Journal of Crystal Growth 311 (2009) 1997–2001

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Growth of free-standing GaN layer on Si(1 1 1) substrate

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A R T I C L E I N F O

Available online 8 November 2008

PACS:
81.05.Ea
81.15.Hi
68.55.−a
68.55.Ln
78.55.Et
68.37.Lp

Keywords:
A1. Funnel-like nano-rods
A1. Free-standing GaN
A3. RF-plasma molecular beam epitaxy
A3. Metalorganic chemical vapor deposition

A B S T R A C T

This investigation demonstrates the epitaxial growth of a free-standing GaN layer on Si(1 1 1) using a funnel-like GaN nano-rod buffer structure. The funnel-like GaN nano-rods were directly grown on Si substrates by RF-plasma molecular beam epitaxy. Free-standing GaN layers were achieved through the coalescence of funnel-like GaN nano-rods by the metalorganic chemical vapor deposition. This study examines the structure, optical characteristics and stress of GaN nano-rods and free-standing GaN layers. The *c*-axis lattice constant of the strain-free Ga-face GaN layer on Si is 5.1844 Å, as determined by high-resolution X-ray diffraction. The fully relaxed band edge at 3.468 eV without deep-level emission around 2.3 eV, was revealed in a free-standing GaN layer on Si, using photoluminescence.

1. Introduction

The III-nitride semiconductors are promising materials with great potential for high-power device and optoelectronic applications. Because of the lack of suitable substrate, most GaN layers have been grown on sapphire (0 0 0 1) substrates, which have some disadvantages, such as unavailability of large sizes, their insulating property and their hardness. The growth of gallium nitride on Si(1 1 1) has attracted considerable academic and commercial interest in recent years. The advantages of Si substrates include their low cost, large available sizes, high crystalline quality and the potential for mature device processing and device integration with Si circuits. However, growing device-quality GaN epilayers on Si substrates raises more difficulties than using sapphire because of the large difference between the lattice constants (20%) and thermal expansion coefficients (56%) of GaN and Si. These difference cause serious problems associated with stress, which induces a piezopolarization field and crack in the thick GaN epilayer, which degrade the electrical and optical properties of the devices. Accordingly, stress control in hetero-epitaxial GaN on Si remains an unsolved problem, preventing improvement in nitride technology. To overcome these problems, various treatments have been adopted to reduce the stress in the GaN epilayer on Si(1 1 1) substrate. Zhang et al. [1] demonstrated that, in addition to lowering the growth temperature, the growth of an AlN interlayer under Al-rich conditions is critical to the crack-free growth of GaN on Si(1 1 1) substrates. Cong et al. [2] investigated the effect of the AlN thickness and number of low-temperature AlN interlayers on the stress relaxation and the crystalline quality of GaN epilayers grown on Si(1 1 1) substrate. Krost and Dadger [3] employed square-patterned Si(1 1 1) using Si_xN_y mask to suppress cracks in the GaN layer. Kusakabe et al. [4] grew unstrained GaN films on (0 0 0 1) sapphire substrates using self-organized GaN nano-column buffer. In contrary, an effective method of reducing stress in GaN layer on Si by integrating RF-plasma-assisted molecular beam epitaxy (RF-MBE) and metalorganic chemical vapor deposition (MOCVD) has not been described.

This investigation, describes an approach for growing free-standing GaN films on Si substrates by integrating RF-MBE and MOCVD. A self-organized GaN nano-rod structure, grown by RF-plasma MBE, is employed as a buffer layer for subsequent MOCVD GaN growth. Overgrown GaN layers on nano-rods were

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doi:10.1016/j.jcrysgro.2008.10.099

obtained through the coalescence of GaN nano-rods. The growth morphology from GaN nano-rods to the thin film was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The residual strain in overgrown GaN layers was evaluated by high-resolution X-ray diffraction (HRXRD) and photoluminescence (PL) measurements.

