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PHASE SEPARATION IN InGaN/GaN MULTIPLE QUANTUM WELLS

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ABSTRACT

Evidence is presented for phase separation in $In_{0.27}Ga_{0.73}N$/GaN multiple quantum wells (MQW's). After annealing for 4 min at a temperature of 1100 ^{o}C, the absorption threshold at 2.95 eV is replaced by a broad peak at 2.65 eV. This peak is attributed to the formation of In-rich InGaN phases in the active region. X-ray diffraction measurements show a shift in the diffraction peaks toward GaN, consistent with the formation of an In-poor phase.

INTRODUCTION

The development of blue light-emitting diodes (LED's) [1] and laser diodes (LD's) [2] has focused a great deal of research activity on GaN-based III-V nitrides. The band gaps of $In_xGa_{1-x}N$ alloys cover a wide spectral range, from red (InN) to UV (GaN), making this alloy system ideal for numerous optoelectronic applications [3]. The active region in GaN-based LED's and LD's consists of $In_xGa_{1-x}N/In_yGa_{1-y}N$ multiple quantum wells (MQW's). In this paper, we report evidence of phase separation in annealed InGaN/GaN quantum wells. The formation of In-rich InGaN precipitates yields a low energy peak in the optical absorption spectrum of the MQW's.

Evidence of phase separation was reported previously in polycrystalline InGaN films that were annealed at temperatures below 700°C [4,5]. Thick (0.3 μm) InGaN layers grown by molecular beam epitaxy (MBE) contain regions of pure InN for atomic In concentrations greater than $x = 0.3$ (Ref. 6). 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 [7]. In GaN/InGaN/GaN double heterostructures, however, atomic In concentrations up to $x = 0.8$ can be incorporated without phase separation [6].

EXPERIMENT

Experimental details

In this study, phase separation was investigated in InGaN/GaN MQW structures. The first structure consists 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. The thickness of the well plus barrier was determined by the spacing between satellite peaks in the x-ray diffraction (XRD) spectrum. The barrier-to-well thickness ratio of 2:1 was measured with transmission electron microscopy (TEM). The In concentration in the InGaN quantum wells was determined by Rutherford backscattering spectrometry (RBS), by assuming the absence of In within the GaN

barriers. Samples underwent a rapid thermal anneal in a Heatpulse thermal processor. Prior to annealing, a SiN cap was deposited over the GaN to prevent decomposition.

RBS was performed with a 1.95 MeV He^+ beam generated by a 2.5 MeV Van de Graff accelerator. The backscattered He ions were collected by a Si surface barrier detector located at 165° with respect to the ion beam. Optical transmission spectra were obtained with a Shimadzu UV-3101PC scanning spectrophotometer, with an instrumental resolution of 1 nm and an aperture diameter of 2 mm.

Structural Characterization

The spacing between (0006) satellite peaks in the as-grown XRD spectrum (Fig. 1) indicates a superlattice period of 60 Å. The zero-order diffraction peak for as-grown material corresponds to an average In concentration in the active region (wells plus barriers) of $x = 0.14$, with the assumption of relaxed layers. The average In concentration measured by RBS, on the other hand, is given by $x = 0.09$. This discrepancy can be explained by the fact that the layers in the active region experience significant biaxial strain that results from the lattice mismatch between InGaN and GaN. Biaxial compression of the InGaN wells leads to an increase in the lattice spacing along the *c*-axis.

