

## Pressure dependence of optical transitions in $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}/\text{GaN}$ multiple quantum wells

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The effects of hydrostatic pressure on optical transitions in  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}/\text{GaN}$  multiple quantum wells (MQW's) have been studied. The optical transition associated with confined electron and hole states in the MQW's was found to shift linearly to higher energy with pressure but exhibit a significantly weaker pressure dependence compared to bulklike thick epitaxial-layer samples. Similar pressure coefficients obtained by both photomodulation and photoluminescence measurements rule out the possibility of the transition involving localized states deep in the band gap. We found that the difference in the compressibility of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  and GaN induces a tensile strain in the compressively strained  $\text{In}_x\text{Ga}_{1-x}\text{N}$  well layers, partially compensating the externally applied hydrostatic pressure. This mechanical effect is primarily responsible for the smaller pressure dependence of the optical transitions in the  $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$  MQW's. In addition, the pressure-dependent measurements allow us to identify a spectral feature observed at an energy below the GaN band gap. We conclude that this feature is due to transitions from ionized Mg acceptor states to the conduction band in the *p*-type GaN cladding layer rather than a confined transition in the MQW's. [S0163-1829(98)51940-6]

The  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloy system and related heterostructures such as quantum wells (QW's) have been attracting much attention because of their importance in both scientific and technological aspects.<sup>1-3</sup> One of the fundamental issues is the evolution of the pressure dependence of the energy band gap for the alloy system. The most-recent experimentally determined values of pressure coefficient for the direct band gap of GaN are  $(3.9-4.2) \times 10^{-3}$  eV/kbar.<sup>4-6</sup> Christensen and Gorczyca predicted a pressure coefficient of  $3.3 \times 10^{-3}$  eV/kbar for the band gap of InN based on their self-consistent band-structure calculations.<sup>7</sup> Pressure-dependent photoluminescence studies on bulklike  $\text{In}_x\text{Ga}_{1-x}\text{N}$  epitaxial layers, which have yielded the pressure coefficients of near-band-edge luminescence emission from layers with small InN mole fraction ( $0 < x < 0.15$ ), do not substantially differ from that of GaN.<sup>8,9</sup> However, recent pressure-dependent studies of the optical properties of  $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$  QW's have found that the pressure coefficients of luminescence emission depend on QW sample structure and the In concentration.<sup>10,11</sup> Perlin and co-workers reported that the pressure coefficients of PL and EL emissions from  $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}/\text{Al}_x\text{Ga}_{1-x}\text{N}$  QW samples are much smaller than those of the GaN band gap.<sup>10</sup> The results were explained by assuming that highly localized states, with small pressure coefficients, are involved in the emission processes in their QW's.

In this paper we present the results of a high-pressure study of optical transitions in an  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}/\text{GaN}$  multiple-quantum-well (MQW) sample by performing photomodulated transmission (PT) and photoluminescence (PL) measurements. Since it is well known that in most instances,

deep localized states have a pressure dependence smaller than the band-edge states, a comparison between the pressure dependence of the absorption process probed by PT and that of the emission process measured by PL can provide direct insights into the nature of the states involved.

The  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}/\text{GaN}$  MQW sample used in this work is a laser diode structure prepared by metalorganic chemical vapor deposition. It consists of a 10-period  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}/\text{GaN}$  superlattice grown on a 4- $\mu\text{m}$ -thick GaN layer deposited on a sapphire substrate, and capped by a 0.2- $\mu\text{m}$  GaN:Mg *p*-type layer. The thicknesses of the well and the barrier are 18 and 62 Å, respectively. These values were derived from x-ray-diffraction (XRD) measurements of the superlattice period (80 Å) and the ratio of the well/barrier growth times (35/120). The averaged In concentration was determined by Rutherford backscattering spectrometry. The MQW structure is pseudomorphically strained to the underlying GaN layers.<sup>12</sup>

Photomodulation spectroscopic measurements were performed in a transmission geometry using a 150 W xenon lamp as probing light source and a chopped HeCd laser beam (3250 Å) as modulating light. PL signals resulted from excitation by the laser and were dispersed by a 1-M double-grating monochromator. Application of hydrostatic pressure was accomplished by mounting small sample chips with sizes of  $\sim 200 \times 200 \mu\text{m}^2$  into gasketed diamond anvil cells. A small ruby chip was also placed in the diamond anvil cell (DAC) for pressure calibration. All the spectra reported in this work were recorded at room temperature (295 K).

