Dependence of composition fluctuation on indium content in InGaN/GaN multiple quantum wells

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The information on the variations of indium composition, aggregation size, and quantum-well width is crucially important for understanding the optical properties and, hence, fabricating efficient light-emitting devices. Our results showed that spinodal decomposition could occur in InGaN/GaN multiple quantum wells with indium content in the range of 15%–25% (grown with metal–organic chemical-vapor deposition). A lower nominal indium content led to a better confinement of indium-rich clusters within InGaN quantum wells. The InGaN/GaN interfaces became more diffusive, and indium-rich aggregates extended into GaN barriers with increasing indium content. It was also observed that indium-rich precipitates with diameter ranging from 5 to 12 nm preferred aggregating near V-shaped defects. © 2000 American Institute of Physics.

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There are now strong evidences showing that InGaN alloy inhomogeneities play a key role in high-efficiency emission of nitride-based light-emitting diodes grown on sapphire.^{1–3} In many articles, it was proposed that nanoscale indium composition fluctuations, due to indium aggregation of phase separation, acted as quantum dots (QDs) in optical characteristics.^{4–6} In the QDs, carriers are deeply localized and their migration toward nonradiative defects (dislocations) is hindered. Therefore, high-luminescence efficiency is expected if the density of QDs is much higher than that of dislocations. Indium compositional fluctuation or QD formation may arise from several mechanisms, including strain-induced island formation,^{7,8} spinodal decomposition,^{9–12} composition pulling effect,¹³ and surface segregation effect.¹⁴ It is uncertain which mechanism dominates for the formation of the compositional fluctuations. The influences of the size and distribution of QDs on the optical properties of InGaN alloys or InGaN/GaN quantum wells (QWs) are also unclear. In this letter, we report the effects of nominal indium content on the compositional fluctuation and structure defects in InGaN/GaN multiple-quantum-well (MQW) structures. The results include the measurement data of high-resolution transmission electron microscopy (HRTEM), atomic-force microscopy (AFM), energy-dispersive x-ray spectroscopy (EDX), and x-ray diffraction (XRD).

The samples used in this study were grown in a low-pressure metal–organic chemical-vapor deposition reactor. The InGaN/GaN MQW samples consisted of five periods of Si-doped InGaN wells with 3 nm thickness. The designated indium compositions of the samples were 15%, 20%, and

25% (samples I, II, and III, respectively). The Si doping concentration was 10^{18} cm^{-3} . The barrier was 7 nm GaN. In each sample, the QW layers were sandwiched between a 1.5 μm GaN buffer layer on a sapphire substrate and a 50 nm GaN cap layer. The growth temperatures were 1050 and 740 °C for GaN and InGaN, respectively.

The HRTEM investigations were performed using a Philips CM 200 electron microscope with an acceleration voltage of 200 kV. All high-resolution micrographs were taken at Scherzer defocus. The samples were viewed along a [11–20] zone axis and bright-field images were taken in our study. To verify that the precipitates are indium rich, EDX microanalysis was utilized to determine the chemical composition of the precipitates and the surrounding matrix. We have checked the indium composition with microprobe analysis (EDAX-DX4) near the QW region with the probe size or resolution of 2 nm. XRD measurements were carried out using $\text{Cu } K_\alpha$ radiation, monochromated by the (111) reflection of a Ge single crystal. The alloy composition of $\text{In}_x\text{Ga}_{1-x}\text{N}$ was determined by calculating the lattice spacing from the (0002) Bragg reflection peak, and assuming Vegard's law is applicable for the InN and GaN system. The surface morphologies were examined by AFM operating in the tapping mode.

Figures 1(a)–1(c) show XRD patterns of samples I, II, and III, respectively. The GaN peaks, identified as D, are mainly from cap and barrier layers. The other two peaks, A and C, corresponding to indium-rich and indium-poor phases, provide direct evidences of phase separation, which is attributed to spinodal decomposition. The extended distributions between A and C, including the features B and E, indicate strong indium compositional fluctuations with broad variations in size, shape, and indium content in the samples.

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FIG. 1. XRD patterns of samples I (a), II (b), and III (c).

