Corrigendum: “Influence of surface nitridation and an AlN buffer layer on the growth of GaN nanostructures on a flexible Ti metal foil using laser molecular beam epitaxy” [Jpn. J. Appl. Phys. 58, SC1032 (2019)]

Chodipilli Ramesh1,2, Prashant Tyagi1,2, Govind Gupta1,2, Muthusamy Senthil Kumar1,2, and Sunil Singh Kushvaha1,2*

1CSIR-National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi 110012, India
2Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India
*E-mail: kushvahas@nplindia.org

Received May 30, 2019; accepted June 3, 2019; published online June 17, 2019

The following corrections are incorporated in this article:

1. On page 1, the sentence “Reference 29 reported the enhancement of GaN nanocolumn alignment when a thin AlN buffer layer was introduced on a graphene-layered Si substrate” is incorrect.
   It should read “Reference 28 reported the enhancement of GaN nanocolumn alignment when a thin AlN buffer layer was introduced on a graphene-layered silica glass substrate”.

2. On page 2, the sentence “Reference 28 reported that native oxide layers on TiN caused by exposure to air only disappear after isothermal annealing at 1000 °C in an ultra-high vacuum.” is incorrect.
   It should read “Reference 29 reported that native oxide layers on TiN caused by exposure to air only disappear after isothermal annealing at 1000 °C in an ultra-high vacuum”.

© 2019 The Japan Society of Applied Physics
Influence of surface nitridation and an AlN buffer layer on the growth of GaN nanostructures on a flexible Ti metal foil using laser molecular beam epitaxy

Chodipilli Ramesh\textsuperscript{1,2}, Prashant Tyagi\textsuperscript{1,2}, Govind Gupta\textsuperscript{1,2}, Muthusamy Senthil Kumar\textsuperscript{1,2}, and Sunil Singh Kushvaha\textsuperscript{1,2,*}

\textsuperscript{1}CSIR-National Physical Laboratory, Dr. K.S. Krishnan Marg, New Delhi 110012, India
\textsuperscript{2}Academy of Scientific and Innovative Research (AcSIR), Ghaziabad 201002, India

E-mail: kushvahahas@nplindia.org

Received December 29, 2018; revised February 23, 2019; accepted February 27, 2019; published online May 17, 2019

GaN nanorods (NRs) and hollow nanocolumns (HNCs) were grown on flexible Ti foils using laser-assisted molecular beam epitaxy at a growth temperature of 700 °C. The shape, size and density of the GaN nanostructures were tuned by surface nitridation and AlN buffer layer growth temperature on a Ti foil. Sparse (∼ 5.5 × 10^6 cm\(^{-2}\)) GaN NRs were obtained on the bare surface whereas dense (∼ 3.47 × 10^5 cm\(^{-2}\)) GaN NRs were grown on the nitridated Ti foil. The shape of the GaN changed from NRs to HNCs by introducing an AlN buffer layer on nitridated Ti foil. Raman spectroscopy showed the grown GaN nanostructures have a wurtzite crystal structure. Room-temperature photoluminescence spectroscopy measurements show that the GaN nanostructures possess an intensive near band edge emission at ∼ 3.42 eV with a negligible defect-related peak. The growth of tunable GaN nanostructures on flexible metal foils is attractive for flexible optoelectronics and sensor devices.

© 2019 The Japan Society of Applied Physics

1. Introduction

GaN nanostructures are attractive for various energy applications such as light-emitting diodes (LEDs), laser diodes, solar cells and photocatalysts in chemical hydrogen production due to their excellent optoelectronic properties and stability in harsh environments.\textsuperscript{1–3} Recently, the growth of one-dimensional (1D) GaN nanostructures on metal substrates has attracted special attention due to their direct band gap, high optical reflectivity and good thermal and electrical conductivities, which are limited with conventional substrates such as sapphire and silicon.\textsuperscript{8–10} Few reports in the literature have presented the growth of 1D GaN nanostructures on various metal substrates.\textsuperscript{11–16} References \textsuperscript{15} and \textsuperscript{16} successfully fabricated highly efficient 1D GaN LED devices on metal substrates. The utilization of thin metal foil is of special interest for III-nitride growth due to its flexibility and availability in a large size at low cost, as is required for large-scale production. Reference \textsuperscript{17} showed that there is no change in the optical properties of 1D GaN nanostructures after bending of metal foil with a positive radius of curvature of 4 mm. Reference \textsuperscript{18} successfully demonstrated AlGaN-based LEDs on flexible Ta metal foil.

