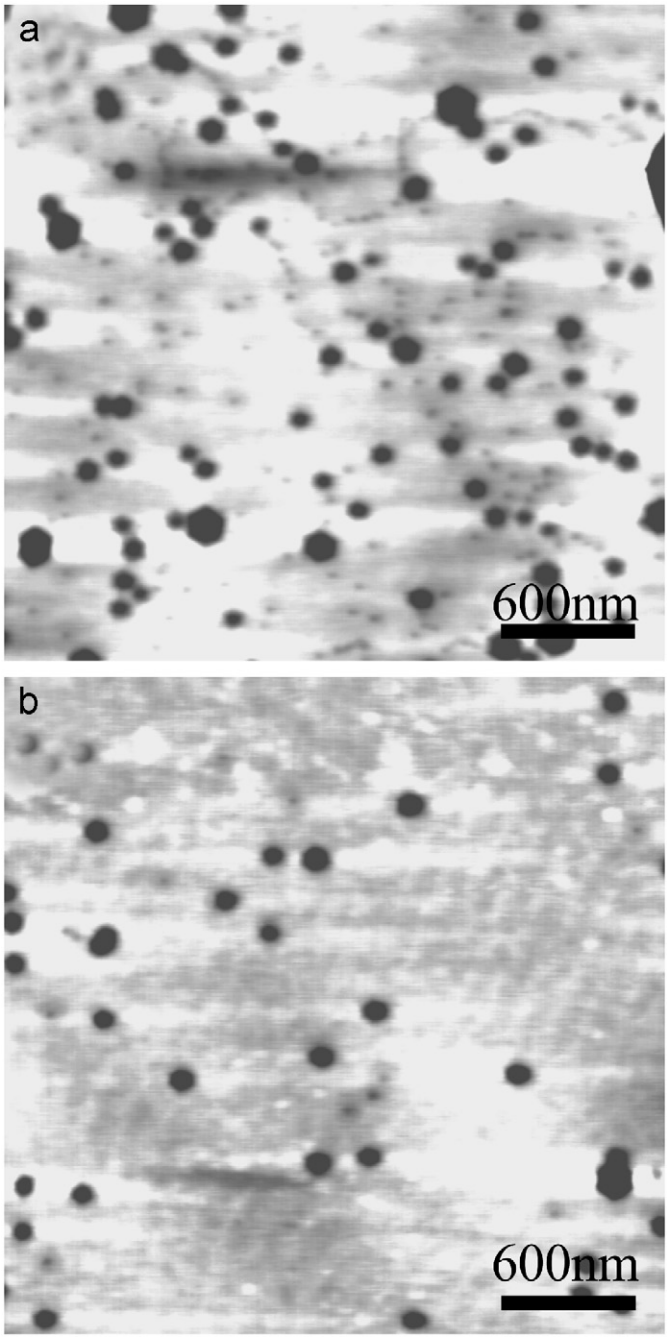

Fig. 4. Etch-pit density data obtained by AFM. A V/III ratio of 1500 (a) and 450 (b) were used during the HT GaN growth to affect the shape of the nucleation islands. A TD density of 2.8×10^9 and $5 \times 10^8\,cm^{-2}$ can be calculated for the two samples, respectively. The scale of the images is $3 \times 3\,\mu m$.

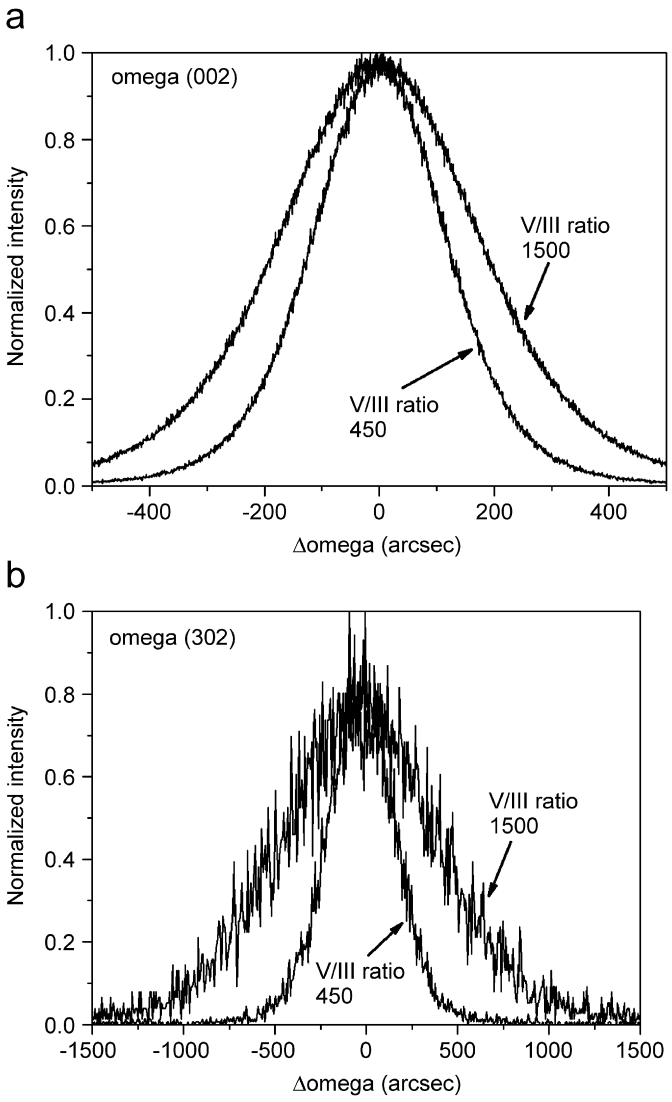

Fig. 5. HR-XRD data from the (a) (0 0 2) and (b) (3 0 2) diffraction of AlGaN. The data were recorded in a rocking curve scan for the two $Al_{0.12}Ga_{0.88}N$ layers in Fig. 4.

such low TD densities in $Al_{0.12}Ga_{0.88}N$ buffer layers grown on a thin GaN NL.

