Comparative study of structural properties and photoluminescence in InGaN layers with a high In content

A. Vantomme[1], M.F. Wu[1], S. Hogg[1], G. Langouche[1], K. Jacobs[2], I. Moerman[2], M.E. White[3], K.P. O'Donnell[3], L. Nistor[4,5,6], J. Van Landuyt[5] and H. Bender[6]

[1]Inst. Kern- en Stralingsfysica, Univ. of Leuven, B-3001 Leuven, Belgium

[2]Dept. of Information Technology, Univ. of Gent-IMEC, B-9000 Gent, Belgium

[3]Dept. of Physics and Applied Physics, Univ. of Strathclyde, Glasgow, U.K.

[4]Institute of Atomic Physics, Bucharest, Romania

[5]EMAT, Univ. of Antwerp (RUCA), B-2020 Antwerp, Belgium

[6]IMEC, B-3001 Leuven, Belgium

ABSTRACT

Rutherford backscattering and channeling spectrometry (RBS), photoluminescence (PL) spectroscopy and transmission electron microscopy (TEM) have been used to investigate macroscopic and microscopic segregation in MOCVD grown InGaN layers. The PL peak energy and In content (measured by RBS) were mapped at a large number of distinct points on the samples. An indium concentration of 40%, the highest measured in this work, corresponds to a PL peak of 710 nm, strongly suggesting that the light-emitting regions of the sample are very indium-rich compared to the average measured by RBS. Cross-sectional TEM observations show distinctive layering of the InGaN films. The TEM study further reveals that these layers consist of amorphous pyramidal contrast features with sizes of order 10 nm. The composition of these specific contrast features is shown to be In-rich compared to the nitride matrix.

INTRODUCTION

InGaN compounds have been used successfully for the fabrication of highly efficient blue, green, amber and red light emitting diodes. The wavelength of the emitted light of these diodes has been correlated with the overall In-content of the ternary nitride [1]. However, from electro- and photoluminescence (PL) experiments, it was suggested that the luminescence originates from In-rich inclusions, the *size* of which determines the wavelength of the emitted light [2]. The size of efficient quantum dots is expected to be of the order of nm [3].

Several groups have tried to find direct evidence of phase separation in $In_xGa_{1-x}N$ layers. In particular, due to their small sizes, the quest for quantum dots is an challenging issue. Recently, evidence was found for segregation of $In_xGa_{1-x}N$ multiple quantum wells (MQW's) and single layers [4-6]. In all of these studies, phase segregation was only observed for In-contents exceeding ~0.30, and it was generally evidenced from extra peaks in X-ray diffraction (XRD) patterns [4-6], from extra spots in the transmission electron diffraction patterns [5], or from energy dispersive X-ray (EDX) analysis [6]. These findings are in agreement with the calculations of Ho and Stringfellow [7], who calculated the critical temperature T_c above which the InN-GaN system is completely miscible. This temperature, 2457 K, by far exceeds the typical InGaN growth temperature at which a maximum In solubility in GaN of less than 6 % is predicted. MQW's were shown to be much more stable than thick single layers, separation only

occurring after annealing at 950°C [6]. This enhanced stability is due to the high elastic strain experienced in thin heterostructures and quantum wells, which results in a significant decrease of the critical temperature for single phase stability [8]. In all of the aforementioned studies, typical precipitate sizes of (several) tens of nanometer were reported, hence too large to result in efficient luminescence [3].

In this paper, we present a correlation between the PL-energy of single $In_xGa_{1-x}N$ thick films and their *overall* and *local* In-content. In particular, we will focus on the effect of local variations of the composition on the nanoscale, resulting in a phase segregation of the ternary nitride.

EXPERIMENTAL

Two $In_xGa_{1-x}N$ layers, each with a laterally varying composition, were grown at 780°C by metalorganic chemical vapour deposition on a thick GaN buffer / Al_2O_3 substrate. The thickness of the layers is about 250 nm. The exact In-content and thickness, as well as the crystalline quality, was mapped by Rutherford backscattering and channeling spectrometry (RBS/C), using a beam spot of approximately 1 mm^2. The crystallinity, azimuthal orientation and the phases present in the sample were further monitored with low (Rigaku system with a rotating anode) and high (Bruker D8 discover) resolution XRD in θ–2θ geometry. PL mapping was performed at low temperature (< 30 K) using an Ar$^+$ laser with a spot diameter of 100 µm. Samples for transmission electron microscopy (TEM) were prepared in cross sections and studied with a Philips CM 30 FEG electron microscope, operating at 300 kV. Electron dispersive X-ray analysis (EDX) was performed with a Link instrument on a Philips CM 20 microscope.
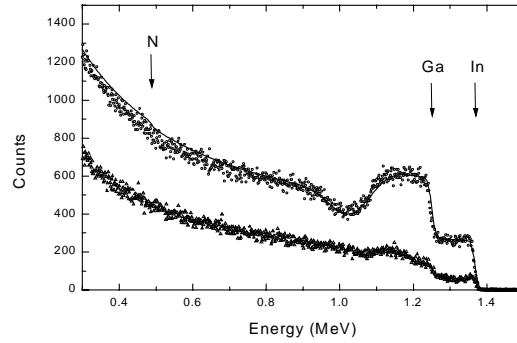