2. Experimental procedure

Self-assembled GaN nano-rods were grown on Si(1 1 1) substrates by RF-plasma MBE (ULVAC MBE system). The 2-in Si(1 1 1) wafers (p-type doping) were chemically cleaned by 10% HF without rinsing in DI water to suppress the oxide formation. The temperature, nitrogen flow rate and plasma power for growing a GaN layer and nano-rods on Si were T_g=900 °C, Φ_N=4.0 sccm and P=500 W, respectively. A clear (7 × 7) surface reconstruction was confirmed by reflection high-energy electron diffraction (RHEED) at a desorption temperature of 830 °C, as presented in Fig. 1(a). The Ga-polar GaN on Si was grown at Φ_{Ga}=1.31 × 10^{-6} Torr, corresponding to nearly stoichiometric conditions. The straight and uniform GaN nano-rods were directly grown on Si(1 1 1) substrates as a nucleation layer under N-rich conditions (Φ_{Ga}=3.21 × 10^{-7} Torr) at 900 °C for 1 h. In contrast to the streaky RHEED pattern observed for the surface of the smooth thin film, the ellipse-like spotty pattern in RHEED observation (Fig. 1(b)) corresponds to the superposition of the diffraction by the top (0 0 0 1) plane and the sidewall of GaN nano-rods, indicating three-dimensional growth morphology. RHEED analysis also directly verified that the nano-rods were wurtzite single crystals structure with same growth orientation on the Si(1 1 1) substrate. Subsequently, funnel-like GaN nano-rods were formed on straight nano-rods under Ga flux conditions (Φ_{Ga}=7.12 × 10^{-7} Torr) at 900 °C for 1 h. RHEED revealed gradual change from an ellipse-like spotty pattern (straight nano-rods) to streaky with ellipse-like spotty pattern (funnel-like nano-rods), as displayed in Fig. 1(c). The streak with a spotted pattern of ellipses contributed to the flat hexagonal terrace and the boundary of hexagonal steps. This phenomenon explains lateral growth as a process of coalescence under high Ga flux conditions. The GaN layer was laterally grown on funnel-like GaN nano-rods for subsequent MOCVD GaN overgrowth under Ga flux conditions (Φ_{Ga}=1.52 × 10^{-6} Torr) at 900 °C for 1 h. Fig. 1(d) shows the streaky RHEED pattern following GaN lateral growth, which contributed to the flatness surface of the layer.

The free-standing GaN films were overgrown by MOCVD on the GaN lateral growth layer/funnel-like GaN nano-rods/Si structure. The sample was desorbed at 900 °C for 1 min in H_2 and 1 min in the mixture of H_2 and NH_3 to clean the contaminated surface. Then, a low-temperature GaN layer was grown at 525 °C for 10 min. The flow rates of hydrogen (H_2), ammonia (NH_3) and triethylgallium (TEGa) were 1000 sccm, 1500 sccm and 8.3 μmol/min, respectively. Then, the GaN was grown at 1000 °C for 20 min at a growth rate of 3.0 μm/h.

Polarity experiments were conducted in a stirred 2 M KOH solution for 30 min, and the etching temperature was maintained at 40 °C. To estimate etch pit densities (EPD), 2 M KOH solution was adopted as a defect etchant in GaN. Samples were etched at 160 °C for 10 min. The evolution of coalescence of GaN was observed under a field-emission SEM (FE-SEM). The residual strain in free-standing GaN layers was evaluated using HRXRD and PL spectroscopy measurements at 13 K.

3. Results and discussion

Figs. 2(a–d) show cross-section and plan view FE-SEM images of the evolution of the self-assembled GaN nano-rods grown on an Si(1 1 1) substrate for beam equivalent pressures (BEP) of the gallium flux from 3.21 × 10^{-7} to 7.12 × 10^{-7} Torr with a fixed amount of active nitrogen at T_g=900 °C. The morphology of the self-assembled GaN nano-rods directly grown on Si(1 1 1) depended strongly on the gallium flux. At a gallium flux of 3.21 × 10^{-7} Torr, the V/III ratio on the Si(1 1 1) surface was highly N-rich. No significant coalescence of individual nano-rods occurred, as presented in Fig. 2(a). The aspect ratio of nano-rods