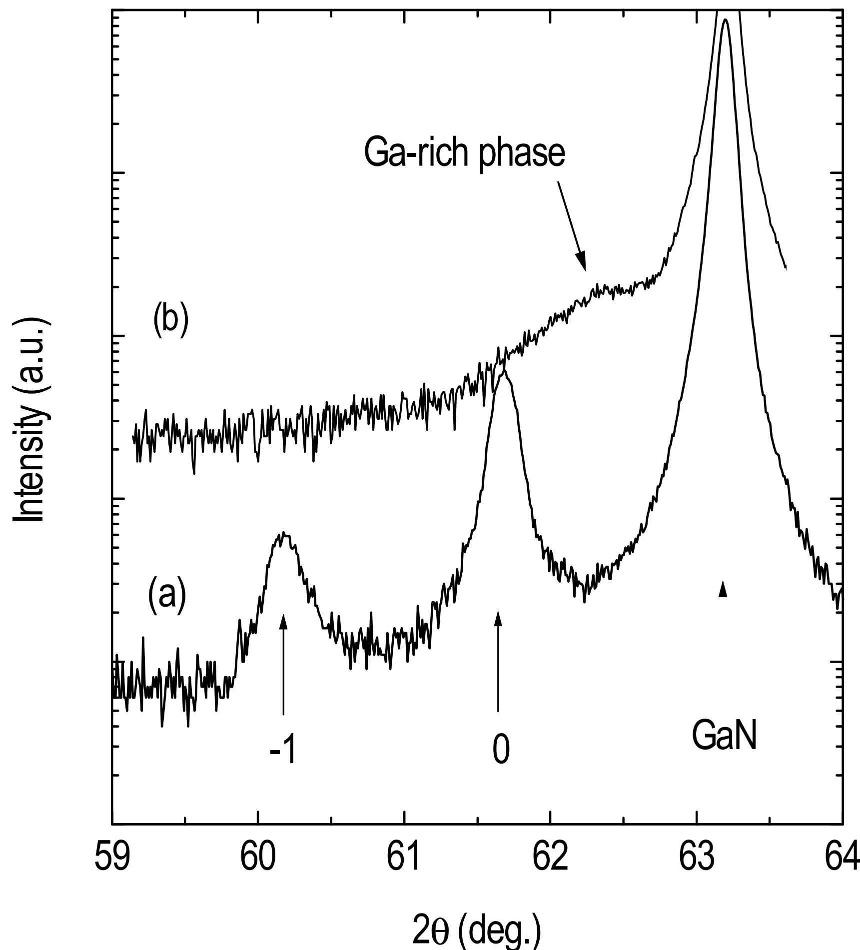

Figure 1. X-ray diffraction (XRD) spectra of $In_{0.27}Ga_{0.73}N$/GaN multiple quantum well structure (a) as-grown and (b) annealed at 1100°C for 4 min.

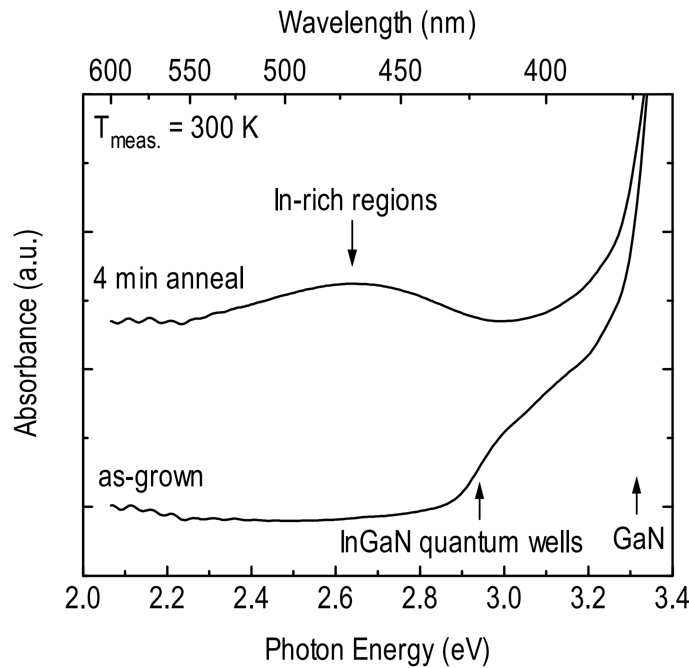

Figure 2. Optical absorption spectrum of $In_{0.27}Ga_{0.73}N$/GaN multiple quantum well structure as-grown and after a rapid thermal anneal at 1100°C.

After annealing at 1100°C for 4 min, the InGaN satellite peaks shift toward the GaN peak (Fig. 1). The superlattice period is unchanged to within the uncertainty of the measurement. The shift of the InGaN peaks indicates the formation of an In-poor phase, with an average In concentration (wells plus barriers) given by $x = 0.10$. In a separate study [8], an additional peak corresponding to an In concentration of $x = 0.42$ is observed in the spectrum for the annealed sample. In-rich InGaN nanostructures are directly observed by TEM and their linear dimensions are approximately 10 nm [8]. Energy dispersive x-ray (EDX) chemical analysis verified that the nanostructures are In-rich as compared to the surrounding matrix [8]. This paper will discuss the optical characterization of phase separated InGaN/GaN MQW's.