The result is supported by HR-XRD data from the same samples. This data is illustrated in Fig. 5(a) and (b) presenting the (0 0 2) and the (3 0 2) rocking curve diffraction peaks for the $Al_{0.12}Ga_{0.88}N$ layers, respectively. The width (FWHM) of the (0 0 2) diffraction peak for sample A and for sample B is 390 arcsec and 270 arcsec, respectively. The corresponding values in the (3 0 2) diffraction are 840 arcsec for sample A and 420 arcsec for sample B. The results demonstrate that the multistep method for AlGaN growth can be utilized to efficiently decrease TD density in thick and crack-free AlGaN epilayers of excellent crystalline quality. Based on the presented data the mechanisms responsible for the drastic reduction in the TD density can be assumed to be similar to the ones reported previously for the multistep GaN growth [10,12].

One of the benefits of using a thin LT NL on sapphire as the starting surface for AlGaN growth is that the theoretical critical thickness of an AlGaN layer on GaN can be substantially exceeded [4]. The cross sectional TEM data in Fig. 6 from sample A illustrates that bundles of TDs are generated at regions where $Al_{0.12}Ga_{0.88}N$ grows directly on top of the highly defective interfacial layer on the sapphire substrate. These are the regions in between the GaN NIs that are exposed for AlGaN growth. Relaxation of films through the generation of TDs at the exposed

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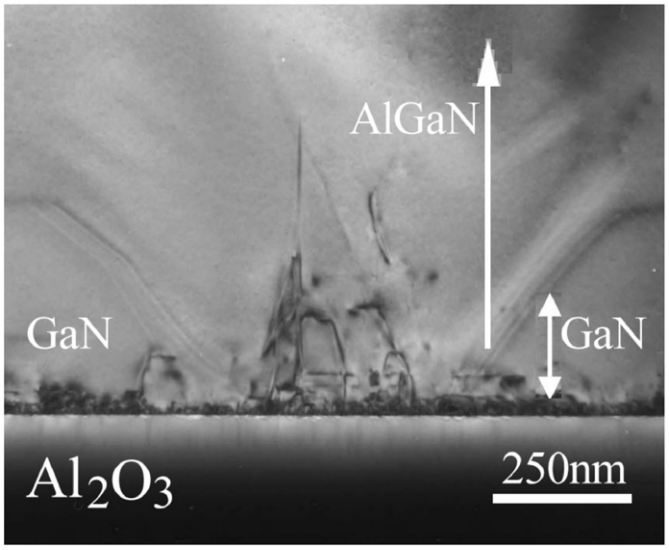

Fig. 6. Cross sectional TEM data presenting TDs generated at the exposed areas of the sapphire interfacial layer in between two GaN NIs. The data were taken from sample A.

regions helps to explain the crack-free growth of the studied $Al_{0.12}Ga_{0.88}N$ layers. The result is in agreement with previous observations indicating that thick AlGaN layers can be grown crack-free either directly on a sapphire substrate or on a thin LT NL [16].

TDs are also able to relax stresses in a heteroepitaxial film by inclination from the vertical growth direction [17]. We suggest that when penetrating into the overgrowing $Al_{0.12}Ga_{0.88}N$ layer some of the TDs are able to retain their inclination further enhancing the relaxation of the film. Detailed behavior of TDs at the interface between GaN NIs and the overgrowing AlGaN layer will be a topic of our future research.

5. Conclusions

A new multistep method for the MOCVD growth of crack-free $Al_{0.12}Ga_{0.88}N$ epilayers on a discontinuous GaN NL was reported. The method was used to improve the crystalline quality of $Al_{0.12}Ga_{0.88}N$ layers by a short HT GaN growth stage. This HT GaN growth increased the size of GaN NIs before the beginning of AlGaN overgrowth.

To reduce the TD density in $Al_{0.12}Ga_{0.88}N$ layers the previously published method for the reduction of GaN NI density was exploited. The reduced NI density allowed prolonged 3D HT growth for the GaN NIs. A low V/III ratio at this stage of the process was utilized to stimulate vertical growth of the NIs and the resulting inclination of TDs towards the high-index facets of the islands. This TD inclination together with the reduced NI density resulted in a TD density of down to $5\times10^{8}\,cm^{-2}$ in crack-free $Al_{0.12}Ga_{0.88}N$ layers of 2 μm thickness.

The discontinuity of the GaN NL enabled the relaxation of the $Al_{0.12}Ga_{0.88}N$ films. Relaxation of the film occurred through generation of TDs at the exposed areas of the highly defective sapphire interface. It was also postulated that the inclination of TDs inside the AlGaN layers could be responsible for further relaxation of the film.

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