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Phase separation in InGaN multiple quantum wells annealed at high nitrogen pressures

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Phase separation was found to occur in $In_{0.33}Ga_{0.67}N/GaN$ multiple-quantum-well structures after annealing at 975 °C in a hydrostatic pressure of 5 kbar N_2 for 4 h. X-ray diffraction (XRD) spectra of the as-grown samples showed superlattice peaks that were replaced by a broad, single-phase peak after annealing. Transmission electron microscopy (TEM) images of the annealed samples show In-rich precipitates and voids that are found only within the quantum-well region. Both TEM and XRD measurements indicated that the formation of voids and second phases were suppressed after annealing in a hydrostatic pressure of 15 kbar. In addition, optical absorption measurements on these samples showed no indication of a peak at 2.65 eV that was observed in previous annealing studies.
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The wide-band-gap range of $In_xGa_{1-x}N$ alloys across the visible spectrum from 2.0–3.5 eV has made these materials attractive for both light-emitting diodes and laser applications.[1] However, the large lattice mismatch between InN and GaN introduces strain in the lattice[2] and phase separation has been observed in thick films using several growth techniques.[3–5] The equilibrium solid solubility limit at typical growth temperatures has been calculated to be less than 6%,[6] although by taking into account the growth kinetics and strain, higher indium contents up to ~50% have been predicted.[7,8] The observed Stokes shift found in $In_xGa_{1-x}N$ multiple-quantum-well (MQW) has been attributed to In rich phases,[9] and more recently to the internal piezoelectric field.[10] If pseudomorphic strain and band-gap bowing[11] of these materials are considered, then lasers that emit at 400 nm have values of $x \sim 0.08$. Recently, Nakamura reported cw laser operation at 450 nm by increasing the indium content.[12]

In this letter, annealing experiments were performed to determine the phase stability and thermal degradation of $In_xGa_{1-x}N$ alloys with high indium content. Previous studies of $In_xGa_{1-x}N/GaN$ MQWs with $x=0.27$ and $x=0.18$ showed that phase separation was found to coexist with void formation.[13,14] The origin of these voids is thought to be due to the loss of nitrogen from the sample. In the present study, hydrostatic pressures of 5 and 15 kbar were applied to $In_xGa_{1-x}N/GaN$ MQW structures with $x=0.33$. In this way, the effect of nitrogen overpressure could be studied to determine whether void formation, and subsequently, phase separation can be suppressed. The values chosen for the overpressure are between the theoretical estimates for the equilibrium vapor pressure over GaN (~10 bar) and InN (~20 kbar) at 1000 °C.[15]

Films were grown by metal organic vapor deposition on *c*-plane sapphire substrates. The structure consists of a low-temperature GaN buffer layer, a 4 μm GaN:Si high-temperature layer, a ten-period 4.5 nm $In_{0.33}Ga_{0.67}N$ well/10 nm GaN barrier superlattice, and a 1 μm GaN:Mg cap layer. 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. The samples were annealed at temperatures ranging from 975 to 1100 °C and pressures from 1 bar to 15 kbar. The high-pressure annealing was done in a sealed furnace with purified N_2 as a pressure-transmitting medium and excess GaN powder in the crucible. Annealing experiments performed at atmospheric pressure were done in a furnace with flowing nitrogen with a GaN sample placed over the InGaN/GaN MQW sample.

The XRD spectra for the as-grown sample and after annealing at 975 °C for 4 h are shown in Fig. 1. In the as-grown

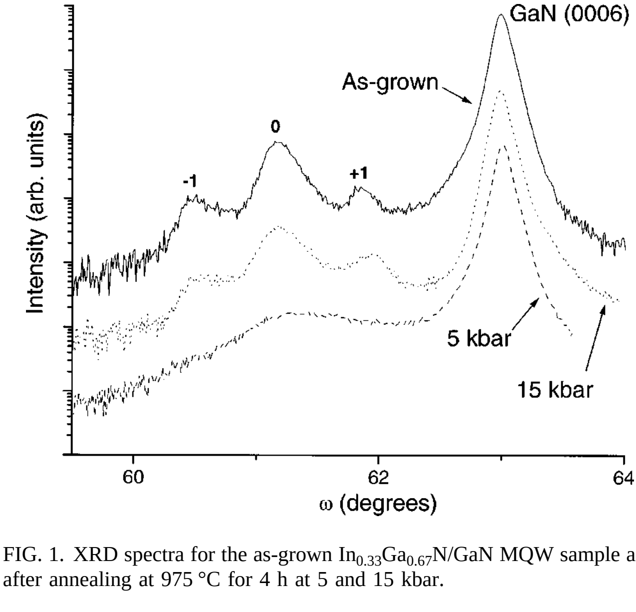

FIG. 1. XRD spectra for the as-grown $In_{0.33}Ga_{0.67}N/GaN$ MQW sample and after annealing at 975 °C for 4 h at 5 and 15 kbar.

