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## **Time, Energy, and Spatially Resolved TEM Investigations of Defects in InGaN**

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### **Abstract**

A novel sample preparation technique is reported to fabricate electron transparent samples from devices utilizing a FIB process with a successive wet etching step. The high quality of the obtained samples allows for band gap - and chemical composition measurements of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  quantum wells where electron beam induced damage can be controlled and shown to be negligible. The results reveal indium enrichment in nanoclusters and defects that cause fluctuations of the band gap energy and can be measured by low loss Electron Energy Spectroscopy with nm resolution. Comparing our time, energy, and spatially resolved measurements of band gap energies, chemical composition, and their related fluctuations with literature data, we find quantitative agreement if the band gap energy of InN is 1.5 – 2 eV.

Keywords: Electron Microscopy, EELS, InGaN, band gap, strain

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## 1. Introduction

Already in early stages of the InGaN growth development for light emitting diodes it was suggested<sup>1</sup> and experimentally verified<sup>2</sup> that indium is inhomogeneously distributed in GaN/InGaN/GaN quantum wells. Successively, a strain mapping procedure was developed<sup>3</sup> for a quantitative analysis of displacement fields that are recorded in lattice images. Such procedures base on the reported knowledge that displacement fields follow closely chemical gradients on an atomic scale<sup>4</sup>. They can be quantitatively accessed<sup>5,6</sup>. The homogeneity of InN-GaN alloys is widely debated<sup>7,8</sup> and the existence of a miscibility gap is postulated that limits the indium solubility in GaN leading to a local formation of In-rich nanoclusters. Concerns were recently raised<sup>9,10</sup> and debated<sup>11</sup> about the use of electron microscopy to investigate the non-equilibrium state of the InGaN system since the exposure of specimens to high-energy electron beams may enhance phase separation.

In this contribution we combine time, energy<sup>12,13</sup>, and spatially<sup>14</sup> resolved electron microscopy to demonstrate that a consistent set of data can be obtained that quantifies the spatial indium distribution as well as the related local band gap fluctuations. Equally important, a sample preparation procedure by Focused Ion Beam milling is described that allows for a fabrication of cross section samples from devices leaving undamaged surfaces. In this case, the electron beam induced damage can be controlled and we find no measurable alteration of the indium distribution for relevant e-beam exposure times of up to 120 s. Consequently, the formation of In rich nanoclusters is determined by the growth process of our samples.

## 2. Experimental results

MOCVD grown samples were investigated that were processed into high efficiency devices<sup>12</sup>. Time series of lattice images were recorded in 15 seconds intervals with the Atomic Resolution Microscope operated at 800 kV and electron exit waves were reconstructed from focal series of images recorded with the One Ångstrom Microscope<sup>14</sup> that provides a spatial resolution of 0.8 Å at 300 kV. Electron energy loss spectra and Z-contrast images were acquired with a monochromated Tecnai G2 at 200 kV (energy resolution: 200 meV).

A commercially available focused ion ( $\text{Ga}^{2+}$ ) beam (FIB) was utilized for routine cross-section site-specific sample preparation from mechanically pre-thinned specimen<sup>15,16</sup>. In our case, the FIB milling was performed in 2 steps: (A) bulk cutting at 30keV using successively 3 different beam currents of 7000pA, 1000pA, and 100pA to obtain 100-200 nm TEM lamella and (B) 'low' energy cleaning at 10kV to obtain perforated membranes that contain ~ 20 nm thick surface damage. Figure 1a shows the phase of a reconstructed electron edit wave of samples prepared in this manner showing that atomic structure imaging is possible but reveals heavy damage.

These FIB membranes were additionally wet chemical etched<sup>12</sup> in a 25% aqueous KOH solution for 3 min at 130 °C. The etch perfectly removes the FIB-induced side-wall damage and surface roughness (Fig. 1b). Figure 1c finally shows that nitrogen and gallium columns can be readily resolved in such samples without any trace of residual damage that - in particular - would disturb the weak signal from the nitrogen columns.

