

# Phase separation in InGaN thick films and formation of InGaN/GaN double heterostructures in the entire alloy composition

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We report the growth of InGaN thick films and InGaN/GaN double heterostructures by molecular beam epitaxy at the substrate temperatures 700–800 °C, which is optimal for the growth of GaN. X-ray diffraction and optical absorption studies show phase separation of InN for  $\text{In}_x\text{Ga}_{1-x}\text{N}$  thick films with  $x > 0.3$ . On the other hand,  $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$  double heterostructures show no evidence of phase separation within the detection capabilities of our methods. These observations were accounted for using Stringfellow's model on phase separation, which gives a critical temperature for miscibility of the GaN–InN system equal to 2457 K. © 1997 American Institute of Physics. [S0003-6951(97)01509-X]

The optimization of InGaN alloys is important for the development of optical devices operating in the visible and near ultraviolet (UV) parts of the electromagnetic spectrum.<sup>1</sup> However, there are only limited studies of the GaN–InN quasi-binary system. The difficulty in growing InGaN alloys with high In content is the significantly higher vapor pressure of nitrogen over InGaN.<sup>1</sup> The first study to address the entire composition of the InN–GaN system was reported by Osamura and co-workers.<sup>2</sup> However, these studies were conducted on polycrystalline films grown at 500 °C on quartz or sapphire substrates. Matsuoka and co-workers<sup>1</sup> reported the growth of InGaN alloys by low temperature (500 °C) metalorganic chemical vapor deposition (MOCVD) with In concentration up to 42%. A number of authors reported the growth of either thick  $\text{In}_x\text{Ga}_{1-x}\text{N}$  films or  $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{In}_y\text{Ga}_{1-y}\text{N}$  heterostructures by MOCVD at temperatures 700–800 °C with maximum In-content of about 30%.<sup>3–6</sup> In this letter, we report the growth of InGaN alloys at the optimized growth temperature of GaN by molecular beam epitaxy. The study addresses issues related to phase separation in these alloys and describes methods to obtain InGaN alloys with up to 80% indium concentration without any detectable phase separation. Some preliminary results on these studies have been reported previously.<sup>7</sup>

InGaN alloys were grown by the electron cyclotron resonance-assisted molecular beam epitaxy (ECR-MBE) method on GaN coated (0001) sapphire substrates. This method of growth has been optimized over the past several years for the growth of GaN.<sup>8–10</sup> The sapphire substrates were subjected to the following processing steps prior to InGaN deposition. (a) Degreased in organic solvents, etched in a hot solution of  $\text{H}_2\text{SO}_4:\text{H}_3\text{PO}_4$  (3:1) for the removal of surface contaminants and mechanical damage due to polishing, rinsed with de-ionized (DI) water, mounted onto a molybdenum block, and introduced in the MBE system. (b) After thermal outgassing in the preparation chamber the substrates were exposed to an ECR nitrogen plasma which converts the surface of  $\text{Al}_2\text{O}_3$  to AlN as described previously.<sup>8–10</sup> (c) Fi-

nally the substrates were coated with GaN deposited in two-temperature steps (a 300 Å GaN buffer at 550 °C and the rest of the film at 800 °C) as discussed in our previous work.<sup>8–10</sup>

Two types of InGaN films were investigated in this study. The first series of InGaN alloys consist of 3000–4000-Å-thick films deposited on GaN films (2000–5000 Å thick). The second series consists of GaN/InGaN/GaN double heterostructures where the thickness of the InGaN layers is less than 500 Å. All the films were grown at growth rates between 10–30 Å/min, which are of the same order as those of InGaN films grown by MOCVD.<sup>4</sup>

