Optical and structural microanalysis of GaN grown on SiN submonolayers

T. Riemann, a) T. Hempel, J. Christen, b) P. Veit, R. Clos, A. Dadgar, and A. Krost
Otto-von-Guericke-University Magdeburg, P.O. Box 4120, 39016 Magdeburg, Germany

U. Haboeck and A. Hoffmann
Technical University Berlin, Hardenbergstrasse 36, 10623 Berlin, Germany

(Received 21 July 2005; accepted 14 November 2005; published online 28 June 2006)

Lateral overgrowth techniques have demonstrated their ability to strongly reduce the dislocation density in GaN grown on a variety of foreign substrates. The in situ deposition of SiN during metal-organic chemical-vapor phase epitaxy (MOVPE) leads to the formation of a randomly distributed mask layer and induces lateral overgrowth similar to conventional epitaxial lateral overgrowth of GaN. Specifically for GaN on silicon substrate, the insertion of SiN submonolayers is a promising method to reduce not only the dislocation density but also the tensile stress upon Si doping. Besides the advantage of uncomplicated in situ mask formation, it allows complete coalescence and planarization of the overgrown GaN within a layer thickness of about 500 nm depending on the mask thickness, thus reducing the liability to cracking. However, the insertion of ultrathin SiN interlayers and, for thicker GaN stacks, additional stress-compensating low-temperature AIN (LT-AIN) leads to a complicated interplay of stress and dislocation density. We systematically study the impact of different interlayer designs on the evolution of stress and dislocation density in GaN on Si(111). Systematic series of samples comprising different SiN coverages, consecutively increasing GaN overgrowth times, and additionally different vertical positions of the SiN interlayer with respect to the substrate and LT-AIN were prepared by MOVPE. The resulting evolution of stress and dislocation density is assessed and correlated by spatially resolved cathodoluminescence microscopy, Raman spectroscopy, and transmission electron microscopy. © 2006 American Institute of Physics. [DOI: 10.1063/1.2150589]

INTRODUCTION

A specific problem of GaN growth on Si(111) is the huge difference by 116% of the thermal expansion coefficients between the silicon substrate and the III-nitrides. This leads to large tensile stress in the epitaxial GaN layers when cooling down from growth temperature, finally resulting in the appearance of microcracks for layers thicker than 1 μm. Additionally, the epitaxial growth is affected by the dissimilar geometric lattice properties of GaN, AIN, and Si(111). As a consequence, dislocations are already created during the stage of GaN nucleation on the AIN buffer layer on Si and further propagate into the epitaxial GaN layers with advancing growth. However, the successful technological application of GaN on Si(111) demands for crack-free material with a low dislocation density in its active layers.

Recently, the insertion of low-temperature AIN (LT-AIN) has been experimentally proven to finally solve the cracking problem.1 The underlying mechanism of stress reduction has been explored,2 and its understanding now allows the careful balancing of internal stresses and the crack-free growth of several microns of GaN on Si(111).3

SiN is one of the potential mask materials for selective area growth and is nowadays implemented in the relevant technologies for dislocation density reduction by epitaxial lateral overgrowth (ELO) of GaN.4 Like the other mask materials for standard ELO GaN,5–9 SiN has to be processed by ex situ lithography into the widely used stripe mask design,10 thus including an interruption of the GaN growth process. Here, masks have clearly defined geometry with a lateral extension on a micrometer scale.

The micrometer dimension of the mask is a great disadvantage for the performance of standard ELO on Si substrate. Even for fastest lateral overgrowth the critical thickness of about 1 μm is usually exceeded before complete planarization, thus leading to cracked ELO GaN.11 Furthermore, the demand for permanently fast lateral overgrowth is detrimental to the mechanism of dislocation bending. As a result, the highly effective two-step-ELO mode12–17 is difficult to implement, and conventional ELO GaN on Si(111) is usually characterized by the uninterrupted propagation of dislocations in the mask openings.18,19