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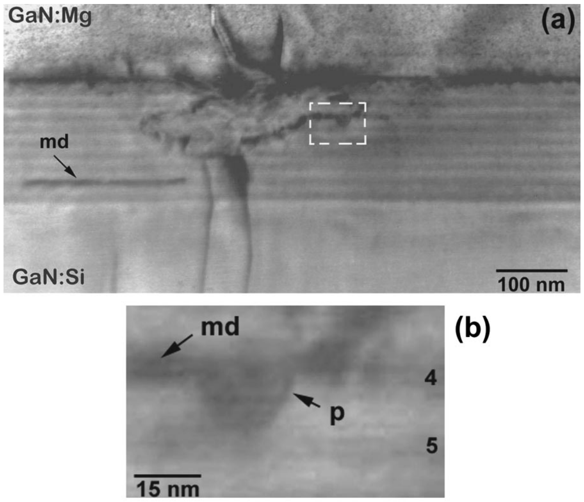

FIG. 2. (a) Bright-field TEM image of the MQW sample annealed at 15 kbar. md is a misfit dislocation. (b) Higher magnification of dotted region in (a) of a precipitate (p) near the fourth (4) and fifth (5) QW.

spectrum, the (0006) reflection for the underlying GaN and the zero- and first-order satellite peaks for the InGaN MQWs are shown. The XRD spectrum for the sample annealed at 15 kbar was unchanged, whereas the spectrum for the sample annealed at 5 kbar shows only a broad, zero-order peak. The In composition in the QWs was found by XRD to be $x = 0.48$, by assuming a relaxed alloy. However, by taking into account that the films are pseudomorphic with the underlying GaN,[2] a value of $x = 0.32$ is obtained which is similar to the RBS measurement. This indicates that the InGaN layers are compressively strained ~3% with respect to the GaN layers. For the sample annealed at 5 kbar, the position of the zero-order peak is found to shift slightly to a lower indium composition corresponding to a *strained* value of $x = 0.29$. This suggests that indium diffused from the quantum wells to form precipitates or there was a loss of indium from the sample.

No indication of phase separation was detected in the as-grown samples by TEM. TEM images for the annealed samples are shown in Figs. 2 and 3. Bright-field (BF) diffraction contrast images were taken ~10° from the $[11\bar{2}0]$ zone axis by using an off-Bragg imaging condition in which the (0002) reflection is weak. Under these imaging conditions, maximum contrast is obtained from regions of different atomic mass density. Figure 2(a) is a BF image taken from the sample annealed at 15 kbar. Misfit dislocations (md) with $\mathbf{b} = \langle 11\bar{2}0 \rangle$ were occasionally observed at the interfaces between the InGaN wells and GaN barriers. This indicates that in some regions of the film partial relaxation occurs which was not observed in samples with lower indium compositions.[13,14] Threading dislocations with a component of its burgers vector **b** along the c axis are also observed to bend at the strained well/barrier interface. This dislocation structure was similar to the as-grown sample and not caused by annealing. Second phases were not present in the majority of the sampling area except in isolated regions near the interface and dislocations. Figure 2(b) is a high-magnification lattice image of the dotted region in Fig. 2(a) showing a small faceted precipitate (~15 nm) along a misfit dislocation near a well/barrier interface.

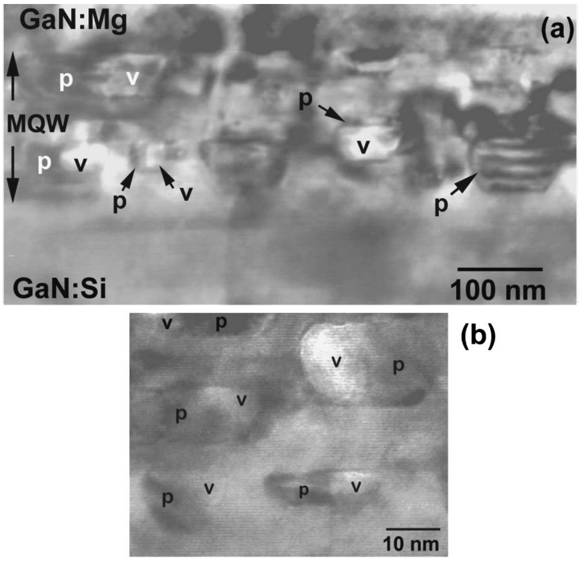

FIG. 3. (a) Bright-field TEM image of the MQW sample annealed at 5 kbar with voids (v) and precipitates (p). (b) TEM lattice image of void/precipitate pairs.