The films were characterized by scanning electron microscopy (SEM), x-ray diffraction (XRD), transmission electron microscopy (TEM), Rutherford backscattering spectroscopy (RBS), and optical absorption measurements. XRD measurements were carried out in a four circle, double crystal x-ray diffractometer with Cu  $K\alpha$  as the excitation source and a curved graphite crystal as the monochromator. The indium concentration in the films was determined by computing the relative shift of the InGaN Bragg peak with respect to the GaN peak and applying Vegard's law. All InGaN films have been examined by SEM and XRD and found to have mirrorlike surface and show no evidence of indium droplets on the surface. The full width at half maximum (FWHM) of the XRD peaks for InGaN (7–9 min) is greater than the FWHM of the corresponding GaN Bragg peaks (3–4 min).<sup>7</sup> The broadening of the InGaN peaks is the combined result of alloying, inhomogeneous strain, and finite domain size effects.<sup>11</sup> X-ray diffraction of the films with the highest In-content ( $x > 0.3$ ) shows an additional peak, which corresponds to pure InN. Such evidence of phase separated InN is shown in Fig. 1

The structure of the investigated InGaN films ( $x > 0.30$ ) was found by TEM to contain high density of dislocations ( $\sim 10^{11} \text{ cm}^{-2}$ ) and planar defects on the basal and prism planes. Selected area diffraction patterns (SADPs) of the film were taken and compared to the GaN buffer layer below. It was observed that the diffraction pattern shows sensitivity to the electron beam which is attributed to beam induced evaporation of parts of the film. Thus the diffraction pattern

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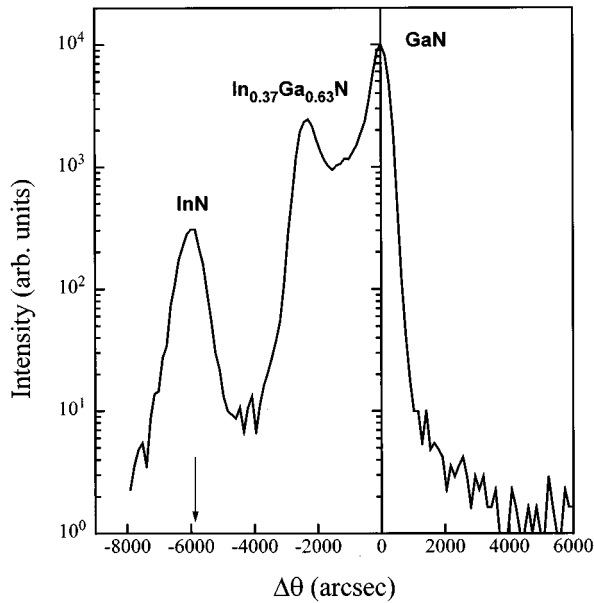


FIG. 1. XRD data for the  $\text{In}_{0.37}\text{Ga}_{0.63}\text{N}$  film plotted in a logarithmic scale. This shows clear evidence of phase separated InN.

changes as a function of beam exposure time. This, together with the high defect density in these films, makes the TEM analysis of phase separation in these samples difficult. The average composition of indium was determined by RBS and it was found that the indium and gallium edges of the RBS data could only be properly modeled if small percentages of InN (<5%) were included in the simulations.

Further evidence of phase separation and thus formation of composite films is also provided by the optical absorption measurements. The optical absorption constant for the film with 37% indium is shown in Fig. 2 and is compared with the optical absorption constants of GaN and  $\text{In}_{0.18}\text{Ga}_{0.82}\text{N}$  film. From this figure, it is apparent that the optical absorp-

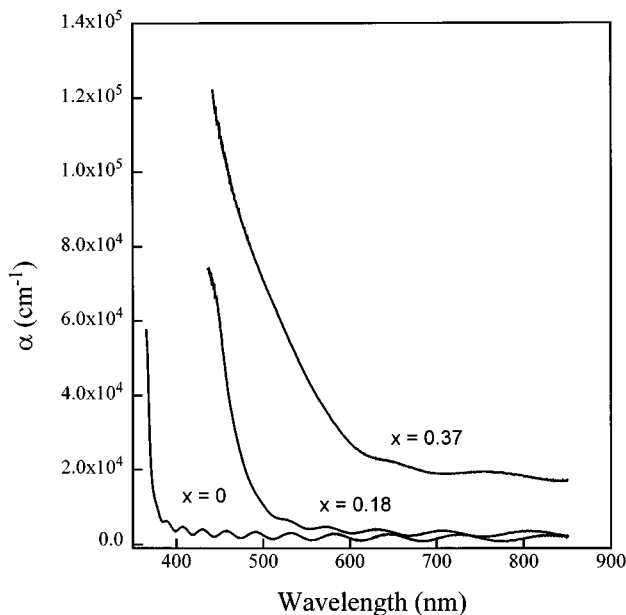


FIG. 2. Optical absorption vs wavelength for (a) GaN, (b)  $\text{In}_{0.18}\text{Ga}_{0.82}\text{N}$ , and (c)  $\text{In}_{0.37}\text{Ga}_{0.63}\text{N}$  film.