Optical Characterization

The optical absorption spectrum for an as-grown InGaN/GaN MQW structure is shown in Fig. 2. The as-grown material shows an absorption onset at 2.95 eV (420 nm), which is attributed to an $N = 1$ valence- to conduction-band transition in the InGaN quantum wells. This value for the band gap is in agreement with photoluminescence (PL) and electroluminescence (EL) measurements. After the optical spectrum was recorded, the MQW structure was annealed at a temperature of 1100°C. As shown in Fig. 2, after an annealing time of 4 min, the absorption threshold at 2.95 eV is replaced by a broad peak at 2.65 eV (465 nm). The same results were obtained when a GaN proximity cap was used instead of a SiN cap. The appearance of the peak at 2.65 eV suggests the presence of In-rich phases of InGaN. The optical absorption of the In-poor phase is probably obscured by the GaN absorption at 3.4 eV.

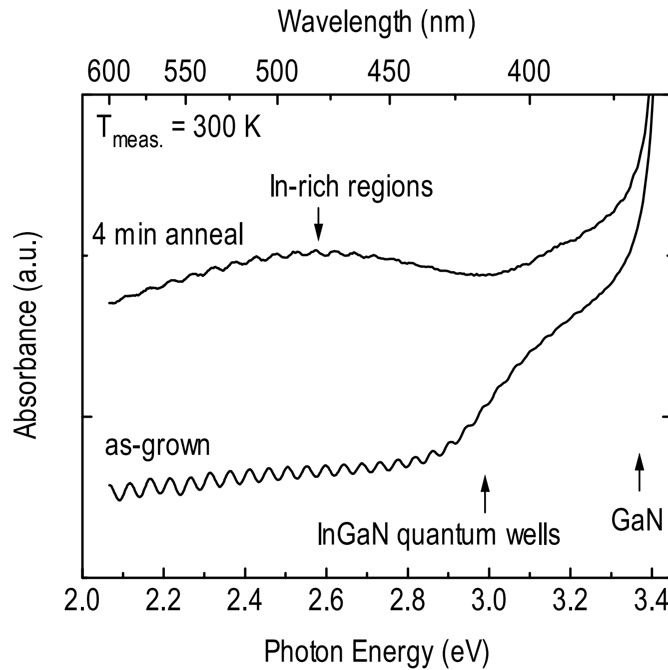

Figure 3. Optical absorption spectrum of $In_{0.33}Ga_{0.67}N$/GaN multiple quantum well structure as-grown and after a rapid thermal anneal at 1100°C.

For thick layers of $In_xGa_{1-x}N$, an In concentration of $x = 0.27$ corresponds to a band gap of 2.8 eV [9], which is lower than the band gap of 2.95 eV that was measured for the $In_{0.27}Ga_{0.73}N$ quantum wells. The observed blue shift of the band gap is attributed to quantum confinement and biaxial compression of the InGaN layers [10,11]. The broad optical absorption peak in the annealed material has a maximum at approximately 2.65 eV. A band gap of 2.65 eV corresponds to an In concentration of $x = 0.35$ for thick layers of $In_xGa_{1-x}N$. If there exists a blue shift due to compressive strain or quantum confinement, however, the actual In concentration in the In-rich regions may be higher than $x = 0.35$. In addition, the large width of the peak (~300 meV) suggests wide variations in the size, shape, and In content of the InGaN precipitates.

Effect of In concentration on Phase Separation

To ascertain the effect of In concentration on the rate of formation for In-rich InGaN precipitates, the annealing study was repeated for a $In_{0.33}Ga_{0.67}N$/GaN MQW structure. The results for this structure are shown in Fig. 3. The as-grown material shows a fairly broad quantum well absorption profile at 2.9 eV, which suggests a greater degree of inhomogeneity than in the previous two examples. The rate of phase separation is similar to that of the $x = 0.27$ structure. After a rapid thermal anneal at 1100°C for 4 min, the quantum well absorption is replaced by a broad peak at 2.55 eV. This energy is slightly lower than that of the $x = 0.27$ case (2.65 eV), which suggests that the InGaN precipitates in the present example contain a higher concentration of In.

CONCLUSIONS

In conclusion, we have characterized phase separation in InGaN/GaN MQW's after post-growth annealing. The formation of In-rich InGaN nanostructures leads to an optical absorption peak centered at 2.65 and 2.55 eV in $In_{0.27}Ga_{0.73}N$ and $In_{0.33}Ga_{0.67}N$, respectively.

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