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Stress distribution in GaN nanopillars using confocal Raman mapping technique

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In this Letter, high-resolution confocal Raman mapping of stress distribution in etched and re-grown GaN nanopillar structures is investigated. Results of the $E_2$(high) phonon line mapping of the top surfaces of individual nanopillars reveal differences in stress between both the center and edge of the nanopillar top surfaces and between the etched and re-grown GaN nanopillar structures. In-plane biaxial compressive stress with the values of 0.36–0.42 GPa and 0.49–0.54 GPa is observed at the center of etched and re-grown GaN nanopillars, respectively. The in-plane biaxial compressive stress decreases from center to edge in re-grown GaN nanopillar due to the tilted facets. Also, the $A_1$(LO) phonon frequency increases from center to edges, or tilted facets, due to the tilt of the c-axis of re-grown GaN nanopillar. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4872056]

Gallium nitride and its compounds are widely used materials in optoelectronics and power electronics applications due to their wide and tunable band gap, large breakdown field, high carrier mobility, and thermal stability. These properties make the material family ideal for devices such as light emitting diodes (LEDs), laser diodes, and high power transistors. Traditional GaN devices rely on lateral layer structures grown by metal organic vapor phase epitaxy (MOVPE) or molecular beam epitaxy (MBE). Recently, there has been a lot of interest towards non-lateral GaN nanostructures which might have a huge potential in optoelectronic applications by both improving the efficiency of III-nitride LEDs and modifying the emission spectra of these devices. For instance, growth of InGaN/GaN quantum wells on patterned GaN nanopillar structures can be used to achieve polychromatic white light emission due to differences of indium incorporation efficiency and growth rate of different crystal planes. The heteroepitaxial growth of lateral III-nitride layers is subjected to a large residual stress from both thermal and lattice mismatch between the epilayer and the substrate. However, it has been shown that GaN nanopillars and other patterned structures can effectively reduce the strain in the epitaxial layer. It has also been proved that the strain relaxation at the surface and sidewalls of the GaN pillars increases the indium incorporation efficiency which opens up possibilities to fabricate more efficient green and yellow LEDs from III-nitride materials. Therefore, it is important to understand the mechanism of strain relaxation in patterned GaN nanopillars. Also, a different dangling bond density and surface energy of different planes can affect indium incorporation efficiency. Previously, strain relaxation in networks of GaN nanopillars has been studied by in-plane x-ray diffraction (XRD) and photoluminescence (PL) measurements. However, these studies focused on structures with different nanopillar height and assumed the top diameter to be constant. A finite element method and linear elasticity theory based models have been proposed to understand the strain distribution in individual GaN nanopillars with different aspect ratios and lateral diameters. It is important to remember that the in-plane stress of the nanopillar is not only affected by the height of the pillar but also the lateral diameter and the shape of the pillar cross-section. The in-plane stress also changes immediately when growth is continued on top of the nanopillar templates. In this work, we study the strain distribution in individual GaN nanopillars with different lateral diameters using the confocal Raman mapping technique. In-plane stress of the nanopillars is determined both before and after the regrowth process to see how growth affects the properties of the structure.