Figure 1 shows PT spectra taken from the  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}/\text{GaN}$  MQW sample and a thick  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$

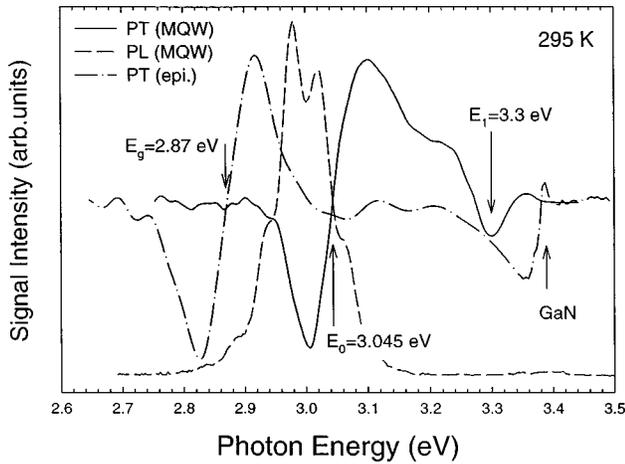


FIG. 1. Photomodulated transmission (PT) and photoluminescence (PL) spectra of the  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}/\text{GaN}$  MQW sample at ambient pressure. PT spectrum taken from an  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  epilayer sample is also shown for comparison.

epilayer sample at ambient pressure, together with the PL spectrum of the MQW sample. Two derivativelike signatures labeled  $E_0$  (3.045 eV) and  $E_1$  (3.3 eV) in the MQW PT spectrum were observed in the energy region between the band gaps of  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  (2.87 eV) and GaN ( $\sim 3.4$  eV). While the  $E_0$  spectral feature can be unmistakably attributed to be the transition between confined electron and hole states in the quantum wells, the identification of the  $E_1$  transition cannot be made immediately. As commonly observed in  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloys and related heterostructure samples, the MQW sample exhibits fairly broad PT and PL spectral line shapes, and a Stokes shift of the PL peak energy (2.99 eV) relative to the transition energy ( $E_0$ ) corresponding to the energy band gap of the sample. The oscillatory features on the PL spectrum are interference fringes primarily caused by the heterointerface between the thick GaN layer and the sap-

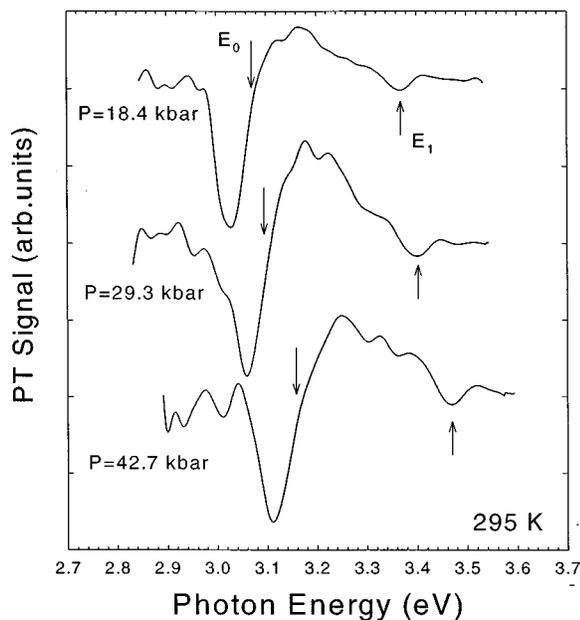


FIG. 2. PT spectra taken at selected pressures. The arrows indicate the spectral features of the  $E_0$  and  $E_1$  transitions.