The broadening phenomenon was found more prominent with increasing designated indium content. It is suggested that phase separation in InGaN QWs was incomplete due to kinetic limitation. The results show that the solubility limit of indium in GaN is roughly 8% for InGaN/GaN QW structures with relatively lower designated indium contents (samples I and II). With a larger indium content (sample III), the second decomposed phase [marked E and Fig. 1(c)] with an indium content of 11% appears. The solubility limit of gallium in InN is less than 5% for all three samples. Doppalapudi *et al.* suggested that at the growth temperature of 750 °C, InGaN was metastable for compositions between 5% and 20% indium (where the phase separation could occur only through nucleation and growth) and unstable for indium composition higher than 25% (where spinodal decomposition was expected).¹⁵ Although we cannot be very accurate about the designated indium content, the results show that spinodal decomposition has occurred with indium composition lower than 25% at the growth temperature of 740 °C. This implies that the behaviors of spinodal decomposition or phase separation in the InN–GaN system need further investigation.

Figure 2 shows three HRTEM pictures of the three samples with parts (a), (b), and (c) for samples I, II, and III, respectively. The variation of contrast in the pictures represents the fluctuation of local indium content. Such indium

FIG. 2. HRTEM pictures of samples I (a), II (b), and III (c). Five quantum wells in each sample can be clearly identified. Fringes represent phase-separated clusters.

composition fluctuation has been confirmed with EDX microanalysis. In all three pictures, five QWs can be well identified. Near these QWs, indium-rich clusters can be clearly seen. From the comparison between the three pictures, one can see that a lower nominal indium content led to a better confinement of indium-rich clusters near InGaN QWs. In sample I, disk-shaped indium-rich precipitates (or dots) can be observed with a diameter ranging from 5 to 8 nm and a thickness ranging from 2 to 4 nm. From parts (b) and (c), one can see that a higher nominal indium content led to the increase of indium-rich cluster size. The interfaces between InGaN and GaN became more diffusive and indium-rich aggregates extended more into GaN barriers as the nominal indium content increased. Meanwhile, a higher nominal indium content resulted in more InN clusters (phase separation), as indicated by fringe patterns. From atomic-scale HRTEM pictures (not shown in this letter), we also observed lattice distortions and planar faults in the samples due to

FIG. 3. HRTEM pictures showing more composition clusters near V-shaped defects for samples I (a) and III (b).

lattice mismatch between InN and GaN. In the selected-area diffraction patterns of samples II and III (not shown either), clear extra spots were also observed, indicating the presence of both phase separation and ordering along the c axis. The density of the aggregates was estimated to be much higher than that of threading dislocation density.

AFM pictures on the sample top surfaces show that the density of V-shaped defects increases with increasing nominal indium content (AFM pictures will be shown in another publication). The V-shaped defect density was about $2 \times 10^9 \text{ cm}^{-2}$ on sample II. Because a higher misfit strain was built with increasing indium content, more V-shaped defects were formed for strain relaxation. Threading dislocations and V-shaped defects were also observed with HRTEM. Figures 3(a) and 3(b) show HRTEM pictures near V-shaped defects in samples I and II, respectively. It seems that the indium-rich InGaIn precipitates with diameter range from 5 to 12 nm prefer aggregating near V-shaped defects or threading dislocations (indicated by dark contrast and fringes). It is believed that the stress field created by the dislocations provides the driving force for the migration of indium atoms toward dislocations. The stress-induced migration may lead to the segregation of indium atoms near dislocations and to the formation of indium-rich clusters. The high density of indium-rich clusters near defects implies that carriers may be trapped in

these aggregations before being captured by the structural defects. The correlation between these structural defects and the indium-rich phase separated clusters deserves further investigation.

In optical analysis among these three samples, we also observed distinct photoluminescence (PL) and amplified spontaneous emission [stimulated emission (SE)] results. Typically, a larger nominal indium content corresponded to a broader PL spectrum. Also, prominent two-peak features were observed in SE spectra from the samples of higher nominal indium contents.¹⁶ These optical characteristics are consistent with the trends of material analysis results in this letter.

In summary, we have demonstrated material analysis results of InGaIn/GaN MQW samples of different nominal indium contents. Our results showed that spinodal decomposition could occur in such a structure with indium content in the range from 15% to 25%. Disk-like indium-rich dots were found to be confined near QWs with a relatively lower indium content. The InGaIn/GaN interfaces became more diffusive with increasing indium content. Meanwhile, the density of V-shaped defects became higher with higher indium contents. The indium-rich precipitates with a diameter range from 5 to 12 nm prefer aggregating near V-shaped defects.

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