Flexible metal foils possess randomly oriented grains with polycrystalline structures. The growth of 1D GaN nanostructures on polycrystalline metal foils leads to the formation of randomly oriented nanostructures due to the different crystal orientations of the grains present in the metal foil. Reference \textsuperscript{18} observed the random formation of GaN nanowires (NWs) at different orientations on a polycrystalline Ti metal foil. These randomly oriented 1D GaN nanostructures are difficult to integrate when it comes to large-scale production. From the point of view of applications, therefore, it is essential to obtain a well-aligned 1D GaN nanostructure on a metal foil. Reference \textsuperscript{19} reported that the pre-nitridation of Ti metal foil favored the growth of well-aligned GaN NWs due to suppression of the influence of the crystal orientation of Ti grains by terminating the Ti top layer in TiN and TiO\(_2\) N. There are only a few reports on the growth of 1D GaN nanostructures on flexible metal foils.\textsuperscript{17–19} Still, there are many challenges involved in improving and controlling the shape, size and density of other GaN nanostructures on flexible metal foils for future nitride-based flexible devices.

Here, we present the effects of substrate nitridation as well as GaN and AlN buffer layer growth conditions on the formation of various GaN nanostructures on flexible Ti metal foils using laser-assisted molecular beam epitaxy (LMBE). In this study, our motivation is to enhance the alignment of the GaN nanostructures on the polycrystalline Ti metal foil and to control the shape and density of the GaN nanostructures. We have introduced GaN and AlN buffer layers at different growth temperatures on nitridated Ti metal foils. Thin AlN film was most commonly used as a buffer layer, especially with a Si substrate.\textsuperscript{8,20–22} The AlN buffer layer worked as a blocking layer for suppression of unwanted interfacial layer formation and also as a seed layer for growth of 1D GaN nanostructures.\textsuperscript{23–27} Reference \textsuperscript{26} showed that the AlN buffer layer improves the alignment of GaN NWs on a Si (111) substrate. Reference \textsuperscript{29} reported the enhancement of GaN nanocolumn alignment when a thin AlN buffer layer was introduced on a graphene-layered Si substrate. Here, we report on tuning of the shape of GaN nanostructures from randomly oriented NRs to a well-aligned GaN hollow nanocolumn (HNC) array on a nitridated Ti metal foil when the growth temperature of the AlN buffer layer is raised from 600 to 700 °C. The possible growth mechanism of various GaN nanostructures obtained on Ti foil is also discussed. The structural and optical properties of LMBE-grown GaN nanostructures on flexible Ti metal foils were studied systematically.

2. Experimental details

Various GaN nanostructures have been grown by the LMBE growth technique on 0.127-mm-thick Ti metal foils (Alfa Aesar, purity 99.99%) on an area of 10 mm × 10 mm by
introducing surface pre-nitridation as well as GaN and AlN buffer layers in the growth sequence. Initially, the Ti metal foil was chemically cleaned with standard organic solvents and degassed in a load lock chamber (base pressure of $2.3 \times 10^{-7}$ Torr) at 230 °C. The degassed Ti metal foil was further thermally cleaned in a growth chamber at 850 °C for 30 min under ultra-high-vacuum (base pressure $2.0 \times 10^{-10}$ Torr) conditions. Nitridation of the Ti foil was performed at 800 °C under a RF nitrogen plasma with a nitrogen flow rate of 1.1 sccm at 400 W plasma power. Here, we prepared two sets of GaN samples: in the first set, GaN was grown directly on bare (sample A0) and pre-nitridated (sample A1) Ti foil. In the second set, various buffer layers were grown on pre-nitridated Ti foils. For example, low-temperature (LT, 600 °C) GaN (sample B0), a LT (600 °C) AlN buffer layer (sample B1) and high-temperature (HT) AlN at 700 °C (sample B2) were grown on the nitridated Ti foil before the growth of the main GaN. A KrF excimer pulsed laser (wavelength 248 nm, pulse 25 ns) was used to ablate the target materials. The GaN was grown by ablating a hydride vapor phase epitaxy-grown polycrystalline solid GaN target (purity 99.9999%) with a laser repetition rate of 20 Hz and laser energy density of about 3 J cm$^{-2}$, whereas the AlN buffer layer was grown by ablating a high-temperature sintered AlN solid target with a laser repetition rate of 10 Hz and a laser energy density of about 5 J cm$^{-2}$. During the growth, additional nitrogen plasma was supplied with a nitrogen flow rate of 0.4 sccm at an applied forward power of 250 W to maintain the nitrogen-rich conditions. The main GaN was grown at 700 °C under nitrogen-rich growth conditions for a duration of 2 h.