An alternative ELO approach20 involves the in situ formation of a random SiN mask. Here, SiN islands are formed self-organized during silane exposure of the bare sapphire surface inside the metal-organic chemical-vapor phase epitaxy (MOVPE) reactor, called SiN treatment.21,22 The island size distribution is influenced by the SiN deposition time and can be adjusted to the nanoscopic dimensions being favorable for low coalescence thickness. Additionally, this process may also take advantage of dislocation bending during growth and coalescence of GaN islands, and has been shown to lead to a reduction of dislocation density similar to standard epitaxial lateral overgrowth of GaN (ELOG).23 In its original concept,21,24 the SiN treatment involves the mass-flow conversion of a low-temperature GaN layer, is specific

a)Electronic mail: till.riemann@physik.uni-magdeburg.de
b)Electronic mail: juergen.christen@physik.uni-magdeburg.de
to the use of sapphire as a substrate, and the SiN forms a compact amorphous mask of several nanometer thickness.

The adaptation of this original concept to GaN on Si(111) has been shown to significantly improve the optical and structural characteristics in terms of luminescence line width and crystal quality.

In further modification of the original SiN treatment, a considerable reduction of dislocation density already appeared during overgrowth of a submonolayer coverage of SiN. The dominant mechanism was explained to rely on masking effects due to the preferential binding of Si atoms at GaN dislocation cores, as well as the annihilation of dislocations by promoted loop formation.

A similar mechanism of dislocation density reduction was evidenced for the insertion of SiN interlayers between subsequent GaN layers using sapphire and Si(111) substrates. Even if no compact amorphous SiN mask could be observed, the presence of the SiN manifested itself in a considerable improvement of the optical and transport properties of GaN on Si(111).

To systematically investigate the impact of the SiN on GaN on silicon substrate and its interplay with LT-AlN interlayers, we prepared by MOVPE series of test structures comprising different interlayer designs.

Both the SiN coverage and the vertical position of SiN interlayers with respect to the substrate and LT-AlN interlayers were varied. These series of test structures include sample setups with the SiN interlayers directly following the AIN nucleation layer as well as the overgrowth of SiN deposited on compressively stressed GaN/LT-AlN/GaN/AlN/Si substrates. For each of these sample setups, the stress state and optical quality of the GaN as well as its lateral homogeneity were investigated by highly spatially resolved cathodoluminescence (CL) microscopy and Raman spectroscopy. The distribution of extended structural defects was determined by cross-sectional and plan-view transmission electron microscopies (TEMs).

Special attention was turned to the gradual evolution of stress and optical quality during advancing GaN growth on the SiN interlayers. For this purpose the growth time of the GaN directly following the SiN interlayer was varied. The MOVPE process was abruptly stopped after growing the template up to the SiN, at the early stages of GaN nucleation in still separated islands, during lateral overgrowth and gradual GaN island coalescence, and finally during the vertical growth of fully coalesced GaN layers. The optical microanalysis of these individual samples by Raman and CL provides a complete image of the GaN evolving on the ultrathin SiN interlayers.

**EXPERIMENT**

Figure 1 schematically illustrates the interlayer design of the samples which were prepared for the structural and optical microanalyses. All samples were grown in an AIX-200/4 RF-S MOVPE reactor on Si(111) substrates.

In set A the SiN is directly deposited on top of the AIN seed layers. The deposition time of the SiN in the MOVPE reactor was varied between 0 and 105 s, i.e., this set includes a reference sample without any SiN interlayer. Even for the longest SiN deposition time of 105 s the AIN is still not completely covered by the SiN. For the AIN:Si seed and the 700-nm-thick final GaN:Si layer the identical growth procedure was used in all samples.

In set B a deposition time of 75 s was chosen for the SiN interlayer which, as in set A, is directly deposited on the AIN seed layer. For all samples of this set the identical growth procedure was used. However, the samples systematically

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**FIG. 1.** Schematic cross section through the sample setup.

**FIG. 2.** Plan-view TEM bright-field image of the reference sample without SiN using an angle of 0.5° and 20° between the c axis and the incident electron beam in (a) and (b), respectively. The imaging plane shows the sample surface after 700 nm GaN growth.
differ from each other in the growth time of the final GaN:Si layer leading to separated GaN:Si islands for short growth times, partially coalesced GaN:Si plateaus, and eventually to fully planarized 700-nm-thick GaN:Si layers.

