Intensive luminescence from a thick, indium-rich In$_{0.7}$Ga$_{0.3}$N film

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1. Introduction

In$_{x}$Ga$_{1-x}$N alloys with an indium composition over 50% have recently gained considerable interest due to their tunable bandgap within the green–red and IR spectral regions. The large difference in decomposition temperature between InN and GaN and the theoretically predicted large region of solid phase immiscibility lead to significant difficulties in achieving homogeneous epitaxial films during InGaN growth. Typically, phenomena such as indium clustering and phase separation are reported. Up to now, there are only a few reports published on In-rich InGaN films with In content $> 50\%$ by metal organic chemical vapor deposition (MOCVD) as well as molecular beam epitaxy (MBE).

Calculated InN/GaN phase diagrams show large miscibility gaps at growth temperatures between 600 and 850 °C being typically applied for MOCVD and MBE.\(^8\) Regarding the low dissociation temperature for InGaN, MBE growth shows advantages over MOCVD for the low temperature regime since nitrogen atoms can be supplied by a plasma source in MBE independent of substrate temperature.\(^10\)–\(^13\) Moreover, it is necessary to keep the growth surface under a metal-rich condition, i.e. In-rich condition for InGaN epitaxy, in order to stay at the two-dimensional growth mode yielding flat surfaces.\(^14\) However, in an In-rich regime, excess indium adatoms may not be evaporated in time giving rise to indium droplet formation on the surface, a common behavior in the case of InGaN growth by MBE.\(^14\)–\(^15\)

A non-uniform distribution of In atoms in the InGaN alloy either by random atomic scale fluctuations and/or in clustering on different length scales results in fluctuations of the local bandgap which has a strong impact on the optical properties due to localization of excess carriers.\(^11\)–\(^16\)–\(^19\) Reference 5 have performed an extensive study with spatially averaging techniques. As an indirect result, an “S-shaped” temperature dependence of the peak wavelength is measured for thick InGaN alloys as well as InGaN quantum well structures.\(^20\)–\(^22\) Here, we use a nm-scale spatially resolved, optical mapping technique to monitor the spatially changing potential landscape as induced by indium fluctuations.\(^23\)\(^24\)

We refer to the pioneering work of Refs. 11, 12, 23 that analyzed films with In-concentrations below 20% containing films. Generally, the weak luminescence of In-rich films and a relatively poor detector efficiency in the IR spectral region make it challenging to directly visualize optical properties of In-rich InGaN films ([In $> 50\%$]) spatially resolved.

In this work, a comprehensive investigation of a 300 nm thick In$_{0.7}$Ga$_{0.3}$N layer deposited on a GaN/sapphire template at 540 °C by MBE has been performed by atomic force microscopy (AFM), X-ray diffraction (XRD), and highly spatially resolved cathodoluminescence (CL).

2. Experimental methods

The InGaN film has been grown by plasma-assisted molecular beam epitaxy (PA-MBE) at 540 °C. A conventional dual filament Knudsen cell is used as Ga and In sources, and a RF $N_2$ plasma cell as the nitrogen source. A GaN layer with a thickness of about 4 µm deposited on a sapphire substrate by MOCVD is the template used for MBE growth. After a 200 nm thick GaN buffer layer is grown on the GaN template, 300 nm thick InGaN films were grown using the growth-temperature-controlled-epitaxy method. More detailed information on the growth technique can be found elsewhere.\(^15\) In-rich growth conditions are required to realize high-quality growth of InGaN. Thus, a high In/Ga flux ratio has been used in this work and the composition of indium is actually determined by the growth temperature. From our previous study, we expect to have a residual background concentration of 10$^{19}$ cm$^{-3}$.\(^20\)

The surface morphology was characterized by a Bruker Dimension Icon AFM. The crystal quality, strain state and averaged In composition was determined by XRD measurements in a Bruker D8 X-ray diffraction system. The investigation of the optical properties has been realized by highly spatially-resolved CL in a home-built CL-SEM system.\(^27\)
In our plan-view CL experiments, the kinetic energy of the incident electron beam was set to 5 keV leading to a penetration depth of about 360 nm.\(^{28-30}\) Realizing a scanning-transmission-electron-microscopy-(STEM) mode-like configuration inside our SEM, the cross-section measurements were performed at a SEM-acceleration voltage \((V_{\text{acc}})\) of 25 kV on a 100–300 nm thin specimen, where the majority of the incident electrons are transmitted. The sample was prepared following conventional TEM preparation recipes (mechanical polishing followed by Ar\(^+\) ion milling in a liquid-nitrogen-cooled precision ion polishing system) and was mounted on a dedicated SEM holder with a hole as well as an electron absorbing graphite plate for STEM mode configuration.