The surface morphology of LMBE-grown GaN samples was investigated using field emission scanning electron microscopy (FESEM) (FIB, Zeiss, Germany) with an operating voltage of 5 kV. Room-temperature Raman spectroscopy was employed to find the crystal phase of the GaN nanostructures on Ti metal foil by exciting the samples with an excitation laser source of wavelength 514.5 nm. The optical emission properties were analyzed using photoluminescence (PL) spectroscopy measurements at room temperature with a 325 nm He–Cd laser as the excitation source.

3. Results and discussions

Figure 1(a) shows the 45° tilt-view FESEM image of LMBE-grown GaN on thermally cleaned bare Ti metal foil without any pre-nitridation. It reveals the growth of randomly distributed GaN NRs on untreated Ti metal foils at the kink sites or steps of thermally cleaned Ti foil.\(^1\) The length, width and density of GaN NRs were statistically analyzed using several FESEM images and were obtained as 170–650 nm, 20–60 nm and $\sim 5.5 \times 10^{6}$ cm$^{-2}$, respectively. In Ref. 19, randomly oriented GaN NWs were obtained on bare Ti foil that had a rough surface; in our case, vertically oriented growth of GaN NWs was observed on steps or kinks on bare Ti foil. High-density, well-aligned GaN NRs were obtained when GaN was grown on pre-nitridated Ti metal foil [Fig. 1(b)]. The grown GaN NRs are closely packed and the NRs were found to coalesce with neighbors at a few locations. The inset of Fig. 1(b) shows the cross-sectional FESEM image. The length, width and density of GaN NRs were in the ranges 220–320 nm, 90–150 and $\sim 3.47 \times 10^{6}$ cm$^{-2}$, respectively. These observations reveal that the adsorption of laser-ablated Ga and growth of GaN$_{1-x}$N$_x$ adatoms are highly enhanced on nitridated Ti metal foil compared with bare Ti foil. Reference 19, using ex situ X-ray photoelectron spectroscopy (XPS), reported the formation of TiN and TiO$_2$N in the uppermost layers after pre-nitridation of Ti metal foil. Reference 28 reported that native oxide layers on TiN caused by exposure to air only disappear after isothermal annealing at 1000 °C in an ultra-high vacuum. These observations show that the possibility of surface oxidation of nitridated Ti foil cannot be ignored after exposure to ambient conditions and it requires systematic in situ XPS measurements to better understand the chemical composition and species present on the uppermost layer of nitridated Ti metal foil.

Further, we have studied the effect of GaN and AlN buffer layers on GaN nanostructure formation and its surface modification when grown on pre-nitridated Ti foil. Figure 2(a) shows GaN growth on the LT-GaN buffer layer (sample B0). A GaN film consisting of nano-islands was grown and the lateral sizes of these islands were found to be in the range of 50–170 nm. This reveals that the LT-GaN layer suppresses the 1D elongated growth. For the LT-AlN buffer layer on nitridated Ti foil, GaN NRs were obtained after GaN growth at 700 °C, as shown in Fig. 2(b). The cross-sectional FESEM image presented in the inset of Fig. 2(b) shows the randomly oriented growth of GaN NRs. The GaN NRs grown on LT-AlN have a length, width and density in the range of 80–130 nm, 20–50 nm and $\sim 5.66 \times 10^{7}$ cm$^{-2}$, respectively. For GaN grown on pre-nitridated Ti metal with a HT-AlN buffer layer, the surface morphology changes from inclined NRs to vertically aligned HNC structures as seen in Fig. 2(c). The height, top width and density of GaN HNCs are in the range of 220–330 nm, 110–200 nm and $\sim 3.78 \times 10^{7}$ cm$^{-2}$, respectively. The density of the GaN