In set C the growth time of the final GaN was varied in the same way as in set B. In contrast to set B, set C was grown on a template containing a LT-AIN interlayer embedded between GaN:Si underneath the SiN.

Spectrally resolved CL plan-view mappings were taken at helium temperature. While the focused electron beam of a scanning electron microscope (SEM) is digitally scanned over typically $256 \times 200$ pixels, a complete CL spectrum is recorded at each pixel and stored for subsequent data evaluation. The evaluation of the CL data set $I_{CL}(x,y,\lambda)$ yields sets of CL intensity images integrating over a chosen spectral range, local CL spot spectra as well as CL wave-length yields (CLWIs), i.e., mappings of the local CL emission peak wavelength $\lambda_{\text{max}}$.

Raman spectroscopy measurements were carried out in backscattering geometry at room temperature with a triple-grating Dilor XY 800 spectrometer using a charge-coupled device (CCD) for detection. The $488 \text{ nm}$ line of an Ar$^+$/Kr$^+$ mixed-gas laser was used for excitation. With this setup we were able to detect Raman shifts with an accuracy of 0.1 cm$^{-1}$.

The TEM images were taken in a Philips CM-200. Samples were thinned by mechanical grinding, polishing, and subsequent Ar-ion milling for both plan-view and cross-sectional investigations parallel and perpendicular to the $c$ plane, respectively. All plan-view specimens were thinned from the silicon substrate, leaving the very sample surface as the remaining material.

RESULTS AND DISCUSSION

In the following section we first discuss the impact of the SiN interlayer deposition time on the structural and optical surface properties of the subsequent GaN:Si layer, using sample sets A. In the second section we concentrate on the gradual evolution of the GaN:Si during overgrowth of a specific SiN thickness in sets B and C and, in detail, investigate the consequences on stress.

At the surface of the reference sample without any SiN interlayer, the dominating structural defects are threading dislocations (TDs) with a Burgers vector in the $c$ plane and a line direction along $(0001)$. In bright-field TEM images perpendicular to the $c$ plane, as depicted in Fig. 2(a), these dislocations are visible due to their local strain field. As seen in the tilted view in Fig. 2(b), such dislocations appear both randomly distributed and in fencelike accumulations, completely surrounding submicrometer wide areas. Such areas are misoriented with respect to the adjacent GaN due to a twist of several degrees, which is also visualized in cross-sectional TEM investigations and quantified by lattice imaging (not shown here).

Figure 3 compiles overview plan-view TEM images of the three specimens prepared from set A. While image (a) again corresponds to the reference sample without any SiN interlayer, the samples depicted in (b) and (c) both contain a SiN interlayer with deposition times of 75 and 105 s, respectively. All specimens show the GaN near the former sample surface, i.e., the material after 700 nm MOVPE growth.

In Fig. 3(a) the contrast primarily results from a strong inhomogeneous bending of the TEM specimen, leading to nanoscopic fluctuations of the $c$-plane orientation with respect to the incident electron beam. This observation indicates a strong residual in-plane stress in the formerly compact GaN layer, which is partly relaxed by geometric distortion of the thin foil left after the TEM preparation. In Fig. 3(b) this effect almost completely vanishes with the insertion of the SiN interlayer. Also, the misoriented areas which are typical for growth without SiN seem to be sup-
pressed. The TD density decreases from $1.8 \times 10^{10}$ cm$^{-2}$ in (a) to $4.6 \times 10^9$ cm$^{-2}$ in (b). Unfortunately, the overall reduction of defect density is not directly proportional to the SiN deposition time. In Fig. 3(b) already some extended defects running nearly parallel to the $c$ plane can be seen, which are absent for growth without SiN. Additionally, extremely disordered regions appear about 1 $\mu$m apart from each other. For long SiN deposition times, as in Fig. 3(c), a variety of in-plane defects is generated. Furthermore, incomplete coalescence leaves hexagonal pits in the GaN surface. Here, it is disadvantageous that the GaN growth time cannot be arbitrarily extended to compensate for the delayed coalescence, as the GaN layers need to stay below the critical thickness where cracking appears.

