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Phase separation in annealed InGaN/GaN multiple quantum wells

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Abstract

In-rich second phases were detected by transmission electron microscopy (TEM) in $In_{0.27}Ga_{0.73}N$ multiple quantum well (MQW) samples that were annealed at 950°C for 40 h. X-ray diffraction (XRD) measurements showed a shift in the zero-order diffraction peak toward GaN, consistent with the formation of an In-poor phase remaining in the InGaN wells. Voids were also found by TEM in the MQWs after annealing.

1. Introduction

The emission mechanism in $In_xGa_{1-x}N$ blue laser diodes (LD) is important to understand the optimization of device structures. Recently, it has been proposed that In-rich quantum dots spontaneously form in the quantum wells, which leads to a localization of excitons and an enhancement of the laser gain [1]. Evidence of phase separation was reported previously in polycrystalline InGaN films that were annealed at temperatures below 700°C [2,3] and on 0.3 μm thick layers grown by molecular beam epitaxy (MBE) with In concentrations greater than 30% [4]. These experimental results are in agreement with theoretical calculations which predict that InN and GaN are not miscible for typical growth temperatures of around 800°C [5]. In this letter, we report the evidence of phase separation in InGaN quantum wells only after post-growth annealing.

2. Experimental procedure

The samples used in this study consist of a 0.2 μm GaN : Mg layer, a 10 period superlattice of 20 Å $In_{0.27}$ $Ga_{0.73}N$ well/40 Å GaN barrier, and a 4 μm GaN : Si layer on a sapphire substrate grown by metal organic chemical vapor deposition. Samples were annealed up to 40h at a temperature of 950°C in a quartz tube furnace in a nitrogen ambient. Prior to annealing, a 120 nm SiN cap was

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deposited on the surface to prevent decomposition of the GaN.

X-ray diffraction (XRD) measurements were performed at the Stanford Synchrotron Radiation Laboratory with a two-circle diffractometer. Scans of the (0 0 2), (0 0 4) and (0 0 6) reflections were measured, but only the (0 0 2) reflections will be presented in this work. TEM experiments were carried out in a JEOL 3010 microscope operated at 300 kV on samples that were prepared by polishing and then ion milled to electron transparency at low voltages (< 4 kV) with a liquid nitrogen cold stage. Energy dispersive X-ray chemical (EDX) analysis was performed in the TEM, by maintaining a count rate of 200 cps to obtain similar ratios of the Ga K_α to Ga L_α line in order to be able to compare the In L_α emission line in different regions of the sample. The In concentration in the InGaN quantum wells was determined with Rutherford backscattering spectrometry (RBS), by assuming the absence of In within the GaN barriers. Optical transmission spectra was performed in a scanning spectrophotometer with an instrumental resolution of 1 nm. and an aperture diameter of 2 mm.

3. Results and discussion

XRD spectra of $In_xGa_{1-x}N$ /GaN MQW structures before and after annealing are shown in Fig. 1. The zero-order diffraction peak for as-grown material corresponds to an average In concentration (well and barrier combined) of $x = 0.14$, by assuming relaxed layers and Vegard's law. Since the well-to-barrier ratio is 1 : 2, this indicates that the In composition in the wells is $x = 0.42$. This value is higher than the composition of $x = 0.27$ obtained from RBS. After annealing at a temperature of 950°C for 40 h, the satellite peaks shift towards the GaN peak indicating that the composition in the wells is reduced to $x = 0.30$. The superlattice *period* is unchanged to within the uncertainty of the measurement. An additional peak is also observed in the spectrum for the annealed sample at a lattice spacing corresponding to an In composition of $x = 0.42$. The width of this peak corresponds to a precipitate size of ~ 10 nm.

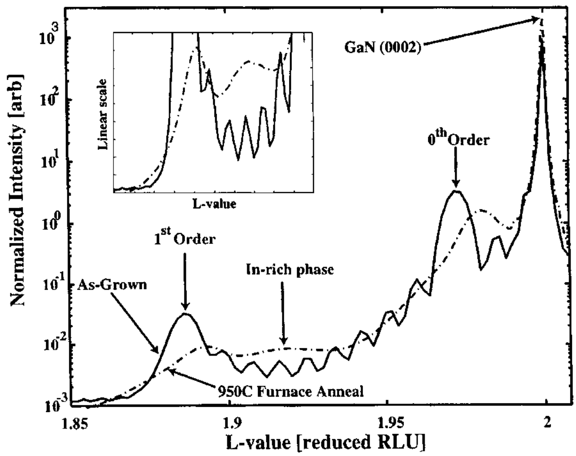

Fig. 1. X-ray diffraction spectra of $In_{0.27}Ga_{0.73}N$ multiple quantum well (MQW) structures showing the as-grown and after annealing at 950°C for 40 h. The inset is a linear scale of the XRD intensity near the d-spacing corresponding to the In-rich phase.

