Phase separation in InGaN/GaN multiple quantum wells

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Evidence is presented for phase separation in $In_{0.27}Ga_{0.73}N$/GaN multiple quantum wells. After annealing for 40 h at a temperature of 950 °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. A diffraction peak corresponding to an In-rich phase is also present in the annealed material. Nanoscale In-rich InGaN precipitates are observed by transmission electron microscopy and energy dispersive x-ray chemical analysis. © *1998 American Institute of Physics.* [S0003-6951(98)00614-7]

The development of blue light-emitting diodes (LEDs)[1] and laser diodes (LDs)[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 LEDs and LDs consists of $In_xGa_{1-x}N/In_yGa_{1-y}N$ multiple quantum wells (MQWs). In this letter, 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 MQWs.

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]

In this study, phase separation was investigated in an InGaN/GaN MQW structure grown by metalorganic chemical vapor deposition (MOCVD). The structure consists of a 0.2 μm GaN:Mg layer, a ten 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 were annealed in a quartz tube furnace at a temperature of 950 °C. Prior to annealing, a SiN cap was deposited over the GaN to prevent decomposition.

The optical absorption spectrum for an as-grown InGaN/GaN MQW structure is shown in Fig. 1. The absorption profile for the as-grown material is similar to that observed by Scholz *et al.*[8] The as-grown material shows an absorption onset at 2.95 eV (420 nm), which is attributed to the band gap of the InGaN quantum wells. After the optical spectrum was recorded, the MQW structure was annealed at a temperature of 950 °C. As shown in Fig. 1, after an annealing time of 40 h, 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.

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,[9,10] which is lower than the band gap of 2.95 eV that was measured for

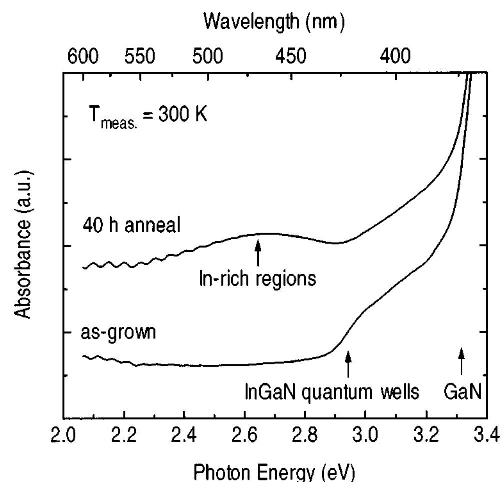

FIG. 1. Optical absorption spectra of InGaN multiple quantum well (MQW) structures before and after annealing at a temperature of 950 °C.

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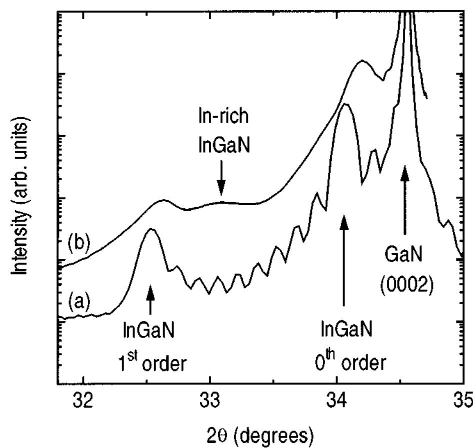

FIG. 2. XRD spectra of InGaN multiple quantum well (MQW) structures, (a) as-grown and (b) after annealing at 950 °C for 40 h.

the $In_{0.27}Ga_{0.73}N$ quantum wells. The observed blueshift of the band gap is attributed to quantum confinement and biaxial compression of the InGaN layers.[11,12] 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 blueshift 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.

XRD spectra of InGaN/GaN MQW structures before and after annealing are shown in Fig. 2. The spacing between (0002) satellite peaks in the as-grown spectrum indicates a superlattice period of 60 Å. Smaller interference fringes are also observed, with a periodicity consistent with the width of the MQW active region (600 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.