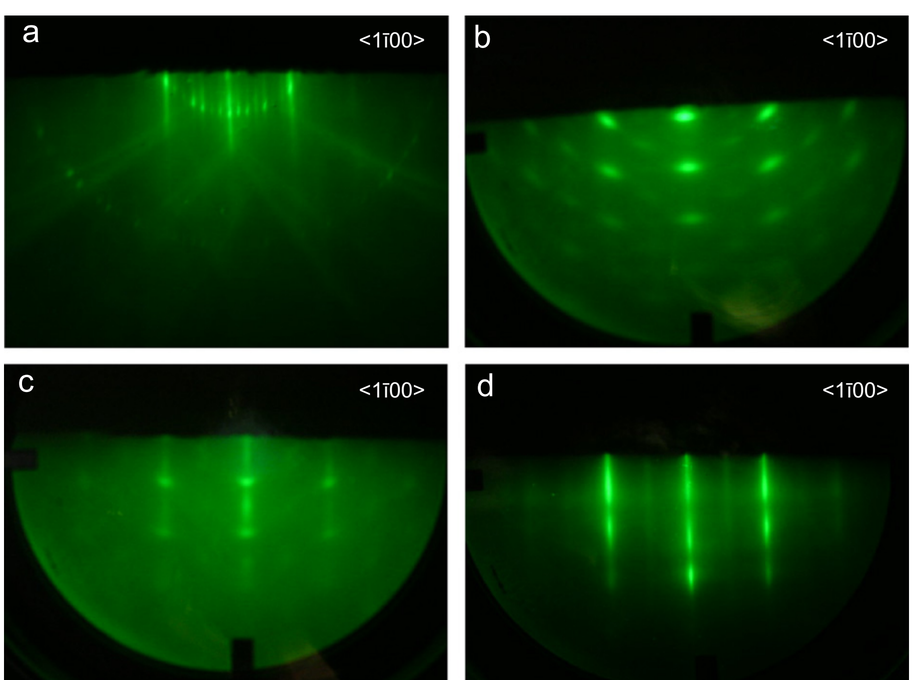

Fig. 1. The evolution of RHEED pattern along the ⟨1 $\bar{1}$ 0 0⟩ azimuth (a) is the Si(1 1 1) 7 × 7 surface, (b) straight and uniform GaN nano-rods, (c) funnel-like GaN nano-rods and (d) GaN lateral growth layer.

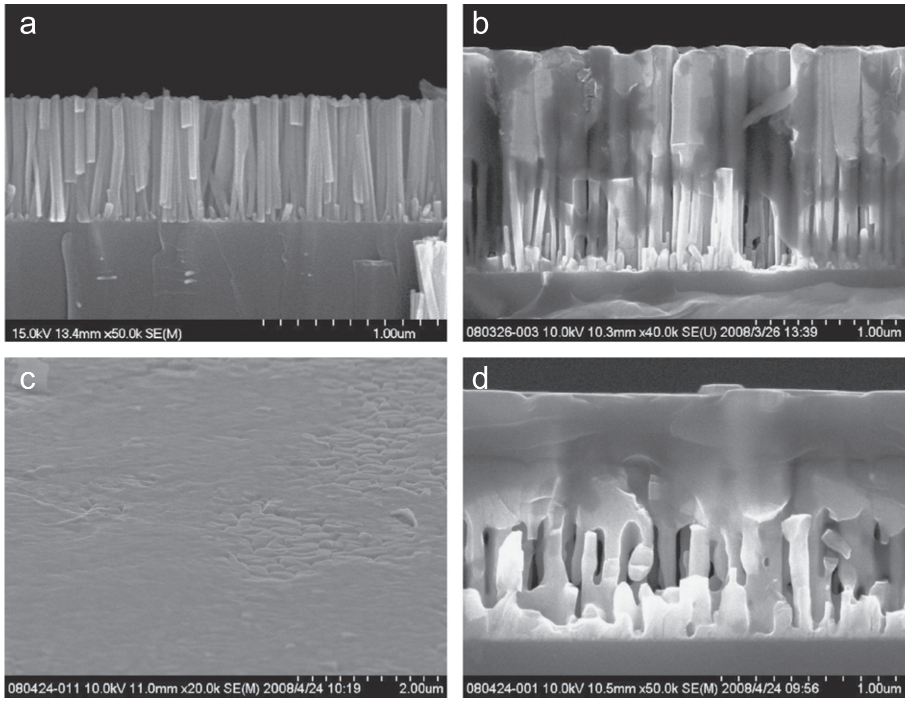

Fig. 2. FE-SEM images of the self-assembled GaN nano-rods directly grown on Si(111) by MBE. Cross-section view of (a) straight GaN nano-rods, and (b) funnel-like GaN nano-rods, (c) PLAN view of GaN lateral growth layer and (d) cross-section view of GaN lateral growth layer on funnel-like GaN nano-rods.