Figure 1. *Random (o), aligned (Δ) and simulated (solid line) RBS spectra of the $In_{0.25}Ga_{0.75}N/GaN/Al_2O_3(0001)$ layer. All TEM results shown further have been obtained from this part of the specimen.*
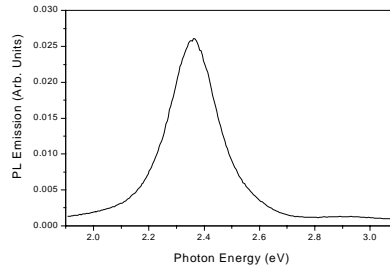
RESULTS AND DISCUSSION

Figure 2. *Low temperature PL spectrum of the same sample as shown in Fig. 1.*

Using RBS, the exact In-fraction of the $In_xGa_{1-x}N$ layers was mapped at a large number of distinct points on the samples, x-values in the range from 0.2 to 0.4 were found [9]. Figure 1 shows the random and aligned RBS spectra of a particular area of the sample which will be discussed in detail below. From the random spectrum, a composition of $In_{0.25}Ga_{0.75}N$ and a thickness of 290 nm are deduced. The spectrum measured with the incoming beam aligned along the <0001> direction indicates that the minimum yield χ_{min} of the $In_{0.25}Ga_{0.75}N$ layer is 20 % (this is the ratio of the backscattering yields of the aligned and random spectra, and is a measure for the crystalline quality of the layer). The value of χ_{min} is found to increase with the In-content
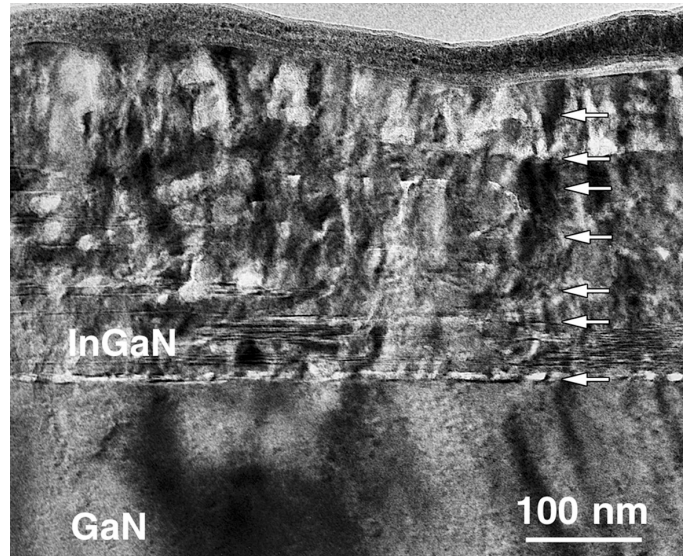

Figure 3. *TEM image of a cross section of the InGaN layer. Rows of pyramidal-shaped inclusions of brighter contrast, parallel to the interface with the GaN buffer layer are marked with arrows.*

(i.e. increasing lattice mismatch with respect to the GaN buffer layer), indicating a deteriorating crystallinity.
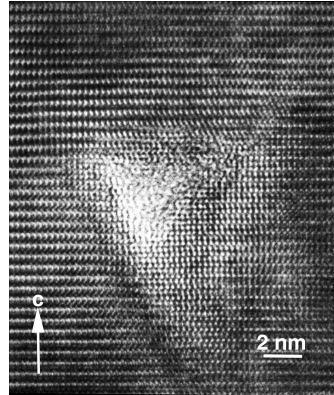

Figure 4. *HREM image along the [01$\underline{1}$0] zone axis showing structural details of a pyramidal-shaped inclusion.*

PL measurements revealed a direct, linear relationship between PL peak energy and In content [9]. Taking into account the linear variation of the PL peak with band gap [10], this result implies that band bowing is absent. The indium content measured by RBS is systematically lower than that expected from previous estimates based on a comparison of PL with X-ray diffraction [11]. As an example, an indium concentration of 40%, the highest measured in this work, corresponds to a PL peak of 710 nm, strongly suggesting that the light-emitting regions of the sample are very indium-rich compared to the overall In content of the nitride, as measured by RBS. On the other hand, the region with an In-concentration of 25 % results in a PL peak energy of 525 nm (Figure 2).