---

**Fig. 1.** (Color online) 45° tilt-view FESEM images of GaN NRs grown on (a) bare (sample A0) and (b) nitridated (sample A1) Ti metal foils. The inset of (b) shows the cross-sectional FESEM image of sample A1.
HNCs is close to the directly grown aligned GaN NRs on nitridated Ti metal foil. The FESEM studies clearly reveal that the AlN buffer growth temperature plays an important role in the shape transition of GaN nanostructures from NRs to HNCs. The change in GaN nanostructure morphology can be understood on the basis of the influence of surface modification by pre-nitridation and GaN and AlN buffer layer growth on Ti metal foil. The GaN grown on bare Ti metal foil forms sparse GaN NRs with a wider size variation, probably due to limited nucleation of GaN at a specific location such as Ti grain boundaries or kink sites [Fig. 1(a)].\textsuperscript{19} The chemical reaction of Ti metal atoms with impinging GaN adatoms suppresses GaN nucleation on Ti metal.\textsuperscript{19} As growth progresses under nitrogen plasma, new nucleation sites can be formed on Ti foil and can lead to a wider size distribution (170–650 nm) of GaN NRs on bare Ti metal foil. With pre-nitridation of Ti metal foil, the nitridated layer is likely to reduce the chance of a direct reaction between Ti metal and the impinging adatoms and thus enhances the GaN nucleation sites on Ti metal foil, resulting in high-density growth of GaN NRs. In addition to the surface nitridation of Ti metal foil, the introduction of a HT-AlN (700 °C) seed layer modifies the morphology of grown GaN from NRs to HNCs. The shape transition may occur due to the formation of stacking faults and partial stress, which originates at the HT-AlN nucleation sites.\textsuperscript{27} For a LT-AlN (600 °C) buffer layer, inclined GaN NRs were formed on Ti metal foil [seen in Fig. 2(b)].\textsuperscript{27} The AlN buffer layer grown at low temperature forms a smooth-grained AlN film due to the short diffusion length of AlN growth adatoms.\textsuperscript{27} The GaN grown on the LT-AlN buffer layer forms a coalesced dense film as a wet layer and further promotes GaN NRs at the grain edges under nitrogen-rich conditions.\textsuperscript{23,27} A similar behavior is observed when LT-GaN was used as a buffer layer on nitridated Ti metal foil, as we can see in Fig. 2(a), promoting dense growth of nano-islands.

Structural analysis of GaN nanostructures grown on Ti foil was carried out by micro-Raman spectroscopy measurements under backscattering geometry at room temperature. Raman spectroscopy is a convenient technique for identifying the crystal phase of GaN nanostructures.\textsuperscript{30–32} For example, the E2 (high) Raman peak for GaN is dominant for the wurtzite GaN structure whereas shift of the E2 (high) peak position shows the stress present in GaN.\textsuperscript{30} Figure 3(a) illustrates the Raman spectra of GaN nanostructures for samples A1, B1 and B2. The Raman spectra were fitted with the Lorentzian function for identification of various peaks and estimation of full width at half maximum (FWHM) values for E2 (high) peaks [Fig 3(b)].\textsuperscript{30} Here, the prominent Raman E2 (high) phonon peak was observed for samples A1, B1 and B2 at 566.37, 566.57 and 566.96 cm\textsuperscript{-1}, respectively. These E2 (high) peak values are close to the stress-free wurtzite GaN E2(high) peak value of 567.6 cm\textsuperscript{-1}.\textsuperscript{32–34} The presence of a Raman E2 (high) phonon peak reveals that the GaN nanostructures grown on Ti foils possess a wurtzite crystalline phase. The redshift values of the Raman E2 (high) peak of GaN samples A1, B1 and B2 are 1.23, 1.03 and 0.64 cm\textsuperscript{-1}, respectively, with respect to stress-free GaN. The stress (\(\sigma\)) present in GaN nanostructures can be estimated from the following equation:\textsuperscript{34,35}

\[
\sigma = \frac{\omega - \omega_0}{4.3}
\]

where \(\omega\) and \(\omega_0\) are the E2 (high) peak positions of the measured samples and stress-free GaN (567.6 cm\textsuperscript{-1}), respectively. The estimated values of tensile stress for samples A1, B1 and B2 are 0.28, 0.24 and 0.15 GPa, respectively. Here, sample B2 has a lower tensile stress than samples A1 and B1. These observations reveal that the AlN buffer layer affects the stress present in GaN and it is lower for a HT-AlN buffer.
layer. Reference 32 showed that GaN NRs grown on a graphene-layered Si substrate with a thin AlGaN buffer layer had a tensile stress at the bottom of the NR and this tensile stress decreased from the bottom to the top.

