Strain relaxation in GaN nanopillars

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In this work, we demonstrate the direct measurement of the strain state at the surface of nanostructures by in-plane X-ray diffraction. GaN tapered nanopillars have been fabricated by dry etching of a highly strained epilayer. The strain of the surface as function of pillar height shows an exponential relaxation which can be described by a single relaxation parameter. Additionally, we have simulated the strain relaxation and distribution of nanopillars. The impact of the pillar geometry on the strain relaxation has been discussed. In agreement with the measurements, an exponential relaxation of the strain is observed. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4772481]

GaN-based light-emitting diodes (LEDs) emitting at UV and visible wavelengths have been accomplished, following the progress in epitaxy technology and structural design of the active layers. Nanostructuring has been proposed to improve the performance of III-nitride LEDs. For instance, lateral growth of InGaN/GaN quantum wells (QWs) on GaN nanopillars can be used to achieve a broader emission spectrum due to the differences in indium incorporation and QW growth rate at the different crystal planes. Additionally, nanostructuring of the surface can enhance the light extraction of LEDs due to the enlarged interface area and improved light scattering. Another application of nanostructuring is the strain relaxation of the strained epilayers due to abundant free surface area and high-aspect ratio. The heteroepitaxial growth of III-nitride LED structures is subject to large residual strain from the thermal and lattice mismatch between the epilayer and the substrate. Nanostructuring of the surface is an effective approach to prepare a strain-free template for subsequent epitaxial growth. Recently, it has been demonstrated that the strain relaxation at the surface and sidewall of the GaN columns/pillars increases the indium incorporation in the succeeding QW growth, which is essential for the III-nitride LEDs to extend the emission wavelength.

An improved insight in the strain relaxation of nanostructured GaN is therefore important. Measuring the strain at the nanostructure surface is however challenging. It requires high accuracy and good vertical spatial resolution. (Micro-)photoluminescence (PL) or (micro-)Raman spectroscopy has been used in the investigation of the strain relaxation in the GaN (nano)pillars. However, the strain state and strain variation at the nanostructure surface cannot be precisely determined due to a relatively long penetration depth of the probing light beam in these technologies (typically 100–200 nm for PL). Grazing incidence in-plane X-ray diffraction (GIIXD) has been exploited to characterize the in-plane alignment and lattice spacing of nanostructures. In this letter, we demonstrate the direct measurement of the strain state of the surface of nanostructures and the strain relaxation as function of pillar height. We have fabricated GaN tapered nanopillars by dry etching of strained epilayers, which leads to strain relaxation, and measured the strain state accurately using a standard laboratory high resolution diffractometer in the grazing incidence configuration with an incoming angle below the critical angle of reflection. Furthermore, the strain distribution of different nanopillar geometries was simulated to obtain additional information on the strain relaxation and distribution.

Metal organic chemical vapor deposition (MOVPE) was used to grow the GaN epilayer on the Si (111) substrate. Field-emission scanning electron microscopy (SEM) (Nova NanoSEM) was used to assess the surface morphology. The in-plane lattice spacing was measured with a standard laboratory high resolution X-ray diffractometer (Panalytical X’Pert) in the grazing incidence configuration. The schematic illustration of the GIIXD measurement of GaN nanopillars is shown in Fig. 1. The incoming X-ray beam angle (α) was chosen below the critical angle (αc) of the total reflection to limit the penetration depth. The diffraction angle (2θ) was measured accurately by using a triple axis monochromator in front of the detector. The energy of the X-ray beam was 8047.8 eV. The GaN epilayer was used to fabricate tapered nanopillars by dry etching using self-assembled Ni clusters as mask. A SiO2 layer of 100 nm was deposited on the GaN epilayers, followed by the deposition of a Ni film of 10 nm. The samples were subsequently