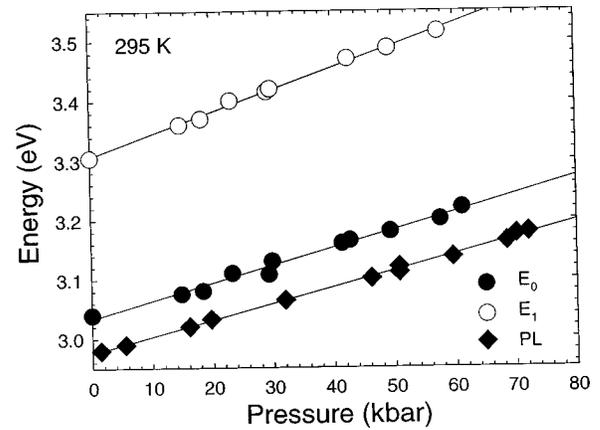


FIG. 3. Energy changes of the optical transitions observed in the MQW's sample as a function of pressure. The solid lines are the best linear fits to the data.

phire substrate. The PL peak position was determined by fitting its line shape to a Gaussian profile.

Under applied pressure, all spectral features shift to higher energy. PT spectra taken at a few different pressures are shown in Fig. 2 as an example. The pressure-induced energy shifts for the  $E_0$  and  $E_1$  transitions, along with the PL emission of the sample, are plotted in Fig. 3. The solid lines in the figure are least-squares fits to the experimental data using the linear-fit function

$$E(P) = E(0) + \alpha P, \quad (1)$$

where the energy  $E$  is in eV and the pressure  $p$  is in kbar. The pressure coefficients for the  $E_0$  and  $E_1$  transitions were determined to be  $3.0 \times 10^{-3}$  and  $3.7 \times 10^{-3}$  eV/kbar, respectively. A best fit to the data yields a pressure coefficient of  $2.8 \times 10^{-3}$  eV/kbar for the PL emission in the sample. We note that the pressure dependence of the interband  $E_0$  transition and the PL emission in the MQW sample is much weaker than that of thick, bulklike  $\text{In}_x\text{Ga}_{1-x}\text{N}$  epitaxial layers (see Table I). Although weaker pressure dependences of PL emissions in  $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$  quantum wells were previously reported,<sup>10,11</sup> this is the first time that a significantly smaller pressure dependence of an interband absorption in  $\text{In}_x\text{Ga}_{1-x}\text{N}/\text{GaN}$  MQW's has been observed. The fact that the pressure coefficient obtained by PT measurements is very similar to that derived from PL measurements infers that the possibility of the PL transition involving deep localized states can be ruled out safely and it further demonstrates that the PL process originates from the effective-mass band-edge states in the MQW sample. The observation of the PL peak

TABLE I. Pressure coefficients of PL emission in  $\text{In}_x\text{Ga}_{1-x}\text{N}$  epilayer samples.

	$E_{\text{PL}}(0)$ (eV)	$\alpha = dE/dP$ ( $10^{-3}$ eV/kbar)
GaN (10 K)	3.481	3.9
$\text{In}_{0.04}\text{Ga}_{0.96}\text{N}$ (10 K)	3.250	3.9
$\text{In}_{0.08}\text{Ga}_{0.92}\text{N}$ (10 K) <sup>a</sup>	3.085	3.5
$\text{In}_{0.08}\text{Ga}_{0.92}\text{N}$ (295 K) <sup>a</sup>	3.043	3.6
$\text{In}_{0.11}\text{Ga}_{0.89}\text{N}$ (295 K)	2.862	4.0

<sup>a</sup>Samples were from two different wafers.

below the band-gap energy can be explained in terms of alloy composition and well-thickness fluctuations and therefore large spatial fluctuations in energy potential. In a PL process, photoexcited carriers relax to the lowest available energy states associated with local minima in the conduction band induced by potential fluctuations, then recombine with holes, leading to the redshift of the PL peak from the averaged band gap determined by PT measurements.<sup>13</sup>

Several effects, including the increase of the electron effective mass with pressure, the mixing of QW and barrier wave functions, and the difference in bulk pressure coefficients of the band gaps of the barriers and the wells, could influence the pressure dependence of transitions confined in QW's and give rise to smaller pressure coefficients compared to those of the well materials in bulk form.<sup>13–19</sup> However, a simple  $\mathbf{k}\cdot\mathbf{p}$  calculation points out that the upper limit of these effects can only result in a reduction of approximately 10%, and cannot account for the big difference in the pressure coefficients between the  $E_0$  transition confined in the MQW's and those listed in Table I.