The effect of the SiN insertion on structural defects and internal stress, as seen in TEM, has a tremendous impact on the optical properties. Figure 4 compares the CL maps of sample set A. The upper row of Fig. 4 visualizes the lateral distribution of the near band-gap CL intensity, spectrally integrated from 355 to 366 nm. All images are scaled from 0 to their individual maximum intensities, given in the upper right corner of the images. Obviously, the CL intensity, i.e., the quantum efficiency, rises monotonously with increasing SiN deposition time. Compared to the SiN-free reference sample, the total rise in intensity reaches one order of magnitude. This is in agreement with the reduction of the TD density derived from TEM, which should lead to a reduction of nonradiative recombination channels. The average size of the bright spots also increases from (a) towards (d), indicating an increase of size of defect-free areas. However, the rise of CL intensity saturates at long SiN deposition times, as expected from the additional defect generation seen in TEM. The CLWIs [(e)–(h)] in the lower row of Fig. 4 show the local CL peak maximum position, which is directly related to the local stress. A quantitative analysis of the histograms of these CLWIs evidences a monotonous shift of the mean peak position with the SiN deposition time from 362 nm (3.43 eV) in Fig. 4(e) to 359 nm (3.45 eV) in Fig. 4(h). Using a parameter of 27 meV/GPa band-gap shrinking with biaxial tensile stress$^{35}$ we derive a reduction of mean tensile stress by 0.7 GPa from Figs. 4(e)–4(h). The assignment of the CL peak shift to stress reduction is in agreement with the TEM observation of reduced in-plane stress in Fig. 3. This reduction is attributed to the larger relative distance of the initial GaN islands during nucleation on a SiN interlayer compared to direct growth on the AIN seed. This larger distance directly leads to a larger lateral extension of the initial GaN islands before coalescence occurs. Hence, fewer coalescence boundaries are formed during the transition to a flat layer, and consequently less growth induced tensile stress is incorporated in the GaN film.

The portion of stress resulting from the difference of the thermal-expansion coefficients between GaN and Si substrates should not be affected by this mechanism. Accordingly, even for the longest SiN deposition time in Fig. 4(h) the mean CL peak position still indicates residual tensile stress.

From both the structural and optical data evaluations of set A in terms of dislocation density, stress, and quantum efficiency, an optimum SiN deposition time of 75 s was derived. This SiN time of 75 s was subsequently used for the deposition of the SiN interlayers in the sample sets B and C.

Figure 5 shows SEM images in a tilted view by 45° of four samples from set B. While in (a) the GaN growth on the SiN interlayer was interrupted after 0.5 min, samples (b), (c), and (d) correspond to 1, 2, and 4 min GaN growth times. Figure 5(a) proves that in the initial stage of GaN growth

![FIG. 5. Scanning electron microscopy (SEM) images of set B. The GaN growth times in (a), (b), (c), and (d) were 0.5, 1, 2, and 4 min, respectively. Images were taken in a tilted view under 45° with respect to the $c$-axis orientation.](image)

FIG. 5. Scanning electron microscopy (SEM) images of set B. The GaN growth times in (a), (b), (c), and (d) were 0.5, 1, 2, and 4 min, respectively. Images were taken in a tilted view under 45° with respect to the $c$-axis orientation.

![FIG. 6. (Color) Plan-view maps ($T = 6$ K) of set B showing the evolution of a 700-nm-thick GaN layer on the SiN/AIN/Si(III) template: [(a)–(d)] SEM images as well as [(e)–(h)] corresponding CLWIs for GaN growth times of 2, 4, 14, and 22 min, respectively.](image)

FIG. 6. (Color) Plan-view maps ($T = 6$ K) of set B showing the evolution of a 700-nm-thick GaN layer on the SiN/AIN/Si(III) template: [(a)–(d)] SEM images as well as [(e)–(h)] corresponding CLWIs for GaN growth times of 2, 4, 14, and 22 min, respectively.
isolated islands are formed on the flat surface of the SiN-covered AlN seed layer. These GaN islands have pyramidal shape with tilted side facets. Partially, the \(0001\) GaN facet appears at the flattened pyramid tops. With advancing growth time the GaN islands expand laterally. Already after 1 min of GaN growth in Fig. 5(b) the majority of the islands exhibit a pronounced \(0001\) top facet. After 2 min adjoining islands clearly start to merge, as displayed in Fig. 5(c). In (d) coalescence is well advanced, and the AlN seed layer is almost completely covered by GaN. As clearly seen in the tilted view (d), adjacent micrometer-wide areas differ in the height of their \(c\)-plane top facet, which may account for the additional generation of extended in-plane defects during final coalescence.