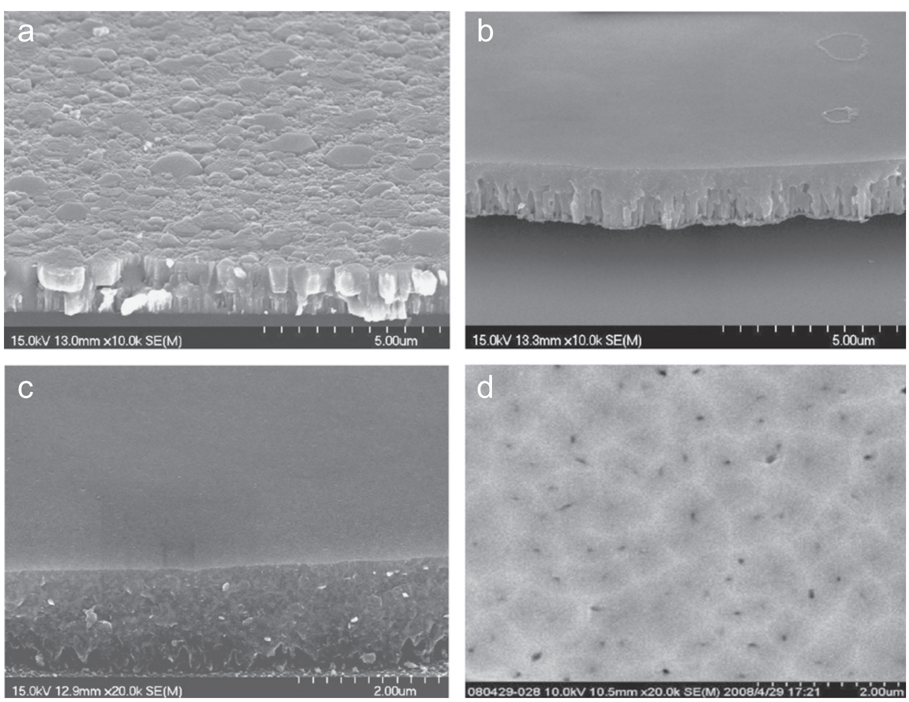

Fig. 3. FE-SEM images of (a) after 2 M KOH etches of MBE-GaN lateral growth layer, and (b) as-grown free-standing GaN layer. (c) After 2 M KOH etches of free-standing GaN layer. (d) Etch pit of MOCVD free-standing GaN layer on funnel-like GaN nano-rods.

is simply controlled by the V/III ratio. The straight GaN nano-rods exhibit mean diameter of 50 nm, a gap space of <100 nm and a density of approximately $8.8\times10^{9}\,cm^{-2}$. As the gallium flux increased, the coalescence of individual nano-rods into nano-rod bundles, increasing the diameter and reducing the gap, were observed. The tensile strain in the sample with a diameter of nano-rods about 350 nm (a gap space of around 5 nm) was observed by HRXRD. Hence, the nano-rod bundles cannot be used as a relaxer buffer to overgrow a low-stress, free-standing GaN layer on Si. In this investigation, free-standing GaN films were grown using the funnel-like GaN nano-rods buffer structure as shown in Fig. 2(b). The straight GaN nano-rods were grown initially under N-rich conditions and then under higher Ga flux conditions. The individual nano-rods gradually coalesced to become funnel-like GaN nano-rods. Thereupon, the GaN thin film with a hexagonal surface grew laterally, displayed in Fig. 2(c).