The patterning of nanopillar templates was performed on planar 3 μm-thick undoped GaN layers grown by MOVPE on c-plane sapphire substrates using a standard two-step growth process. Trimethyl-gallium (TMGa) and ammonia (NH$_3$) were used as gallium and nitrogen sources, respectively. For the nanopillar fabrication, a 200 nm-thick silicon dioxide (SiO$_2$) mask layer was first deposited onto a GaN layer by plasma enhanced vapor phase deposition (PECVD) followed by deposition of a 20 nm-thick nickel (Ni) layer by e-beam evaporation. The Ni/SiO$_2$/GaN structure was subjected to rapid thermal annealing (RTA) at 850°C for 2 min in N$_2$ ambient to form self-assembled Ni islands. The used Ni layer thickness and annealing parameters resulted in elliptically shaped islands with average diameters ranging between 250 and 600 nm. The purpose of the SiO$_2$ mask was to enhance the island formation and improve the uniformity of the island size and shape. SiO$_2$ layer also improved the adhesion of the Ni droplets to the sample surface during the etching process steps. The Ni islands together with the SiO$_2$ layer served as an etch mask to form GaN nanopillars by reactive ion etching (RIE) and inductive couple plasma (ICP) etching. RIE was used to etch through the SiO$_2$ layer followed by Cl$_2$/Ar based ICP etching of the GaN layer. The GaN layers were etched down to the thickness of 1 μm resulting in a nanopillar height of 2 μm. The residual Ni mask and SiO$_2$ were removed by wet etching in aqua regia (3:1 mixture of hydrochloric acid and nitric acid) and diluted hydrofluoric acid (HF) solutions. Before the GaN re-growth on the nanopillar template, the wafers were...
cleaned by piranha etchant and hydrochloric acid (HCl) solution. The GaN re-growth was performed by MOVPE at 1080 °C for 80 s in H₂ ambient with a V/III ratio of 1250. The resultant film thicknesses varied between 40 and 120 nm depending on the crystal plane. During re-growth, the pillar cross-sections are transformed from elliptical to hexagonal due to the diverse growth rates of different crystal planes. Also, as desorption at high temperature H₂ ambient is crystal plane dependent hexagonal pillar formation is further promoted. The re-grown GaN nanopillar has a flat top facet (0001) plane and six smooth tilted facets of hexagonal structure with {1–101} planes (see Fig. 1(c)). Raman mapping analyses were performed on the top of individual etched GaN nanopillars and re-grown GaN nanopillars. The \( \frac{z(C0_0)}{C2z} \) backscattering geometry with \( z \) parallel to the c-axis was used. In this backscattering geometry, the selection rule for wurtzite structure allows \( E_2^\text{(high)} \) and \( A_1^\text{(LO)} \) phonon scattering. The spectra were acquired at room temperature with a confocal Raman backscattering technique using a 532 nm line from a frequency-doubled Nd:YAG laser for excitation. The laser light was coupled into the microscope using a single-mode fiber and brought on to the sample using a dichroic mirror and a 100× microscope objective (NA 0.9). The spatial resolution is about 300 nm with a spectral resolution of 0.02 cm⁻¹. The measurement tool was focused to get the maximum intensity from the top surface of the pillars which strongly reduces the intensity of the Raman signal from the background of the underlying GaN layer. Also, the measurement depth is about 1 μm as has been determined by laser excitation wavelength, material refractive index, pinhole size, and objective numerical aperture. In the detection beam path, Rayleigh-scattered light was filtered out using an edge filter and a 50 μm core-diameter fiber was used as a confocal pinhole. The backscattered light was then directed to an ultrahigh-throughput spectrometer equipped with an 1800 g/mm grating and thermoelectrically cooled electron-multiplication charge coupled device detector. The XY-positioning of the sample was achieved using a piezo-electric scanning stage, and a stepper motor was used for focus control. The scanning area was 5 μm × 5 μm. The scanning area is divided into 220 lines with 180 measurement points/line.

Figures 1(a) and 1(b) show the top and tilted view scanning electron microscopy (SEM) images of GaN nanopillars after ICP etching and mask removal. The top view of etched GaN nanopillar template shows the pillars have asymmetrical cross-sections which is due to the shape of the Ni nanodroplets used as etch masks. The side walls of the 2 μm-high pillars are nearly vertical with an average side wall angle of 88°. Side walls and the areas between the pillars have some etch induced damage. Figures 1(c) and 1(d) show the top and tilted view SEM images of GaN nanopillars after re-growth using the etched GaN nanopillars as the growth template. The hexagonal geometry is clearly visible after the re-growth. The average diameter (including tilted crystal planes) of an individual pillar is varying from 370 to 860 nm. The angle between tilted sidewall facets and the (0001) plane is measured to be about 61° ± 0.8° which has been associated with \{1–101\} planes. Insets (a) and (b) of Fig. 2 show the Raman intensity mapping of the etched GaN nanopillar template and the re-grown GaN nanopillar structure, respectively, measured in the range of 500 cm⁻¹–800 cm⁻¹ from the same area as shown in the SEM images in Figs. 1(a) and 1(c). The measurement areas are chosen from the edges of the wafers to