FIG. 1. Schematic illustration of grazing incidence in-plane X-ray diffraction measurement of GaN nanopillars. Inset (a) shows the cross section of the pillar with the presence of light evanescence into the pillar and inset (b) shows the top view of the pillar with the presence of diffracting planes.
annealed at 850 °C in N₂ environment for 1 min to transform the Ni film into nanoclusters. The pattern of the self-assembled Ni clusters was transferred to the SiO₂ layer using a SF₆-based inductively coupled plasma (ICP) dry etching. Subsequently, the GaN layer was etched into nanoclusters using a Cl₂-based ICP dry etching. The Ni nanoclusters and remaining SiO₂ were finally removed by wet etching, resulting in GaN nanoclusters. Figs. 2(a) and 2(b) show the SEM images of the GaN tapered pillars at top view and at 80°, respectively. The average top diameter is 250 nm with a size dispersion of 40 nm. The bottom diameter of the tapered pillars is increased by 0.4 nm when the pillar height is increased by 1 nm (Δbottom=Δtop+0.4 × pillar height in nm). For the in-plane XRD configuration, the incident beam angle was fixed at 0.13° which is significantly below the critical angle (0.33°) for the total external reflection. The penetration depth of the incoming X-ray beam in GaN is calculated to be 5 nm. 21 As this configuration lowers the intensity of the diffracted X-ray beam that reaches the detector, a relatively long integration time of 77 s per step was chosen to achieve sufficient intensity and to reduce the noise level. Fig. 3(a) shows the normalized XRD spectra of the GaN tapered pillars with different pillar heights, scanned at the GaN (1010) reflection. The measured spectrum is fitted by two Gaussian curves. The right peak of the spectrum attributes to the X-ray diffraction at the top surface of GaN pillars. For increasing pillar height, the diffraction peak position shifts towards higher 2θ values indicating a reduction in the in-plane spacing. The sub-peak centered at 16.174° in all pillar spectra which shifts slightly from the position of as-grown GaN peak (16.169°) is originated from the X-ray diffraction at the edge of the pillar samples. Limited by the fabrication approach, the sample edge was not covered by the Ni clusters after the annealing and was hence etched blankly. Although the ICP dry etching etches uniformly, the etched surface can be still roughened from few angstroms to few nanometers, 23 resulting in the slightly relaxed surface than the initial epilayer. The full width at half maximum (FWHM) of the pillar spectra is found all larger than the as-grown GaN. FWHM of the XRD spectrum for the GaN nanostructure is commonly reported increased after the dry etching process. 24,25 The bombardment of energetic ions accelerates the atom removal at the layer surface during the dry etching and simultaneously introduces the ion-induced damages at the interface and near-surface region, deteriorating the crystalline quality of the nanostructure surface. The in-plane lattice spacing (a-spacing) has been derived from the angular position of the XRD peak using Gaussian fit, and is plotted as function of pillar height in Fig. 3(b). The error is the fitting error. The residual in-plane stress of the GaN epilayer grown on Si was calculated to be 780 MPa for the in-plane lattice spacing of 3.194 \text{	extperthinspace A}. Our measurements show that the strain relaxes exponentially as function of pillar height. The relaxation of the a-spacing as function of pillar height (x in nm) has been fitted by the equation \( a(x) = a_0 + b e^{-\frac{x}{R}} \), resulting in the following fit: \( a_0 = 3.1892 \text{	extperthinspace A}, b = 0.0050 \text{Å}, \) and \( R = 22.0 \text{ nm} \). For larger pillar heights \( x \gg R \), this results in \( a(\infty) = a_0 \), indicating that \( a_0 \) is the in-plane spacing of fully relaxed GaN. For \( x \) equal to 0 nm, \( b \) has to be equal to the difference in lattice spacing between the strained \( a(x) = 0 \) and relaxed value \( a_0 \). The strain relaxation as function of pillar height can therefore be described by

\[
e_a(x) = \frac{a(x) - a_0}{a_0} = e^{-\frac{x}{R}}. \tag{1}
\]

For \( x \) equal to \( R \), the strain reduces to 1/e (37.3%). The parameter \( R \) can therefore be defined as the relaxation depth at which the strain relaxes to 1/e of the initial strain \( (e_0) \). The relaxation depth \( R \) depends on the pillar geometry and the material properties. In the case of GaN tapered pillars of 250 nm diameter at the top, we find a relaxation depth of 22.0 nm. Additional to GaN heteroepitaxially grown on Si, we have fabricated the tapered nanoclusters from GaN grown on sapphire substrates. The XRD results of the GaN pillars and epilayers on Si and sapphire are summarized in Table I. The difference in lattice spacing and thermal expansion for Si and sapphire substrates results in different residual strain for the GaN epilayers grown on these substrates. For sapphire and silicon, the residual strain of the GaN layer is compressive and tensile, respectively. However, the measured a-spacing shows both converge to the same value that characterizes strain-free GaN when both pillars are fully relaxed.
TABLE I. Measured lattice spacing and calculated stress of GaN epilayers and pillars (diameter = 250 nm) on Si and sapphire, derived from in-plane and symmetric XRD measurements. $\sigma_s$ and $\varepsilon_s$ denote the in-plane stress and in-plane strain, respectively.