Figure 3(b) shows the Raman spectrum of GaN NR sample A1 fitted with the Lorentzian function. Apart from the E₂ (high) peak, we can observe forbidden E₁ (TO) and A₁ (TO) peaks at ∼556.93 and ∼529.2 cm⁻¹, respectively. The obtained E₁(TO) peak position for LMBE-grown GaN NRs on Ti foil is very close to previous reports on the free-standing GaN NRs grown (557.8 cm⁻¹) by MBE36) The appearance of Raman E₁ (TO) and A₁ (TO) peaks is due to either sidewall scattering of the incident beam or inclined GaN nanostructures.30–33) We have also estimated the FWHM value for the Raman E₂ (high) peak to find out the structural quality of samples A1, B1 and B2 and their FWHM values; the results are listed in Table I. Sample A1 has a lower FWHM value, indicating the good structural quality of GaN NRs.

Figure 4(a) shows the PL spectra of GaN nanostructure samples grown on pre-treated Ti foil. Intense near band edge (NBE) emission is observed for all the GaN samples. The PL NBE peak positions of the GaN nanostructures are 3.42, 3.36, 3.43 and 3.43 for samples A1, B0, B1 and B2, respectively. Compared with the NBE position of bulk GaN (3.4 eV),37) GaN samples A1, B1 and B2 show a blue shift of 20, 30 and 30 meV, respectively, whereas sample B0 shows a redshift of 40 meV, as we can see in the normalized PL spectrum in Fig. 4(b). The blue shift of GaN nanostructure samples A1, B1 and B2 mainly occurs due to variation of stress from the bottom to the top of the GaN nanostructures.32,38) The redshift of the PL NBE peak in sample B0, i.e. GaN film, may due to the generation of point defects during the coalescence of GaN islands.39)

Here, sample A1 exhibits a high PL intensity with a negligible yellow luminescence (YL) peak compared with the other samples [Fig. 4(a)]. However, the GaN nanostructures with an AlN buffer layer showed a significant YL peak of the PL spectrum, with a maximum of ∼2.26 eV. The GaN PL
spectrum indicates that the transition of optically excited electrons from the conduction band to deep acceptor states is negligible for samples A1 and B0.\textsuperscript{40–42} The prominent YL defect band in samples B1 and B2 is probably due to the presence of surface point defects.\textsuperscript{31,43} The broadening of the PL NBE peak was resolved by Lorentzian fitting analysis, and the FWHM values are listed in Table I. Samples B0, B1 and B2 show high PL NBE peak broadening (280–340 meV) whereas sample A1 shows a slightly lower PL NBE peak broadening (230 meV). The broadening of the PL NBE peak is due to variation of tensile stress in the nanostructures together with the superimposed luminescence intensity.\textsuperscript{30,32}

Overall, the Raman and PL spectroscopy studies imply that the GaN sample A1 has good structural and optical properties compared with the other samples. These results demonstrate that the shape and size of the GaN nanostructure can be tuned on Ti metal foil by pre-growth surface modifications such as surface nitridation and an AlN buffer layer.

4. Conclusions

GaN NRs and HNCs have been successfully grown on flexible Ti metal foil using the LMBE growth technique by tuning the surface conditions of the Ti metal. The surface morphology studies with FESEM measurement revealed that surface pre-nitridation and an AlN buffer layer play an important role in determining the size, shape and density of GaN nanostructures. Pre-nitridation of the Ti metal foil helps to increase the density of GaN NRs and also enhances their uniformity in size and shape. The growth temperature of the AlN buffer layer on nitridated Ti metal is found to change the morphology from NRs to HNCs. Raman spectroscopy analysis indicates that the grown GaN nanostructures are in the wurtzite crystal phase and possess minimal tensile biaxial stress. Room-temperature PL spectroscopy shows that the GaN NRs grown on nitridated Ti metal foil have a high NBE peak intensity compared with the other GaN nanostructures. The growth of controllable GaN nanostructures on flexible Ti metal can be attractive for flexible high-efficiency light-emitting diodes, laser diodes, solar cell and photo-electrochemical water-splitting applications.

Acknowledgments

The authors are grateful to the Director, NPL for his constant encouragement and support. The authors would like to thank Dr N. Dilawar, Dr M. Saravanan and M. Kaur for their help in characterizations. CR and PT would like to thank CSIR for the senior research fellowship (CSIR-SRF) award. CR thanks SERB-DST (file no. ITS/2018/005054) for financial support to present this work in IWN-2018, Japan.

ORCID iDs

Sunil Singh Kushvaha © https://orcid.org/0000-0003-0698-7486