After annealing at 950 °C for 40 h, the InGaN satellite peaks shift toward the GaN peak (Fig. 2). 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 $x=0.10$. An additional peak corresponding to an In concentration of $x=0.42$ is observed in the spectrum for the annealed sample. The width of this peak is consistent with the presence of In-rich precipitates with linear dimensions on the order of 10 nm.

A bright-field TEM micrograph of the MQW structure after annealing is shown in Fig. 3. The image is taken $\sim 10°$ from the [11–20] zone axis under an off-Bragg imaging condition in which the (0002) diffraction spot is very faint in the diffraction pattern. Under these imaging conditions, the image is sensitive to atomic mass density. Moire fringes arise from In-rich InGaN precipitates, due to the difference between the lattice constants of the precipitates and the surrounding matrix. As shown in Fig. 3, the precipitates have a width of ~ 10 nm along the *c* axis and a length of ~ 25 nm in the *c* plane. Voids are also observed within the MQW region of the annealed material, with dimensions similar to those of the precipitates. Voids and precipitates of this type are not found outside the MQW region or in the as-grown material.

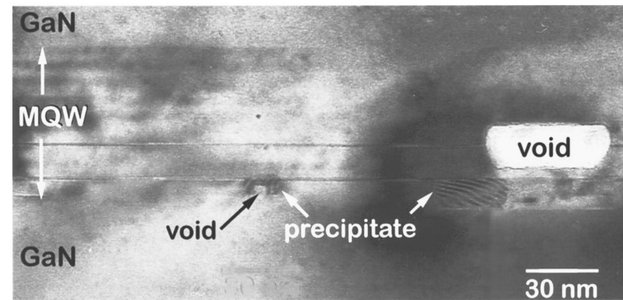

FIG. 3. TEM micrograph of an InGaN MQW structure that was annealed at 950 °C for 40 h, showing precipitates and voids.

To verify that the precipitates are In-rich, energy dispersive x-ray (EDX) analysis was utilized to determine the chemical composition of the precipitates and the surrounding matrix. The count rate was maintained at 200 cps so that the intensity ratio of the Ga $K\alpha$ to Ga L_α emission lines was constant throughout the measurements. As shown in Fig. 4, the precipitates are clearly In rich as compared to the surrounding matrix. The estimated concentration of In within the regions of the precipitates is $x=0.4$, in good agreement with the XRD data.

In conclusion, we have characterized phase separation in InGaN/GaN MQWs after postgrowth annealing. The formation of In-rich InGaN nanostructures leads to an optical absorption peak centered at 2.65 eV. For samples annealed at 950 °C, phase separation was detectable after 8 h, which is very long compared to typical growth times. If the MQW active region of a laser diode heterostructure never experi-

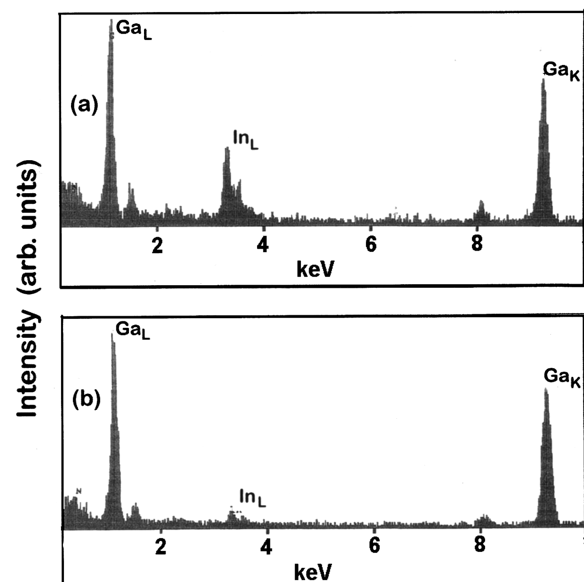

FIG. 4. EDX spectra showing analysis in the region of (a) the precipitate and (b) the surrounding matrix.

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ences growth temperatures above 900 °C, our results suggest that significant bulk phase separation will not occur as a result of annealing during growth for In concentrations of $x \leqslant 0.27$.

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