A bright field TEM micrograph of the MQW structure after the anneal is shown in Fig. 2. The image is taken at ~ 10° from the [1 1 –2 0] zone axis by using an off-Bragg imaging condition with the (0002) diffraction spot faintly visible in the diffraction pattern. Under these imaging conditions the image is sensitive to atomic mass density. Moire fringes can arise from the region containing the precipitate due to a difference in lattice constant with the matrix. Precipitates were found to appear as slabs that were ~ 10 nm wide and up to 25 nm long. EDX analysis showed that the composition of the precipitates were In-rich (Fig. 3a) compared to the surrounding matrix (Fig. 3b). Composition analysis taken from several 10 nm thick precipitates, was estimated to have an In concentration of $x = 0.40$, which is in agreement with the XRD data. The composition of the surrounding matrix was estimated to have an In concentration of $x = 0.10$. Voids, with similar dimensions as the precipitates, were also found within the QW region of the annealed sample.

Phase separation in the annealed samples was also consistent with optical absorption measurements. Optical absorption for the as-grown $In_{0.27}Ga_{0.73}N$ sample showed an onset at ~ 2.9 eV (420 nm), which is attributed to an $N = 1$

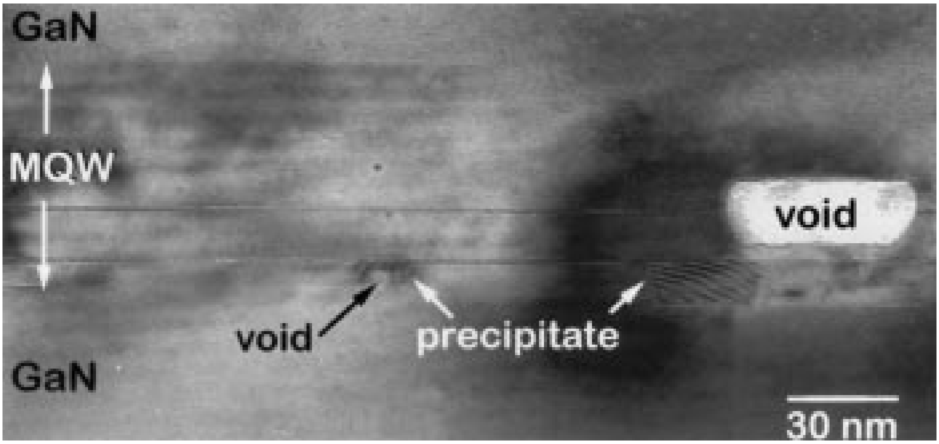

Fig. 2. TEM micrograph of $In_{0.27}Ga_{0.73}N$ MQW that was furnace annealed at 950°C for 40 hr showing precipitates and voids.

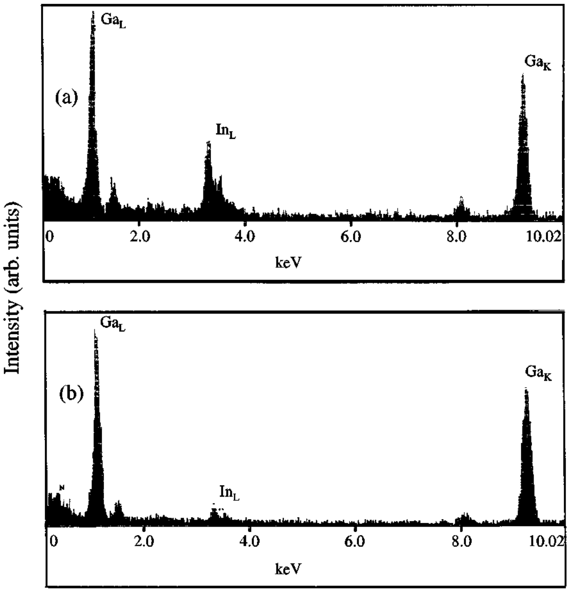

Fig. 3. (a) EDX spectra showing analysis in the region of the precipitate and (b) the surrounding matrix.

valence-to-conduction band transition in the InGaN quantum wells. For the same sample annealed at 950°C for > 8 h, the onset of a peak at 2.65 eV was observed suggesting the presence of an In-rich phase. The optical absorption of the In-poor phase is probably obscured by the GaN absorption at 3.4 eV. A band gap of 2.65 eV corresponds to an In concentration of $x = 0.35$ in thick layers of $In_xGa_{1-x}N$. The intensity of this peak increased by further annealing to 40 h. In addition, the width of the peak was broad ($\sim$ 300 meV) indicating wide variations in the size, shape, and In content of the In-rich regions.

4. Conclusions

In-rich precipitates were identified by TEM and EDX analysis for $In_{0.27}Ga_{0.73}N$ multiple quantum well (MQW) samples that were annealed at 950°C for 40 h. Optical absorption showed a signature of this In-rich phase for annealing times > 8 h. Since the MQW active region of a laser diode heterostructure is grown at temperatures below 900°C, our results suggest that negligible phase separation occurs as a result of annealing during growth.

Acknowledgements

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