Figure 3(a) is an image taken from the sample annealed at 5 kbar in which precipitates (p) and voids (v) are observed only within the QW region. Most precipitates appear as regions of dark, uniform contrast. However, the larger precipitates (>50 nm) contain moiré fringes due to the differences in lattice constant with the matrix. EDX analysis was used to verify that the precipitates were higher in indium content than the surrounding matrix. The In/Ga ratio in these second phases (r_p) ranged from above the matrix composition ($r_m = 0.08$) to $r_p = 0.70$. No InN or Ga precipitates were detected by EDX or selected area diffraction (SAD). Microdiffraction of the second phases showed the same hexagonal crystal orientation as the matrix, although it was difficult to distinguish precipitate spots in SAD probably due to the wide variations in In composition. Voids and precipitates are often found as pairs and faceted as shown in the lattice image in Fig. 3(b). Facets are observed predominately along the $\{10\bar{1}1\}$ and $\{0001\}$ planes and occasionally along the $\{10\bar{1}0\}$ planes. This is consistent with facets observed in bulk single-crystal growth of GaN. The presence of In-rich phases at the voids may be similar to the In segregation that drives the formation of pits in pseudomorphic thick InGaN films[2] and QWs.[16] Northrup and co-workers performed total-energy calculations that show In atoms have a strong tendency to segregate to the {0001} and {10-11} facets.[17,18] Void precipitate pairs have been observed in other III–V systems such as Zn-diffused GaAs and InGaAsP lasers.[19,20]

The sizes of the voids suggest that their formation is due to the loss of material in the QW region. Since void formation can be suppressed by applying a large hydrostatic N_2 overpressure of 15 kbar, the simplest possibility is the loss of N during high-temperature annealing. Since no pure In or Ga precipitates were observed by TEM, it is also possible that Ga and In diffused out of the sample or that any Ga or In precipitates would have been removed during TEM sample preparation. The diffusion paths for these elements are likely to be along the dislocations or heterointerfaces where the initial stage of voids and precipitates were observed [recall

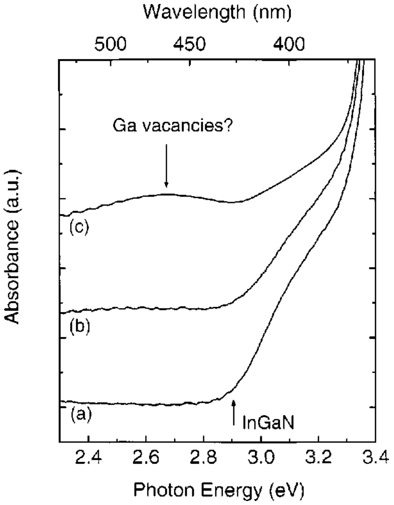

FIG. 4. Optical transmission spectrum for an (a) as-grown $In_{0.33}Ga_{0.67}N$/GaN MQW, (b) $In_{0.33}Ga_{0.67}N$/GaN MQW sample annealed at 5 kbar, and (c) $In_{0.27}Ga_{0.67}N$/GaN MQW annealed at atmospheric pressure for 40 h at 950 °C (from Ref. 13).

Fig. 2(b)]. SEM analysis of the surface showed that the morphology of the as-grown and annealed samples were similar, with no indication of pitting.

The formation of voids in the presence of In-rich precipitates may be understood by considering the strain field that such a precipitate would produce in the surrounding GaN matrix. Since the chemical potentials required to stabilize bulk GaN are increased near the precipitate (due to the strain field), the formation of a void is most likely to occur near the precipitate. Conversely, the In-rich precipitate can itself relax more completely if it is bounded partially by a void. This explanation for the void–precipitate pair formation requires that the Ga and N chemical potentials at the high temperature and low N_2 pressure annealing are too low to stabilize strained GaN in the region near the In-rich precipitate.

The optical transmission spectrum for an as-grown $In_{0.33}Ga_{0.67}N$/GaN MQW structure is shown in Fig. 4(a). An absorption onset is observed at 2.95 eV (420 nm), which is attributed to a valence- to conduction-band transition in the quantum wells. The sample annealed at a pressure of 15 kbar showed a nearly identical spectrum (not shown), whereas annealing at 5 kbar shows a slight broadening of the bandgap absorption onset [Fig. 4(b)]. Previous studies on an $In_{0.27}Ga_{0.67}N$ MQW annealed at atmospheric pressure for 40 h at 950 °C (Ref. 13) showed a broad peak centered at 2.65 eV (465 nm) [Fig. 4(c)] in addition to the conduction-band onset. This peak was not present in GaN samples annealed under the same conditions or MQW structures annealed under high pressures. Since the high-pressure furnace also provides a gallium overpressure, the formation of gallium vacancies may be suppressed. The 2.65 eV peak is, therefore, tentatively ascribed to an electronic transition involving gallium vacancies in the MQW region that is supported by the observations of Hoffman *et al.*[21] They observed an absorption profile which peaked at ~2.8 eV. If the yellow luminescence band arises from gallium vacancies, then this peak may result from the excitation of electrons from gallium–vacancy acceptor levels to the conduction band. Although the peak observed by Hoffman *et al.* is 0.15 eV higher than that observed in this study, the presence of nearby indium could account for the difference.