FIG. 1. SEM images of etched GaN nanopillar (a) top view and (b) tilted view. SEM images of re-grown GaN nanopillars (c) top view and (d) tilted view. The scale bar corresponds to 1 μm in (a) and (c), 2 μm in (b) and 300 nm in (d).
simplify the detection of the same location in different characterization tools. This explains the rather low density of pillars for some parts of the analysis area. The Raman mapping clearly shows the distribution of the GaN nanopillars on the background GaN surface. The corresponding Raman spectra measured from the top of individual etched and re-grown GaN nanopillars together with the underlying GaN layer are shown in Figure 2. The Raman spectrum of the etched GaN nanopillar reveals a sharp $E_2$(high) phonon mode at 568.6 cm$^{-1}$ and $A_1$ (LO) phonon mode at 736.5 cm$^{-1}$. In addition, there is also a peak located at 703.8 cm$^{-1}$. Previously, this has been reported as the surface optical (SO) phonon mode in GaN nanostructures. From the re-grown GaN nanopillar, the $E_2$(high) phonon and $A_1$ (LO) phonon modes can be observed at 569.3 cm$^{-1}$ and 737.0 cm$^{-1}$, respectively. The $E_2$(high) phonon mode is at a higher wavenumber in the re-grown GaN nanopillar and the underlying GaN layer compared to the etched GaN nanopillar. This indicates that the top of the re-grown GaN nanopillar is compressively stressed compared to the top of the etched GaN nanopillar. The intensities of $E_2$(high) and $A_1$ (LO) phonons are lower in the underlying GaN layer compared to the etched and re-grown GaN nanopillars due to a slightly out of focus measurement geometry.

To gain more understanding about the stress distribution in individual etched and re-grown GaN nanopillars, a detailed Raman mapping was performed from 563 to 580 cm$^{-1}$ to cover $E_2$(high) phonon frequencies. In order to obtain the precise $E_2$(high) phonon frequency position, the measured spectra were fitted with Lorentzian line shapes. Insets of Figs. 3(a) and 3(b) show the Raman image of $E_2$(high) phonon frequency position fitted with Lorentzian line shape of etched and re-grown GaN nanopillars. Figure 3(a) shows $E_2$(high) phonon frequency as a function of position (black line) in the area of two etched GaN nanopillars having a different cross-sectional diameter and includes the underlying GaN layer between the pillars. The measurement line is shown in the Raman image in the inset. The frequency profile shows that the maximum of $E_2$(high) phonon is observed at 569.6 cm$^{-1}$ on the underlying GaN layer. The $E_2$(high) phonon frequency decreases when moving from the center towards the edges of the GaN nanopillars. The $E_2$(high) phonon frequency value is strongly dependent on the GaN nanopillar lateral geometry. The $E_2$(high) phonon frequency value at the center of the pillar top is smaller for smaller cross-sectional diameter GaN nanopillar compared to the larger one. Figure 3(b) shows the...
respectively. The maximum of the E₂(high) phonon frequency is located at 569.15 cm⁻¹ on the underlying GaN layer. The relation between E₂(high) phonon frequency shift and the residual diameter increases from 380 nm to 620 nm. The relation between E₂(high) phonon frequency shift and the residual diameter is heavily dependent on the pillar diameter. The frequency at the center of the pillar is heavily dependent on the lateral dimension of the nanopillar and it does not have a clear correlation with the pillar diameter. The frequency at the center of the nanopillar shows higher crystalline quality compared to the etched GaN nanopillars and 0.49–0.54 GPa in the center of the re-grown GaN nanopillars. Figure 4 shows the residual stress at the center of the etched and re-grown GaN nanopillars as a function of pillar diameter from 200 to 650 nm. It is evident that the stress in the middle (0001) plane of the nanopillar increases as soon as re-growth process is started. The average difference of the biaxial compressive stress is about 0.1 GPa for etched and re-grown GaN nanopillars with the same lateral diameter. The increase of stress in the re-grown GaN nanopillar compared to the etched GaN nanopillar may be related to etch induced damage releasing the stress inside the pillar. The FWHM value of about 4.7 cm⁻¹ in the re-grown GaN nanopillar shows higher crystalline quality compared to the value of 5.1 cm⁻¹ measured in the etched GaN nanopillar. During re-growth, the overall crystal quality of the pillar and electrical properties are improved, resulting in higher compressive stress in the pillar. In previous studies, a finite element method and continuous media approach have shown that the in-plane stress is sensitive to the geometry and aspect ratio of the nanopillars. It has been shown that the part more accessible to the free surface is more flexible to release strain. Recently, Le Boulbar et al. have studied the strain relaxation of etched and re-grown GaN nanorods using Raman spectroscopy. They show that the GaN nanorods are fully relaxed in etched and re-grown structures. Re-growth of GaN onto the etched nanorods does not re-introduce strain in their studies. However, in our case, with the confocal Raman mapping technique, we are able to experimentally determine the stress distribution at the surface of the individual nanopillars with different diameters and surface geometries. Based on our results, the stress in the re-grown GaN nanopillar depends strongly on the geometry.