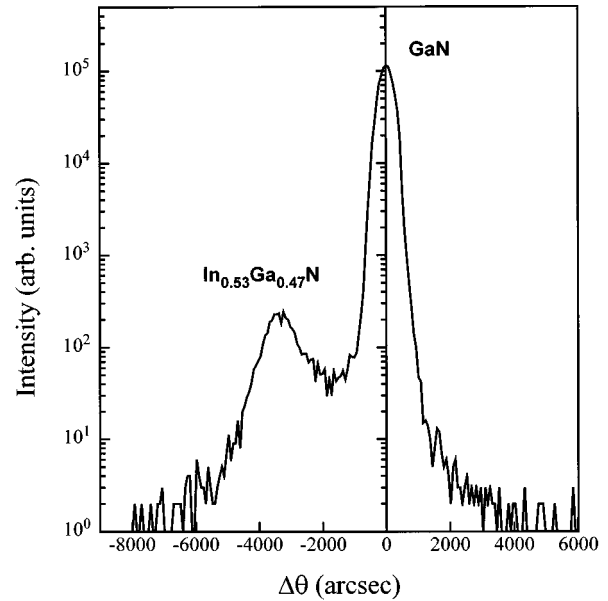


FIG. 3. XRD data for a  $\text{GaN}/\text{In}_{0.53}\text{Ga}_{0.47}\text{N}/\text{GaN}$  double heterostructure. There is no detectable evidence of phase separated InN.

tion constant of the  $\text{In}_{0.37}\text{Ga}_{0.63}\text{N}$  is not as sharp as that of GaN and the InGaN film with smaller indium concentration. A determination of the optical gap for this alloy using the convention,  $E_g \cong h\nu$  (at  $\alpha \sim 2-3 \times 10^4 \text{ cm}^{-1}$ ) results in the energy gap of about 2 eV, which is the same as that of pure InN. Thus the optical gap of these composite films is determined by the optical properties of the phase separated InN. We believe that this finding also accounts for the results of Matsuoka,<sup>1</sup> who observed an energy gap of 2.0 eV for  $\text{In}_{0.42}\text{Ga}_{0.58}\text{N}$  alloys. Thus the observed phase separation in InGaN alloys is independent of the growth method.

The second series of films consists of  $\text{GaN}/\text{InGaN}/\text{GaN}$  double heterostructures. Figure 3 shows the XRD data for one of these double heterostructures. The indium concentration in this InGaN film is 53% with no evidence of phase separated InN. These data provide a practical route of how to form InGaN alloys with high indium concentrations. Using the same approach and increasing the In/Ga ratio, we were able to make InGaN films with up to 81% indium in a double heterostructure, which is the highest yet reported by any growth method (see Fig. 4).

Phase separation in the InN–GaN pseudo-binary system is thermodynamically expected because of the large difference in lattice parameter between GaN and InN (11%). Similar findings have been widely reported for the InGaAsP system.<sup>12</sup> An estimate for the critical temperature for miscibility in this system can be obtained using the delta lattice parameter model (DLP), developed by Stringfellow.<sup>13,14</sup> This model is based on the dielectric theory of Phillips and Van Vechten<sup>15,16</sup> and has been successfully used to calculate and predict the miscibility in a number of binary, ternary, and quaternary systems in their zinc blende structures. The model assumes that the alloy system obeys Vegard's law and thus the lattice constant ( $a$ ) is related to the mole fraction ( $x$ ) by the following linear expression:

$$a_{\text{In}_x\text{Ga}_{1-x}\text{N}} = xa_{\text{InN}} + (1-x)a_{\text{GaN}}. \quad (1)$$