This sample preparation process allows for HRTEM observations of large-areas that are free of preparation-induced defects (Fig 2a), which is essential if electron beam induced damage must be probed. The comparison of two lattice images of a time series shown in

Figures 2a and 2b establishes that beam induced sample damage cannot be observed within the first 120 seconds of our experiments. Moreover, we can extract displacement fields from InGaN quantum wells including defects<sup>3</sup> yielding identical results as shown by the insets. Therefore, we conclude that any compositional indium distribution observed in our samples reflects the as-grown stage of the sample.

Figure 3 combines calibrated displacement measurements with electronic structure measurements by low loss EELS. Lattice images (as well as HAADF STEM images not shown here<sup>12</sup>) consistently reveal the presence of In-rich nanoclusters in quantum wells with an average concentration  $x_{\text{In}} = 0.17$  and a fluctuation  $\Delta x_{\text{In}} = \pm 0.04$ . Moreover, localized defects with  $x_{\text{In}} = 0.38$  are present in some of our materials. Band gap and band gap fluctuation measurements by low loss EELS with a monochromated microscope agree very well with strain measurements from HRTEM images if literature data are considered that report a InN band gap of about 1.5 - 2eV<sup>12,13</sup>. It is noted that the debated InN band gap of 0.7 eV would require that the green light emission of our samples is caused by an average indium concentration of only  $x_{\text{In}} \sim 0.09$ . This is an unreasonable assumption that apparently excludes low band gap values of InN.

### 3. Conclusions

A novel sample preparation procedure was developed to produce electron transparent GaN-InGaN samples in cross section geometry from devices. The method utilizes a focused ion beam process with a successive wet etching step in a 25% aqueous KOH solution at elevated temperature (~130 C). The etching process removes entirely residual surface damage and leaves atomically flat surfaces.

Samples that are prepared in this manner are ideally suited to study radiation induced phase separation effects in In GaN quantum wells because the recorded images are not disturbed by surface roughness that is otherwise common. It is shown that 800 keV electrons do not cause measurable damage during an illumination time of up to 2 minutes. Indium segregation observed and quantified from strain maps agree with local band gap measurements by low loss EELS in such samples.

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Fig. 1

Exit-wave phase images of GaN [11 $\bar{2}$ 0]:

(a) before, and (b) after applying the wet chemical etch to the FIB prepared sample.

Insets show contrast variations in radians. Contrast variations shown by the inset in b) correspond to 3-5 Å of surface roughness.

(c) magnified EW phase image showing separation of Ga and the N atomic columns (see crystal model in upper right inset). Columns are 1.13 Å apart in this projection.

Fig. 2

2 high-voltage (800kV) HRTEM lattice images of the active region of an InGaN/GaN based LED from a time series of images. [11 $\bar{2}$ 0] zone axis orientation and Scherzer defocus = -52.5nm. InGaN quantum wells (QWs) are labeled ("QW").

(a) initial image. (b) a lattice image taken after 2 min of constant e-beam irradiation.

Insets show a defect in a QW and strain maps recovered from the images that do not depend on e-beam irradiation time. Largest strain values of ~ 8% are reached at the defects.

Fig. 3

Gray level representation of the indium distribution in a quantum well. Top interface is rough. Bottom interface is sharp. The average In concentration can be extracted to be  $x_{In} = 0.17 \pm 0.04$  with peak concentrations reaching 0.38 around the defects shown in Figure 2. Indium depletion around the defects is visible. Bottom left: conversion of average strain values to concentrations<sup>3,5</sup>. Bottom right: local band gap measurements with a 1.5 nm probe revealing the band gap of GaN and of InGaN of one particular composition<sup>12</sup>. Local band gap measurements of InGaN vary<sup>12</sup>.