In order to understand the biaxial compressive stress relaxation from the center to the edges, or tilted facets, of re-grown GaN nanopillars, we have performed A₁(LO) phonon mapping. The inset of Figure 4(b) shows the Raman image of the A₁ (LO) phonon frequency position fitted with

![Graph and images](image-url)
Gaussian line shape from 720 cm\(^{-1}\) to 750 cm\(^{-1}\). The corresponding peak position is shown with the red line. Also, the E\(_2\)(high) frequency position is shown in dotted line for comparison. The A\(_1\)(LO) phonon position and E\(_2\)(high) phonon line positions show a clear relation. A\(_1\)(LO) phonon frequency is observed at about 736 ± 1.02 cm\(^{-1}\) at the center of the top of the GaN nanopillars having different diameters of 380 nm and 620 nm. This indicates that the center of the top of the re-grown GaN nanopillar is along the (0001) axis. Moreover, the A\(_1\)(LO) phonon frequency shifts to higher wavenumbers when moving from the center to the tilted facets of the GaN nanopillars. On the other hand, A\(_1\)(LO) phonon frequency is observed at about 740 cm\(^{-1}\) from the underlying GaN layer. Previously, the shifting of A\(_1\)(LO) phonon position towards the E\(_1\)(LO) phonon position has been reported as quasi longitudinal (QLO) modes due to the tilting of crystal axes relative to the phonon propagation direction.\(^{20}\) The intermediate energies of the QLO mode between the A\(_1\)(LO) and E\(_1\)(LO) phonon mode can be calculated using\(^{21}\)

\[
\omega^2_{QLO}(LO) = \omega^2_{A1(LO)} \cos^2(\theta) + \omega^2_{E1(LO)} \sin^2(\theta),
\]

where \(\theta\) is the angle between the phonon propagation direction and the c-axis of the sample. The LO phonon has a frequency between that of the A\(_1\)(LO) mode (phonon propagation along the c-axis, \(\theta = 0^\circ\)) and that of E\(_1\)(LO) phonon mode (\(\theta = 90^\circ\)). The phonon propagation at the center of top of GaN nanopillar is observed to 736 ± 1.02 cm\(^{-1}\) meaning that this has (0001) axis. On the other hand, the shifting of A\(_1\)(LO) phonon to higher wavenumbers when moving from center to the tilted facets of the GaN nanopillars is due to light refraction away from normal incidence.\(^{20}\) Furthermore, as ICP processing etches uniformly the GaN layer, the underlying GaN layer (not covered by Ni) area becomes very rough due to ion bombardment. The bombardment of energetic ions during dry etching accelerates the atom removal at the layer surface and introduces ion induced damages, deteriorating the crystalline quality. This roughened underlying GaN layer thus scatters the light from the normal incidence which in turn shifts the polar-sensitive A\(_1\)(LO) to a higher wavenumber.\(^{22}\) The material under the tilted facets of the pillars is grown in both the lateral and vertical (0001) growth directions during the re-growth process. The crystal quality in this area is very high due to homoepitaxial growth. Therefore, the mechanism of stress relaxation when moving from center to edge in the re-grown GaN nanopillars is due to the growth direction. On the other hand, etching induced damage and dislocations may cause increased stress relaxation when moving from center to edges in the etched GaN nanopillars. Moreover, the part more accessible to the free surface area causes stress relaxation in both etched and re-grown GaN nanopillar.

In summary, the stress distribution of individual etched and re-grown GaN nanopillars have been studied by confocal Raman mapping. The biaxial compressive stress in etched and re-grown GaN nanopillars is shown to strongly depend on the nanostructure geometry. The stress relaxation is observed when moving from center to edge in both the etched and re-grown GaN nanopillars. In the re-grown GaN nanopillar, the stress relaxation from center to edge is attributed to the tilted facets. The A\(_1\)(LO) phonon shifts to a higher wavenumber, due to light refraction in the tilted facets of re-grown GaN nanopillar, which supports the stress relaxation mechanism.

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