The funnel buffer structure is so called because it is shaped like a funnel wide at the top and narrow at the bottom. As the GaN nano-rod buffer was deposited on the Si substrate, the GaN nano-rods (straight) were initially isolated far from each other, and then this spacing gradually shrunk as the diameters of the rods (funnel-like) increased. Accordingly, no new nano-rod or nano-rod bundle was formed on the Si surface following the MBE lateral growth process. The wide terraces on top of the funnel-like structures prevented the formation of new nano-rod bundles during subsequent MOCVD GaN overgrowth. Fig. 2(d) depicts the cross-sectional FE-SEM image of laterally grown GaN on funnel-like GaN nano-rods. Lateral growth occurred only at the topmost surface of the funnel-like nano-rods. The top surface was flat after 1 h of MBE lateral growth.

To study the polarity of the MBE laterally grown GaN layer and the free-standing GaN film, 2 M KOH solution was used to etch the GaN films. The polarity of the GaN epitaxy layer has already been demonstrated, exploiting advantage of the fast etching of N-face in KOH aqueous solution [9]. The surface morphology of as-grown MBE laterally grown GaN differs from that after etching, as shown in Figs. 2(c) and 3(a). The root mean square (RMS) values of roughness as-grown and etched sample, were 25.8 and 210.0 nm, respectively, according to AFM analysis. In contrast, the free-standing GaN film in the as-grown and etched samples had smooth surfaces, as shown in Figs. 3(b and c). The MBE laterally grown GaN was N-polar, while the free-standing GaN film was Ga-polar. The dislocation density was examined by etching with KOH. A rough estimate of the EPDs in the etched free-standing GaN film is approximately $6 \times 10^8\,cm^{-2}$, as presented in Fig. 3(d). In this work, a GaN layer with a thickness of about 0.6 μm was necessary to enable the gap spaces to coalesce by MOCVD overgrowth. The large area free-standing GaN layer was lifted-off after etching with 2 M KOH solution without the need for a conventional laser lift-off process, greatly benefiting device applications.

To estimate the residual strain in free-standing GaN films, HRXRD was employed in $\theta - 2\theta$ scan mode, as shown in Fig. 4. The (0 0 0 2) peak indicates that the GaN layer had the wurtzite structure. The GaN epilayer on the Si(1 1 1) substrate is typically regarded as exhibiting in-plane tensile strain due to the difference between thermal expansion coefficients. However, a c-axis lattice constant of MBE-GaN on Si(1 1 1) of 5.1801 Å has been demonstrated, revealing that MBE-GaN on Si (1 1 1) exhibits some in-plane compressive strain [10]. However, the c-axis lattice constant of the free-standing GaN film was 5.1844 Å, approximating the strain-free value of 5.185 Å. The (0 0 0 2) 2θ value of a free-standing GaN film, determined by XRD reciprocal space mapping, is 34.5625°, which also is consistent with the result of HRXRD. This finding suggests that nano-rods effectively reduce the biaxial strain localized at the interface of MOCVD GaN/nano-rods and Si substrate, because the strain energy in the epitaxial layer can be significantly reduced by combining the effects of nano-structuring [5–7].

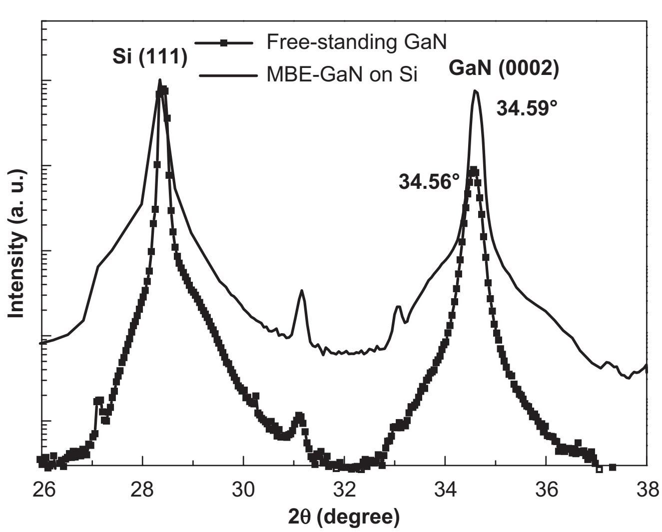

Fig. 4. HRXRD in the $\theta - 2\theta$ scan mode of MBE-GaN on Si(1 1 1) and MOCVD free-standing GaN layer on Si.