The CL maps of sample set B in Figs. 6(e)–6(h) give access to the stress state of the GaN islands during their advancing coalescence. As in this sample set the template does not contain any GaN, all of the GaN luminescence can be entirely attributed to the layer evolving on the SiN. As a consequence, in Fig. 6(e) GaN luminescence is only detected when exciting at the positions of GaN islands, giving the brighter contrast in the corresponding SEM image in Fig. 6(a). In the CLWI in Fig. 6(e) the peak position of the GaN luminescence is always found near 357 nm, the very position of \((D^0,X)\) in relaxed GaN.\textsuperscript{36} Thus, the GaN islands on SiN appear to be almost stress-free and obviously decoupled from the underlying AlN seed layer, which should induce compressive stress due to the difference in lattice parameters. With the evolution of the GaN from isolated islands to a fully coalesced layer an overall spectral redshift is observed from Figs. 6(a)–6(h), indicating the gradual builtup of tensile stress. A more quantitative result is provided by the histograms of such CLWIs, depicted in Fig. 7(a). For separated GaN islands the histograms of the CLWIs are centered at 3.472 eV, the position of \((D^0,X)\) in relaxed GaN. With coalescence, the histograms shift towards lower energies which compares to the builtup of tensile stress. Even after the full coalescence around 4 min we observe a further redshift with increasing GaN thickness, i.e., a further rise of tensile stress. In comparison, Fig. 7(b) shows the result of Raman measure-
ments, performed at room temperature on the same sample set B. Here, the energetic shift of the $E_2$ phonon mode is used to determine stress. In Fig. 7(b) the Raman spectra in the vicinity of the $E_2$ mode always consist of a single peak, i.e., showing one dominant stress state of the GaN on SiN. As expected for the pure SiN/AIN/Si(111) template, no signal is detected in this spectral range due to the absence of GaN.

With advancing growth time the $E_2$ mode shifts from the position of 567 cm$^{-1}$, which corresponds to the value of relaxed GaN (Refs. 36 and 37) towards lower wave numbers. The actual peak positions of the CL histograms and the $E_2$ spectra are compared in Fig. 8. The CL results in Fig. 8(a) and the Raman data in Fig. 8(b) show the same trend. Isolated GaN islands on the SiN are nearly stress-free, while stress appears abruptly with island coalescence and, after complete coalescence, further increases with GaN layer thickness.

For sample set C, comprising two GaN layers in the template, the interpretation of the optical data is more complicated. Here, the GaN on top of the SiN as well as both GaN layers in the template emit CL under electron excitation. For short overgrowth times both GaN layers in the template are subject to direct excitation, in addition to the topmost GaN islands. For long overgrowth time the electron-beam energy is completely dissipated in the GaN layer on top of the SiN, excluding the template from direct excitation. Thus, GaN luminescence is present over the whole area of the CL scan in Fig. 9(e). In contrast to sample set B, the CL peak positions near 356 nm are found, giving rise to the violet contrast in Fig. 9(e). The comparison with the sample morphology in the corresponding SEM image in Fig. 9(a) proves that this luminescence is emitted by the template itself. The CL emission of the GaN islands themselves is found at 357 nm in Fig. 9(e). As in set B, after coalescence the final GaN shows a gradual CL redshift with increasing growth time.

