Influence of pressure on photoluminescence and electroluminescence in GaN/InGaN/AlGaN quantum wells

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(Received 15 January 1997; accepted for publication 1 April 1997)

We have measured photoluminescence and electroluminescence in two different types of high-brightness single-quantum-well light emitting diodes manufactured by Nichia Chemical Industries with $In_xGa_{1-x}N$ active layers ($x=0.45$ and $x=0.15$), under hydrostatic pressures up to 8 GPa. We discovered that the pressure shift of the primary luminescence peak in each diode is very small: 12 and 16 meV/GPa for the green and blue diodes, respectively. The observed pressure coefficients are much lower than those characteristic of the energy gap in GaN (≈ 40 meV/GPa) or the energy gap in InN (≈ 33 meV/GPa). This kind of behavior is usually associated with recombination processes involving localized states. These localized states may be associated either with band tails (arising from In fluctuations in the active layer or from high density of defects), and/or with localized excitons of various types. *© 1997 American Institute of Physics.* [S0003-6951(97)02022-6]

$In_xGa_{1-x}N$ ternary compounds are of great interest as materials for present and future optoelectronic applications. Having band gaps that are composition tunable in a large range of energies (2.07–3.4 eV depending on the In content), this material is well suited to form quantum wells (QWs) in many optoelectronic devices based on group-III nitrides.[1] Also, compared to GaN, InGaN is commonly thought to provide better radiative recombination efficiency and to be free from parasitic yellow luminescence. Hence, it is not surprising that this material has been successfully employed in the most recent single-quantum-well (SQW) light-emitting diodes (LEDs) manufactured by Nichia Chemical Industries.[2,3] The first diode laser operating in the blue spectral region was also based on a very similar structure, except that the active region consisted of multiple quantum wells instead of SQW.[4] In contrast to dramatic technological progress resulting in commercial availability of blue and green SQW LEDs, the mechanism of optical emission in InGaN QW diodes is still poorly understood. First, it was observed that light emission in InGaN QWs usually occurs at photon energies smaller than the band gap.[2] At this point, however, it should be stressed that the available information about the dependence of the InGaN band gap on In content is not very accurate. In addition, determination of the average In content in the QW active layer is rather difficult and may involve a large error margin. Second, it was observed that the spontaneous emission linewidth is characterized by a large nonthermal broadening.[2,3,5] Finally, it was established recently that the temperature shifts of the photo- and electroluminescence (EL) peak energies in Nichia green SQW LEDs are opposite to the corresponding shift of the band gap.[6]

All these observations strongly suggest that the recombination in GaN/InGaN/AlGaN SQW LEDs does not have a standard band-to-band character. To account for this, several different recombination mechanisms have been put forth. Chichibu *et al.*[7–9] suggested that the luminescence involves recombination of excitons localized on the potential fluctuations caused by variations in the In content. Perlin *et al.*[6] proposed that the radiative transitions take place between uncorrelated electrons and holes in the band tails of InGaN alloy. Also, from measurements of the photoluminescence (PL) decay lifetime in InGaN, it has been concluded that alloy potential fluctuations and impurity states are the most likely candidates responsible for the PL signal.[10] Last, it was asserted (only for quantum well systems) that the recombination could be related to quantum dots spontaneously formed in the InGaN active layer due to In content fluctuations.[8,11]

In order to shed more light on the nature of the radiative recombination in InGaN QWs, especially focusing on the material used in commercial devices, we performed high hydrostatic pressure measurements of the PL in two types of Nichia SQW LEDs, NSPG-500 and NSPB-500, emitting in the green and blue spectral region, respectively. The active region of these devices consists of a 30-Å-thick $In_xGa_{1-x}N$ layer ($x=0.45$ for the green LEDs, and $x\approx 0.16$ for the blue LEDs), sandwiched between n-GaN and p-$Al_{0.2}Ga_{0.8}N$ layers. The pressure coefficient of the emission peak can reveal whether the radiative transitions have band-to-band character (pressure coefficient should be close to that of the band gap) or whether they involve localized states (a pressure coefficient much smaller than that of the band gap is then expected).