Application of hydrostatic pressure to strained QW's consisting of barrier and well materials with very different bulk moduli will lead to uniaxial strains that make the barriers and the wells experience different effective hydrostatic and axial pressure components.<sup>20,21</sup> Since the MQW structure used in this work was grown on a thick GaN layer, and the GaN barriers are much thicker than the  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  wells, the deformation of the well layers is dominated by the compression of the stiffer GaN under hydrostatic pressure. The bulk modulus of InN ( $\sim 125$  GPa) (Ref. 22) is approximately half that of GaN ( $\sim 210$ – $237$  GPa).<sup>22–24</sup> A linear interpolation gives a bulk modulus of  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  about 7% smaller than that of GaN. Under hydrostatic pressure conditions, a tensile strain will be induced in the compressively strained  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  well layers in the MQW structure to compensate the applied hydrostatic pressure because  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  has a larger compressibility. As a result, the  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  layers effectively experience a smaller hydrostatic pressure and an additional (0001) uniaxial stress. The relative volume change with applied pressure can be estimated using the Murnaghan equation of state:<sup>25</sup>

$$P = (B_0/B'_0)[(V_0/V)^{B'_0} - 1], \quad (2)$$

where  $B_0$  is the bulk modulus and  $B'_0$  is its pressure derivative ( $=dB/dP$ ). For a crystal with wurtzite structure, the relative volume change can be related to the variation of lattice parameters  $a$  and  $c$  as  $\Delta V/V = 2\Delta a/a + \Delta c/c$ . The relative changes of the lattice parameters can further be related through the elastic stiffness coefficients as  $\Delta c/c = -2(C_{13}/C_{33})\Delta a/a$ . Under the conditions that the  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  well layers remain pseudomorphically strained to GaN at high pressures, the variation of the  $a$ -lattice parameter of the well layers has to match the change of the  $a$ -lattice constant of GaN under pressure. Using the first-order (linear) approximation, the relative changes of the  $c$ -lattice constant as a function of applied hydrostatic pressure for a pseudomorphically strained to GaN and strain-free (free standing)  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  layer can be expressed as

$$\Delta c/c = P/B_0^{\text{InGa}} - P/[B_0^{\text{Ga}}(1 - C_{13}/C_{33})^{\text{Ga}}] \quad (3)$$

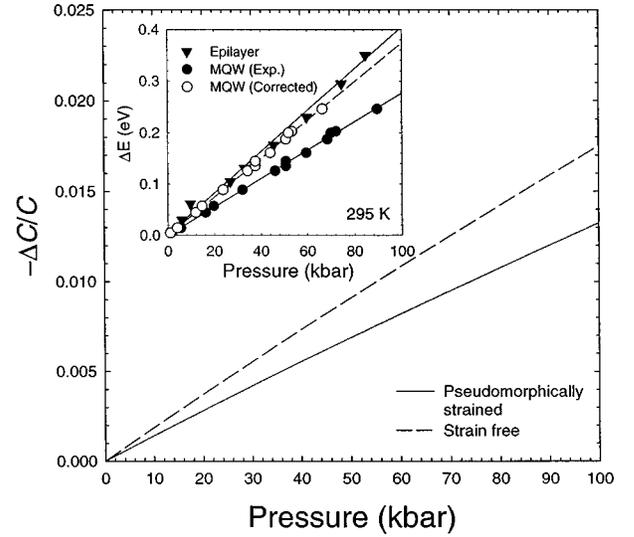


FIG. 4. Relative change of the  $c$ -lattice constant of an  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  layer pseudomorphically strained to GaN (solid line) and a strain-free  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  layer (dashed line) as a function of pressure. The inset shows the mechanical correction (open circles) to the experimental data (filled circles). The effects of pressure on PL from a  $0.2\text{-}\mu\text{m}$   $\text{In}_{0.11}\text{Ga}_{0.89}\text{N}$  epitaxial layer are also shown in the inset for comparison.