<table>
<thead>
<tr>
<th>GaN sample</th>
<th>a-spacing (Å)</th>
<th>c-spacing (Å)</th>
<th>$\sigma_s$ (MPa)</th>
<th>$\varepsilon_s$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epilayer/sapphire</td>
<td>3.1847</td>
<td>5.1881</td>
<td>-660</td>
<td>-0.140</td>
</tr>
<tr>
<td>Epilayer/Si</td>
<td>3.1941</td>
<td>5.1816</td>
<td>780</td>
<td>0.156</td>
</tr>
<tr>
<td>200 nm pillars/sapphire</td>
<td>3.1889</td>
<td>...</td>
<td>...</td>
<td>~0</td>
</tr>
<tr>
<td>250 nm pillars/Si</td>
<td>3.1892</td>
<td>...</td>
<td>...</td>
<td>~0</td>
</tr>
</tbody>
</table>

The strain distribution in the GaN tapered pillars was simulated using a finite element method (FEM), based on the Hooke’s law and GaN’s elastic constants. The in-plane stress of the GaN bulk was set to 780 MPa, as measured by GIIXRD. The top diameter of the tapered pillar was set to 250 nm, and the bottom diameter was set according to the equation $\varnothing_{\text{bottom}} = 250 + 0.4 \times \text{pillar height in nm}$, as the virtual shape of the tapered pillar shown in Fig. 2. The simulated strain distribution in a fully relaxed ($\varnothing_{\text{top}}/\varnothing_{\text{bottom}}/\text{height: 250/250/250 nm}$) and partially relaxed ($\varnothing_{\text{top}}/\varnothing_{\text{bottom}}/\text{height: 250/270/50 nm}$) GaN tapered pillar is illustrated in Figs. 4(a) and 4(b), respectively. In both cases, the surface in the neighborhood of the base around the pillar shows increased tensile strain (light orange and light yellow part) attributing to the inward pulling of the pillar. From our simulation, it is clear that the strain relaxation is highly location-dependent for the partially relaxed pillars. The part more accessible to the surface is more flexible to release the strain. The uniformity of the strain distribution at the top of pillar should reflect in the measured XRD spectrum. The spectrum profile of the fully relaxed pillars in Fig. 3(a) is expected to be narrower than that of the partially relaxed pillars (i.e., 50 nm-high pillars). However, no specific trend of FWHM variation is observed in the pillar spectra. The degradation of the crystalline quality has the dominant impact on FWHM of the pillar XRD spectrum over the strain dispersion at the top of pillar. Fig. 4(c) shows the simulated average in-plane strain at the top of the tapered pillar as function of the pillar height. Similar to the measurements, we have fitted the strain relaxation of the pillars using Eq. (1) and find a value for the relaxation depth of 19.1 nm. The simulation and XRD measurements show a good agreement in the exponential relaxation of the in-plane strain at the top of the pillars as function of pillar height. However, the strain relaxation rate obtained from the XRD measurement is slower than the simulation. To study further the influence of the geometric shape on the strain relaxation, the strain relaxation in the following different nanostructure models, as listed in Table II, has been simulated: a small circular cylinder ($\varnothing = 250 \text{ nm}$), a big circular cylinder ($\varnothing = 350 \text{ nm}$), and an elliptic cylinder ($\varnothing_{\text{shoe}}/\varnothing_{\text{long}} = 250/350 \text{ nm}$). The height of the cylinders varies from 0 to 250 nm. The in-plane strain is calculated by averaging the strain at the top of the pillar. The strain relaxation as function of pillar height is fitted by Eq. (1) and the fitted relaxation depth at the top of the pillar XRD spectrum over the strain dispersion at the top.

In summary, the strain state at the surface of nanostructures has been measured by exploiting in-plane XRD. Tapered nanopillars have been fabricated by dry etching of a highly strained GaN epilayer. The in-plane lattice spacing of the top 5 nm was accurately determined by using high resolution grazing incidence X-ray diffraction with an incoming...
angle below the critical angle of reflection. The in-plane strain at the top of pillars is measured experimentally and shows an exponential relaxation as function of pillar height which can be described by a single parameter, the relaxation depth. Additional to the measurements, we have simulated the strain relaxation and strain distribution of the tapered nanopillars. The simulated exponential strain relaxation shows good agreement with the experimental observation. The impact of the pillar morphology on the strain relaxation has also been discussed.

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