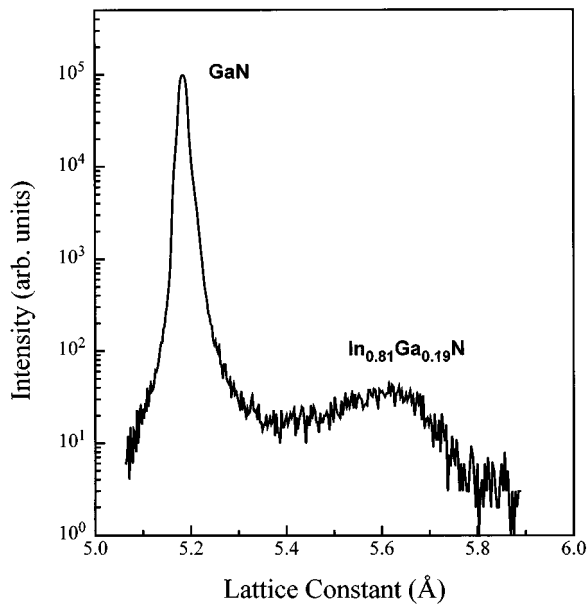


FIG. 4. XRD data for a GaN/In<sub>0.81</sub>Ga<sub>0.19</sub>N/GaN double heterostructure.

The maximum value of the critical temperature ( $T_c$ ) above which the InN–GaN system is completely miscible can be computed from Stringfellow’s equation for a binary system<sup>13</sup>

$$T_c = \frac{8.75K}{4R} \frac{(\Delta a)^2}{(\bar{a})^{4.5}}, \quad (2)$$

where  $\Delta a$  is the difference in the lattice constants of GaN and InN,  $\bar{a}$  is the average lattice of GaN and InN, and  $R$  is the gas constant.  $K$  is the proportionality constant between atomization enthalpy (bonding energy) and lattice constant in the Phillips and Van Vechten formula<sup>15,16</sup>

$$\Delta H^{\text{at}} = K a^{-2.5}. \quad (3)$$

The constant  $K$  was found by Stringfellow<sup>13</sup> by fitting Eq. (3) to experimental data for III–V compounds to have a value of  $1.17 \times 10^7$  cal/mol  $\text{\AA}^{2.5}$ .

GaN and InN in their equilibrium phases have the wurzite structure. However, the cohesive energies of those structures must differ only slightly from their zinc blende counterparts. Evidence for this is provided by the fact that the zinc blende structures can be grown easily by epitaxial stabilization using cubic substrates.<sup>17,18</sup> As a result, the solid solubility of GaN and InN will be approximately the same in the two structures. Thus, the critical temperature,  $T_c$ , was calculated for the zinc blende structures of GaN<sup>17</sup> and InN<sup>18</sup> using Eq. (2) and found to be 2457 K. Based on this estimate, the growth of InGaN bulk alloys at 700–800 °C occurs within the miscibility gap of this system which will explain the observed phased separation.

Phase separation in any alloy requires long range diffu-

sion and thus a correlation should exist between phase separation and length of time required for the growth of the film. We believe this is one of the reasons for the nonobservable phase separation in GaN/InGaN/GaN double heterostructures with thin InGaN layers. Strain associated with thin InGaN quantum wells could also stabilize the alloys against phase separation.

In conclusion, we have grown InGaN alloys by the MBE method at the optimized temperature employed for the growth of GaN films. These studies have shown that up to 30% indium can be easily incorporated in InGaN bulk films ( $>0.3 \mu\text{m}$ ) grown on pre-deposited GaN films. Further increase in indium concentration results in phase separation of InN which is attributed to the growth of InGaN alloys below the critical temperature required for miscibility. An estimate of the critical temperature for complete miscibility in the InN–GaN system using Stringfellow’s DLP model is 2457 K. We also discovered that high indium concentrations in InGaN alloys can be obtained in thin InGaN layers grown as GaN/InGaN/GaN double heterostructures. Using such structures, we incorporated up to 81% indium. Such structures are likely to be used for quantum devices operating in the visible part of the electromagnetic spectrum.

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