Measurements took place at a beam current of \(I_{\text{Beam}} = 1.6 \, \text{nA (plan-view) and } I_{\text{Beam}} = 650 \, \text{pA (cross-section)}, \) respectively, and at liquid helium temperature \((T = 5 \, \text{K})\) recording the emitted luminescence with a liquid-nitrogen-cooled InGaAs array detector.

3. Results and discussion

3.1. Structural characterization

The surface morphology across a \(3 \times 3 \, \mu\text{m}^2\) scanned area obtained by AFM is depicted in Fig. 1. As mentioned above, growth under a In-rich condition may lead to In droplets, which are usually removed by chemical etching after growth.\(^{14,15}\) Remarkably, the InGaN surface presented in Fig. 1 provides a droplet-free, grain-like structure with a rms roughness of about 2.31 nm.

The crystal quality of the InGaN layer has been characterized by high-resolution XRD measurements. By taking an \(\omega - 2\theta\) scan along the (0002) direction yields the GaN(0002) reflection peak at \(\sim 32.1^\circ\) with a FWHM of 470 arcsec. With the help of a reciprocal space map (RSM) around the asymmetric GaN(11-24) reflection plane, the composition as well as the strain relaxation of the InGaN film was analyzed, as shown in Fig. 2. Exclusively one diffraction spot corresponding to the InGaN layer is observed indicating no phase separation in the film. To illustrate the strain relaxation of the InGaN, full and zero relaxation lines are shown in the figure. The RSM yields to 71% of In content in the InGaN film, which agrees well with the intended nominal value. The center of the InGaN reciprocal lattice point is quite close to the full relaxation line indicating an almost fully relaxed InGaN layer with slight residual compressive stress.

3.2. Lateral luminescence distribution

The low temperature \((T = 5 \, \text{K}), \) spatially averaged CL spectrum recorded from the surface is shown in Fig. 3(a) and reveals an intense, but broadened and symmetric luminescence band from the InGaN layer with a peak wavelength at 1185 nm and a FWHM of 63 meV. Sharper linewidths are reported in literature for less Ga-containing layers.\(^{31}\) No emission from the GaN buffer layer can be seen in plan-view due to the large thickness of the InGaN layer. The broad InGaN emission is modulated by Fabry–Pérot-thickness interferences. The luminescence peak energy is in accordance with an In composition range of 68%–78% assuming a bowing parameter in a wide range from 1.8 to 2.8 eV,\(^{63,32}\) supposing that the substrate induced strain can be neglected.

The CL intensity image (CLI) of Fig. 3(b) taken over \(15 \times 12 \, \mu\text{m}^2\) shows an intense and more or less homogeneous distribution of luminescence. We found a few dark lines that are due to scratches during template handling (not shown here). However, these scratches are not seen as morphological features of the InGaN in AFM or SEM images. Structural damage of the buffer layer due to scratching reduces the CL emission intensity of the overgrown InGaN film possibly due to dominant non-radiative recombination at the GaN-MBE/GaN-MOCVD interface. The penetration depth of the incident electron beam perfectly matches the vertical position of the scratches within the layer stack. Other than the network of dark lines, only slight intensity modulations are resolved in the CLI, proving a homogeneous InGaN film in the area between the scratches.

In Fig. 3(c), the CL wavelength image (CLWI), i.e., a map of the local peak emission wavelength across an image of \(256 \times 200 \, \text{points}, \) is depicted. We were able to prove wavelength changes on two different length scales: an
Chemical disorder in III-nitride semiconductor alloys is characterized by fluctuations, which can be statistically analyzed. For a perfectly random alloy, the probability of finding any given number of atoms A and B is given by a Poisson distribution. Beyond the Poisson distribution, inhomogeneity on different length scales is possible: Short-range ordering effects caused by chemical affinities, correlated fluctuations across multiple sites, as well as point and extended defects force deviations from a pure Poisson distribution. On an even larger scale, phase separation and clustering may occur.

In our sample, the continuous wavelength shift in the CLWI is caused by a temperature gradient across the wafer during the growth leading to a slight In-concentration discrepancy. Since, the scanned area in the shown CL map (Fig. 3) is too small, the overall gradient is not recognizable here.