The coexistence of several stress states during the initial stage of overgrowth is imaged in detail in Fig. 10. The CL scans of this partially coalesced sample show a lateral variation of the CL peak position which can be directly correlated with the local morphology. Figures 10(c)–10(e) show the local CL spectra representative for the three different stress states. According to the SEM image in Fig. 10(a), blueshifted luminescence (c) is detected in the still open areas of the GaN/LT-AIN template, indicating compressive stress in its upper part. GaN islands on SiN give rise to luminescence (d) centered at the position of $(D^0,X)$ in relaxed GaN. In fully coalesced areas redshifted CL (e) is found, evidencing tensile stress.

Additionally, Raman spectra of the $E_2$ phonon mode show the coexistence of tensile and compressive stresses in the template before overgrowth. In Fig. 11 the Raman spectrum of the template clearly consists of two spectral components. The main line at 565 cm$^{-1}$ indicates tensile stress. It is followed by a shoulder at 569 cm$^{-1}$, proving the parallel existence of compressively stressed GaN in the template. As the Raman investigations were carried out using laser light with energy below the GaN band gap, it can be assumed that the whole stack of the 700-nm-thick template was excited.
The intensity ratio of the two $E_2$ components agrees nicely with the thickness ratio of the GaN below and above the LT-AIN interlayer. Thus, the dominant tensile stressed component is identified as the initial 500-nm-thick GaN layer. The compressively stressed component of the template is attributed to the 200 nm GaN above the LT-AIN interlayer, in agreement with the CL scans. Due to the strong signal of the LT-AIN interlayer in the template, the comparatively weak $E_2$ intensity of the isolated GaN islands is obscured. However, after evolution of a thick GaN layer on top of the SiN, only a single $E_2$ component is detected. For these thick layers from set C an $E_2$ position of 565 cm$^{-1}$ is found, i.e., the same value as for direct growth on SiN/AIN/Si(111) in set B. That means that the stress accommodated in the GaN on SiN is largely independent of the initial stress state of the template. Unfortunately, this decoupling effect of the SiN submonolayer may prove disadvantageous for intentional stress engineering in thick GaN stacks on silicon substrate. Here, AIN interlayers need to be inserted to additionally establish compressive stress in subsequent GaN layers to avoid cracking. By introducing SiN above the AIN interlayers for dislocation reduction, GaN starts growing in relaxed islands and the effect of the AIN is lost. Consequently, SiN interlayers should be placed in the vicinity of the seed layer away from potential AIN interlayers, as in sample set B. As here the initial dislocation is highest which makes loop formation more probable, also the greatest impact of the SiN interlayer on dislocation density reduction is expected.

If properly optimized, the stress-compensating AIN interlayers may lead to a reduction of TD density by themselves and such may make the multiple insertion of SiN unnecessary. Figure 12 shows a cross-sectional dark-field TEM image of the final sample from set C, where the template was 21 min overgrown by GaN. In Fig. 12 an abrupt reduction of TD density is already achieved at the position of the AIN interlayer in the template. The additional effect of the SiN is quite weak, as at its position the TD density is already too low for effective loop formation.

**CONCLUSIONS**

The insertion of SiN submonolayers is an effective means to decrease the TD density in subsequent GaN layers and to reduce growth-induced tensile stress. However, the amount of deposited SiN needs to be properly adjusted, as long SiN deposition times lead to additional defect generation. According to their CL emission energy and affirmed by Raman measurements, GaN nanoislands on SiN are un-stressed in their initial stages of growth, independent of the stress state of the underlying template. As a result, the effect of stress-compensating LT-AIN interlayers is partly neutralized. The onset of thermal stress coincides with the coalescence of adjacent GaN islands. Even for fully coalesced layers, CL mapping and Raman prove a monotonous increase of overall tensile stress with advancing GaN deposition time, i.e., increasing GaN layer thickness. For such fully coalesced layers, CL visualizes a lateral modulation of the optical properties in domains of different quantum efficiency, i.e., density of nonradiative defects, whose size is influenced by the amount of deposited SiN. The CL results perfectly correlate with the dislocation distribution derived from cross-sectional and plan-view transmission electron microscopy investigations.

**ACKNOWLEDGEMENTS**

Part of this work has been funded by the Deutsche Forschungsgemeinschaft (DFG) under Contract Nos. Kr1239/10-1, Ch87/4-1, and CH 87/4-2.