Figure 1

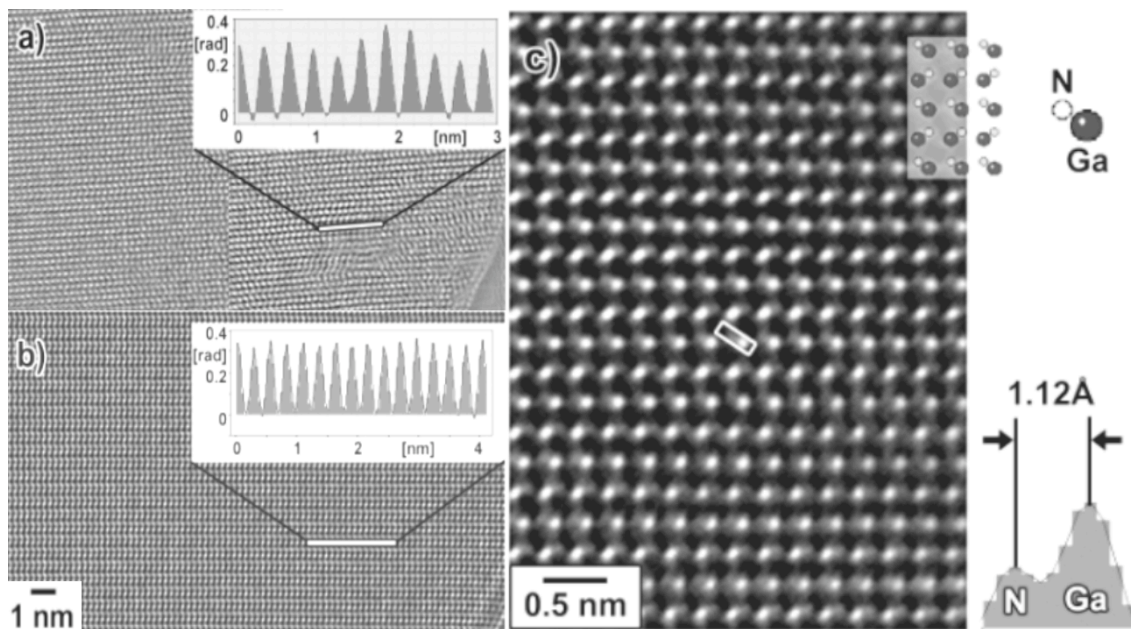


Figure 2

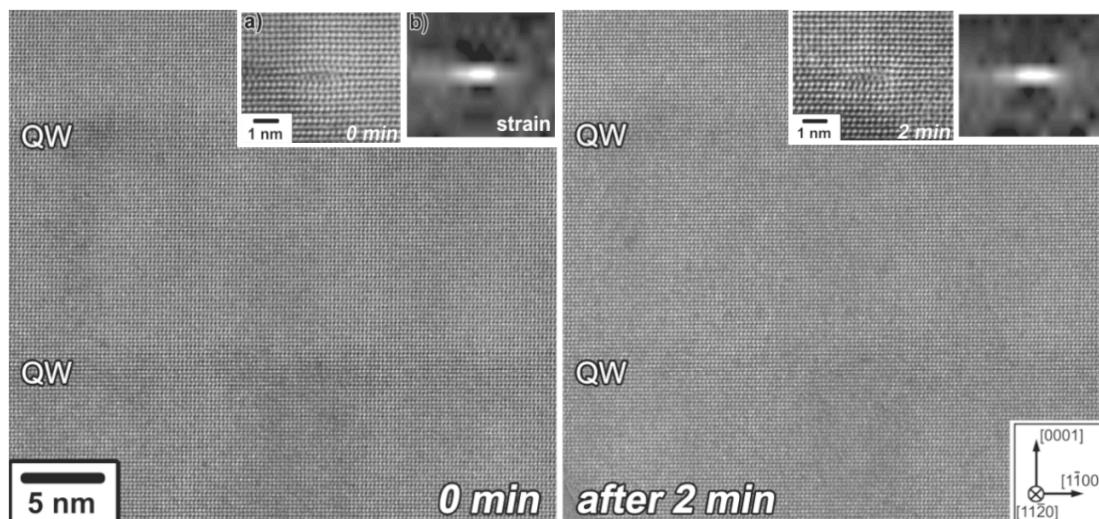


Figure 3