The small wavelength variation below 1 μm is caused by indium fluctuation. To statistically analyze these fluctuations, we calculated the histograms of the CLWI: the frequency of pixels in the CLWI maps emitting at a given peak energy is plotted versus the photon energy for all 51200 pixels of the map. For an alloy without local phase separation but purely statistically local indium fluctuations, a monomodal statistical distribution function results, which converges into a Gaussian distribution for perfect random alloys. The standard deviation σ of the statistical distribution gives information on the disorder in the alloy. For [In] = 50%, the standard deviation should reach its maximum (assuming strain-free conditions). The resulting histogram (dotted red line) is plotted in Fig. 3(a) together with the corresponding spatially averaged spectrum. The maximum of the distribution of wavelength matches with the integral spectrum. The standard deviation σ = 7 meV is relatively large. From the spectrally wide features in the histogram we can conclude that local inhomogeneity of the InGaN layer leads to the broadening of the integral spectrum. The reasons for the broad distribution in the shown CLWI are the local variation of the In-composition on micrometer scale as well as the shift of the In concentration across the wafer.

In agreement with the XRD data, we did not find any indication for phase separation in CL, since the distribution of wavelengths is purely statistical monomodal with a single emission line in the low temperature spectra. Nevertheless, indium clustering is directly visible on a sub-micrometer scale in the wavelength image. On the other hand, alloy disorder on atomic level cannot be resolved here in our experiment as the radiative recombination inherently averages over the distance of the generated excess electrons and holes which is of the order of several lattice constants. Moreover, the spatial resolution of our SEM-CL setup does not match with the required resolution. With the help of STEM-CL, which offers a much higher spatial resolution, such questions can be addressed.

### 3.3. Evolution of emission in growth direction

The volume of the electron beam–solid interaction determines the spatial resolution of a CL experiment and is known as the Bethe range for bulk materials. A drastic reduction of this interaction volume is achieved by using a thin specimen instead of a bulk sample like that used in TEM. Since the InGaN layer in this study is only 300 nm thick, we have applied this approach for the cross-section characterization of our sample to increase the spatial resolution. The InGaN layer was prepared with a manual TEM preparation technique in a face-to-face sandwich configuration to achieve a wedge-shaped specimen. Subsequently, the specimen was analyzed using our standard SEM-CL, but with relatively high acceleration voltage (V_acc = 25 kV) to achieve a STEM mode with a small scattering volume.

![Energy (eV)](image)

*Fig. 3.* (Color online) (a) Spatially averaged CL spectrum (solid line) of InGaN film with histogram (dotted line) shows a broad intense peak at around 1200 nm modulated by thickness interferences. In the histogram, these Fabry–Pérot modes are pronounced visible as well. (b) plan-view CL integral intensity image with corresponding (c) CL wavelength image.
expected Goldstein range, i.e., the range of scattered electrons within the thickness of the specimen is in the order of 10 nm.\(^{(40,41)}\)

Figure 4 displays the CL linescan across the specimen to characterize the luminescence evolution in growth direction. The region, where the two pieces of the sample face-to-face prepared specimen are glued together, is blackened to improve the contrast. The sharp near-band-gap emission of GaN (3rd and 4th order at \(\lambda = 1072\) nm and \(\lambda = 1429\) nm, respectively) as well as the InGaN luminescence is visible. The broad InGaN emission is modulated by Fabry–Pérot-thickness interferences and appears at longer wavelengths (\(\lambda_{\text{peak}} = 1250\) nm) than the plan-view measurements due to the different sample position and the In-composition gradient across the wafer. Nevertheless, a slight shift within the linescan to a longer wavelength from the InGaN/GaN interface to the surface can be obtained (\(\Delta \lambda = 10\) nm). This redshift of emission can be caused either by the relief of substrate-induced stress or more likely, by an increase of In concentration along growth direction (calculated from emission shift: \(\Delta [\text{In}] = 0.5\%\)).\(^{(3,4)}\) We excluded excitation dependent effects through the CL linescan under different beam currents.

4. Conclusions

An analysis by structural and optical means of an MBE-grown, 300 nm thick In\(_{0.7}\)Ga\(_{0.3}\)N layer is presented that excludes the presence of phase separation. While the strain-state of the layer is almost fully relaxed it still exhibits intense emission around 1200 nm allowing for a CL-based mapping of the optical properties. In plan-view, a laterally homogeneous emission intensity is found. Slight In fluctuations as well as a growth-temperature induced compositional gradient across the wafer are revealed. In cross-section STEM-CL experiments, a slight increase of In composition during the growth of the 300 nm thick layer of about 0.5% is observed. These results demonstrate the feasibility for high-quality InGaN materials with In composition over 50% when grown by MBE.\(^{(3–8)}\)

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