In conclusion, phase separation could be detected in $In_{0.33}Ga_{0.67}N$/GaN MQW structures only after using annealing conditions that produced voids in the QW region. Voids and second phases were found to be faceted and initiated at dislocations and heterointerfaces. Void formation, and consequently, phase separation was found to be suppressed by applying a high N_2 overpressure of 15 kbar during annealing. Phase separation in the presence of the voids is explained by a preferential segregation of In atoms to the void as a way to relieve the large compressive strain in the film.

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[1] S. Nakamura and G. Fasol, *The Blue Laser Diode* (Springer, Berlin, 1997).
[2] L. T. Romano, B. S. Krusor, M. D. McCluskey, D. P. Bour, and K. Nauka, Appl. Phys. Lett. **73**, 1757 (1998).
[3] R. Singh, D. Doppalapudi, T. D. Moustakas, and L. T. Romano, Appl. Phys. Lett. **70**, 1089 (1997).
[4] N. A. Masry, E. L. Piner, S. X. Liu, and S. M. Bedair, Appl. Phys. Lett. **72**, 40 (1998).
[5] Y. Sato and S. Sato, Jpn. J. Appl. Phys., Part 1 **36**, 4295 (1997).
[6] I-H. Ho and G. B. Stringfellow, Appl. Phys. Lett. **69**, 2701 (1996).
[7] A. Koukiti, N. Takahashi, T. Taki, and H. Seki, Jpn. J. Appl. Phys., Part 2 **35**, L673 (1996).
[8] S. Y. Karpov, MRS Internet J. Nitride Semicond. Res. **3**, 16 (1998).
[9] S. Chichibu, T. Azuhata, T. Soto, and S. Nakamura, Appl. Phys. Lett. **69**, 4188 (1996).
[10] T. Tetsuya, C. Wetzel, S. Yamaguchi, H. Sakai, H. Amano, I. Akasaki, Y. Kaneko, S. Nakagawa, Y. Yamaoka, and N. Yamada, Appl. Phys. Lett. **73**, 1691 (1999).
[11] M. D. McCluskey, C. G. Van de Walle, C. P. Master, L. T. Romano, and N. M. Johnson, Appl. Phys. Lett. **72**, 2725 (1998).
[12] S. Nakamura, Proceedings at the International Conference on Luminescence and Optical Scattering of Condensed Matter 1999, Osaka, Japan, Paper No. S8-1.
[13] M. D. McCluskey, L. T. Romano, B. S. Krusor, D. P. Bour, N. M. Johnson, and S. Brennan, Appl. Phys. Lett. **72**, 1730 (1998).
[14] M. D. McCluskey, L. T. Romano, B. S. Krusor, N. M. Johnson, T. Suski, and J. Jun, Appl. Phys. Lett. **73**, 1281 (1998).
[15] J. B. MacChesney, P. M. Bridenbaugh, and P. B. O'Conner, Mater. Res. Bull. **5**, 783 (1970).
[16] X. H. Wu, C. R. Blass, A. Abare, M. Mack, S. Keller, P. M. Petroff, S. P. DenBaars, J. S. Speck, and S. J. Rosner, Appl. Phys. Lett. **72**, 710 (1998).
[17] J. E. Northrup, L. T. Romano, and J. Neugebauer, Appl. Phys. Lett. **74**, 2319 (1999).
[18] J. E. Northrup and J. Neugebauer, Phys. Rev. B **60**, 8473 (1999).
[19] W. Jager, A. Rucki, K. Urban, H.-G. Hettwer, N. A. Stolwijk, H. Mehrer, and T. Y. Tan, J. Appl. Phys. **74**, 4409 (1993).
[20] C. W. Snyder, J. W. Lee, R. Hull, and R. A. Logan, Appl. Phys. Lett. **67**, 488 (1995).
[21] D. M. Hoffman, D. Kovalev, G. Steude, B. K. Meyer, A. Hoffman, L. Eckey, R. Heitz, T. Detchprom, H. Amano, and I. Akasaki, Phys. Rev. B **52**, 16702 (1995).