In an attempt to find direct evidence for the phase segregation suggested by the PL measurements, XRD was performed in $\theta-2\theta$ geometry, using a detector angle between 10° and 120°. In none of the low resolution/high intensity diffraction patterns could any trace of In-rich phases be found. However, preliminary high resolution measurements (which also allow us to probe a much smaller – hence perhaps more uniform – part of the inhomogeneous layer) give evidence of a small fraction of In$_x$Ga$_{1-x}$N, with a composition close to x = 0.50. A detailed high-resolution investigation of samples with varying In compositions will be indispensable to understand the mechanism of this phase segragation, and in particular to elucidate whether the value of x = 0.50 gives evidence of ordering in the ternary system.

On the other hand, transmission electron microscopy of the 290 nm thick In$_{0.25}$Ga$_{0.75}$N layer reveals the presence of 10-20 nm islands, aligned at the interface with the GaN buffer layer, and parallel to it at different depths in the InGaN layer. Figure 3 is a cross sectional transmission electron microscopy (TEM) image showing the InGaN layer on the top of the GaN buffer layer. Besides planar defects and strain contrast, the image reveals some pyramidal-shaped zones of a different brighter contrast. Seven such rows of pyramidal islands are visible (indicated by arrows in Fig. 3), the first one lying

near the interface with the GaN buffer layer. The distance between the rows of pyramidal inclusions in the bulk of the film is about 30-40 nm.
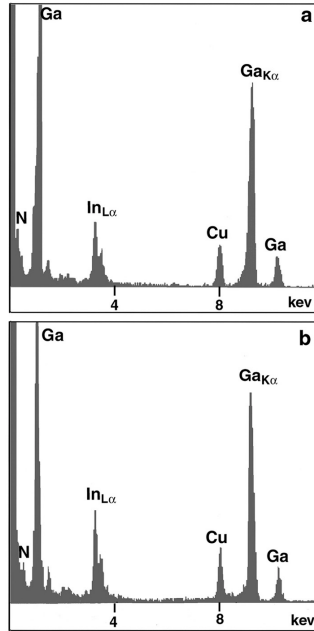

Figure 5. *EDX spectra from the matrix (a) and from a pyramidal-shaped inclusion (b) showing an increased In concentration in the latter.*

In an attempt to obtain more detailed structural information about these precipitates high resolution electron microscopy (HREM) has been performed. Figure 4 shows a HREM image along the [01$\underline{1}$0] zone axis of a region in the InGaN layer containing a pyramidal shaped inclusion. It is clear that the material in these precipitates is amorphous, which rules out a direct correlation to the In-rich phase observed by X-ray diffraction.

To compare the composition of the pyramidal precipitates to that of the surrounding matrix, energy dispersive X-ray (EDX) analysis was performed. The count rate was maintained constant for the different measurements, so that the absolute intensities of the peaks can be compared. The spot size of the electron beam was 15 nm. Care was taken to analyse neighbouring regions of the islands and the matrix, so that the sample thickness could be considered constant from one zone to the other. In this way one can presume that the same volume of specimen was analysed in the islands and in the matrix. The EDX results (Figure 5) show that the amorphous pyramidal-shaped inclusions are In-rich as compared to the surrounding matrix. The relative ratio of the InL_α to GaK_α peak intensities, which is proportional to the In to Ga atomic ratio, is 0.39 in the amorphous pyramidal precipitates and 0.32 in the surrounding matrix. Since the

diameter of the electron beam is of the order of (or larger than) the inclusions, the former value can be considered a lower limit.

SUMMARY AND CONCLUSION

We have studied the composition of $In_xGa_{1-x}N$ layers on a macroscopic (RBS) and microscopic (TEM) level, and compared the indium content to the luminescence of the respective nitrides. A detailed analysis of these data reveals that the luminescence must originate from In-rich inclusions in the InGaN layer. Indeed, partial phase separation has been observed by high-resolution XRD. Moreover, a cross sectional TEM/EDX investigation has indicated the presence of 10-20 nm large pyramidal amorphous precipitates, the composition of which is In-rich. However, according to O'Donnell *et al.* [2,3] the size of these pyramidal islands is too big to expect large quantum effects. Hence we have to look for smaller sized features that could be related to the quantum effects. In a recent plan-view microscopy investigation, features of the order of ~2 nm have been observed. From high-resolution electron micrographs, these inclusions could be positively identified as quantum dots. A full discussion of this TEM investigation, along with a comparison to dot size estimates from PL measurements, will be given elsewhere. Hence, we can conclude that the $In_xGa_{1-x}N$ samples we studied seem to segregate into a wide variety of crystalline and amorphous microstructures and nanostructures, as evidenced with a variety of techniques. The challenging task will be to correlate the observed (optical) properties to the specific spatial patterns of the layers.

ACKNOWLEDGEMENTS

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