and

$$\Delta c/c = P/[B_0^{\text{InGa}}(1 - C_{33}/C_{13})^{\text{InGa}}], \quad (4)$$

respectively. The calculated results are given in Fig. 4. The numerical values of  $C_{13} = 108$  GPa and  $C_{33} = 399$  GPa for GaN and  $C_{13} = 94$  GPa and  $C_{33} = 200$  GPa for InN were used, and no fitting parameters were invoked in the calculations. As is shown in the figure, the overall effect of mechanical strain is to make a strained  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  layer sandwiched by stiffer GaN layers be compressed less than a free-standing layer at a given externally applied hydrostatic pressure. The effective pressure experienced by the well layers is only about 74% of the applied pressure. The effect of the stress reduction caused by the GaN barrier and cladding layers is also shown in the inset of Fig. 4. A pressure coefficient of  $(3.7\text{--}4.0) \times 10^{-3}$  eV/kbar can be derived from this purely mechanical correction. Therefore, we attribute the difference in the compressibility of  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  from that of GaN to be the major factor responsible for the significantly weaker pressure dependence of the confined transition in our MQW sample.

In order to identify the nature of the  $E_1$  transition, the effects of quantum confinement on the energy levels in the MQW's were estimated based on an envelope-function approximation using both the Kronig-Penney single-band model and Kane's three-band model.<sup>26,27</sup> However, the calculated results indicate that there is only one confined level in the conduction band and one in the valence band, respectively, for an  $18\text{-}\text{\AA}$   $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}/\text{GaN}$  quantum well. The large pressure coefficient of  $3.7 \times 10^{-3}$  eV/kbar further suggest that the  $E_1$  transition cannot be related to a transition confined in the well. Otherwise the mechanical correction discussed above would produce an unrealistic pressure coefficient of  $5.0 \times 10^{-3}$  eV/kbar. Therefore, the  $E_1$  transition

has to originate from GaN layers. Since the transition is observed at below-band-gap energy, where GaN is transparent, it is most likely related to a transition involving ionized impurity states. Similar observations of impurity-related below-band-gap transitions in GaAs and  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  bulk materials using high-sensitivity derivative-nature modulation spectroscopy were previously reported by several authors.<sup>28–31</sup> Based on the energy position of the transition and its pressure coefficient, we attribute the transition to Mg acceptors in the *p*-type GaN cladding layer on the top of the MQW structure. The slight difference of the pressure coefficient of this  $E_1$  transition from that of the GaN band gap is primarily caused by the uncertainty in determining the transition energy at different pressures due to the fairly broad spectral line shape and the small signal intensity.

In conclusion, two PT spectral features observed in the energy region between the band gaps of  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  and GaN were found to shift to higher energy under pressure, but at different rates. The spectral feature corresponding to the transition associated with the confined states in the quantum wells exhibits a significantly smaller pressure dependence as

compared to bulklike thick  $\text{In}_x\text{Ga}_{1-x}\text{N}$  epitaxial-layer samples. The very similar pressure coefficients obtained by monitoring two different transition processes, i.e., absorption (PT) and recombination (PL), rule out the possibility of PL resulting from localized states deep in the band gap. The difference in the compressibilities of  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  and GaN, which induces a tensile strain in the  $\text{In}_{0.15}\text{Ga}_{0.85}\text{N}$  well layers, partially compensating the externally applied hydrostatic pressure, was found to be primarily responsible for the smaller pressure dependence observed for the confined transition in the MQW sample. The pressure-dependent measurements also allow us to assign the second spectral feature to the transition from ionized Mg acceptor states to the conduction band in the *P*-type GaN cladding layer rather than to the second confined transition in the MQW's.

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