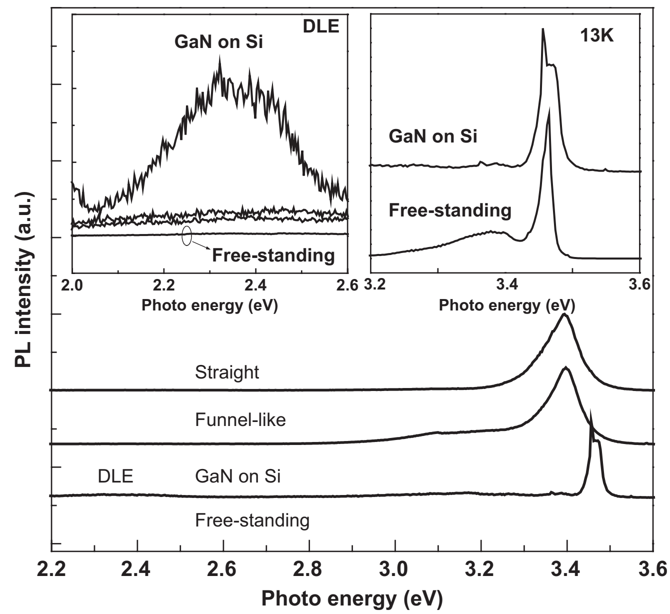

Fig. 5. PL spectra of free-standing GaN layer on Si, funnel-like nano-rods and straight nano-rods at low temperature (13 K).

PL measurements were made at 13 K to investigate the optical properties of the free-standing GaN films, MBE-GaN on Si, funnel-like GaN nano-rods and straight GaN nano-rods, as shown in Fig. 5. Strong excitonic emission is clearly observed at 3.468 and 3.457 eV with full-widths at half-maxima of 14 and 20 meV in a free-standing GaN film and MBE-GaN on Si sample, corresponding to the emission of neutral donor bound exciton ($D^{\circ}X$). The $D^{\circ}X$ at 3.468 eV also represent the full relaxation of the free-standing GaN sample, consistent with the results of Kusakabe [4]. This result, again, is consistent with the strain-free in free-standing GaN film of HRXRD. The polarities of GaN layers on funnel-like nano-rods and on Si are Ga-face, as demonstrated by KOH etching herein this study. However, the strong excitonic emission appeared around 3.397 eV in both funnel-like GaN nano-rods and straight GaN nano-rods samples, because of the zero-phonon transition from the conduction band to the acceptor (e-A) [8]. However, we hypothesize that the peak at 3.397 eV is caused by the N-face effect, which was demonstrated by KOH etching. A comparison of the PL spectrum around 2.3 eV from free-standing sample with that of GaN on the Si revealed no deep-level emission (DLE) around 2.3 eV or yellow-band in the free-standing sample. This difference indicates that the defects density in the MOCVD overgrown free-standing sample is lower than the sample of GaN on Si.

4. Conclusion

The feasibility of growing free-standing GaN on Si (1 1 1) was demonstrated using a funnel-like GaN nano-rods buffer structure. SEM images demonstrate the evolution of coalescence from straight to funnel-like nano-rods. The GaN layer with a thickness of about 0.6 μm was necessary to enable the gap spaces to coalesce by MOCVD overgrowth. The free-standing GaN layers are crack-free and strain-free. A rough estimation of the defects of the free-standing layers is approximately $6\times10^{8}\,cm^{-2}$. The *c*-axis lattice constant of free-standing GaN films is 5.1844 Å, approximating the strain-free value of 5.185 Å. PL analysis reveals full relaxation with no DLE or yellow-band in the free-standing GaN sample. The developed growth approach is very promising for use for GaN device applications.

Acknowledgements

The authors would like to thank Mr. Micheal Chen and Bomin Tu for the experimental assistance. This work was supported by the National Science Council of Taiwan under the Grant nos. NSC-97-2221-E-009-153, NSC 96-2221-E-009-236 and NSC 96-2221-E-009-202-MY3. We also would like to thank ULVAC Taiwan for maintenance supporting.

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