The experiments were performed at 300 K, using a diamond anvil cell with a 4:1 mixture of methanol and ethanol

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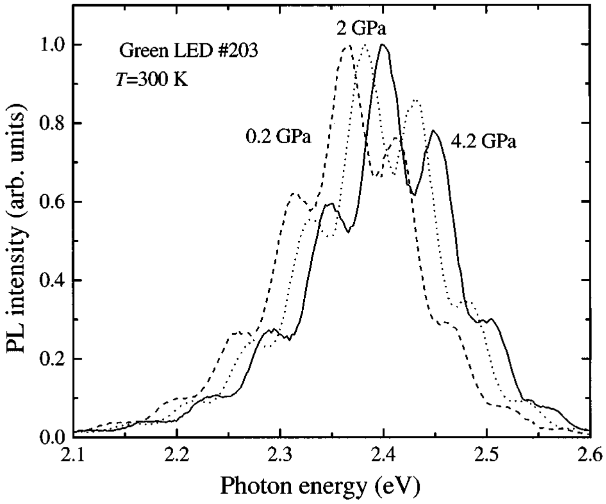

FIG. 1. Photoluminescence (PL) spectra of Nichia NSPG-500 green SQW LED measured at different pressures. Undulations are due to Fabry–Perot resonances. Spectra are normalized for clarity.

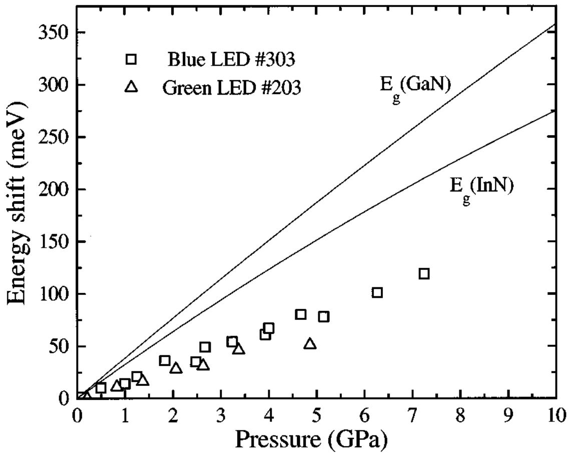

FIG. 3. Peak position of the PL as a function of pressure for both NSPG-500 green (triangles) and NSPB-500 blue (squares) SQW LEDs. Solid lines show the pressure-induced shift of the band gaps in bulk GaN and InN.

as the pressure transmitting medium. The shift of the ruby R-line luminescence (3.65 Å/GPa) was used to calibrate the pressure inside the cell. Prior to the experiment, the diodes were deencapsulated, and part of the sapphire substrate was mechanically removed. Finally, the samples were cleaved and placed in the gasket hole of the diamond anvil cell. The luminescence was excited with an argon ion laser, using the blue 458 nm line in the case of the green LEDs and the UV 363 nm line for the blue LEDs, with the spot size of $\sim 5\ \mu$m.

Figures 1 and 2 show the MPL spectra of the green diode and the blue LEDs, respectively, measured at different pressures. A characteristic feature of the luminescence from both diodes is the presence of Fabry–Perot interference fringes. In both cases, the distance between fringe maxima is close to 50 meV ($500\ \mathrm{cm}^{-1}$). This corresponds to a layer thickness of approximately 5 μm, which is close to the total thickness of 4.6 μm of these GaN/InGaN/AlGaN structures.[2,3] In analyzing the pressure-induced shift of the PL peaks, one should realize that the interference maxima have an added pressure coefficient related to the change of the refractive index. For GaN,[12] this pressure coefficient was calculated to be approximately 6 meV/GPa. Consequently, simple tracking of an interference maximum position would result in a wrong pressure coefficient. In order to determine the PL peak position more accurately, we fit the product of a Gaussian peak profile and a periodic function representing the interference fringes. The obtained peak positions as a function of pressure are shown in Fig. 3. The linear pressure coefficients obtained for these PL peaks are unusually low, 12 and 16 meV/GPa for the green and blue LEDs, respectively. In order to check whether the mechanisms of PL and EL in these diodes are the same, we also performed a high pressure investigation of EL from another green SQW LED. A full-size deencapsulated diode with undisturbed wiring was placed in a ''Unipress'' piston-cylinder liquid cell[13] equipped with sapphire window and electrical connections. Figure 4 shows the obtained EL spectra. We determined that the pressure coefficient of the EL peak position is equal to 15.8 meV/GPa, in agreement with the PL measurements.

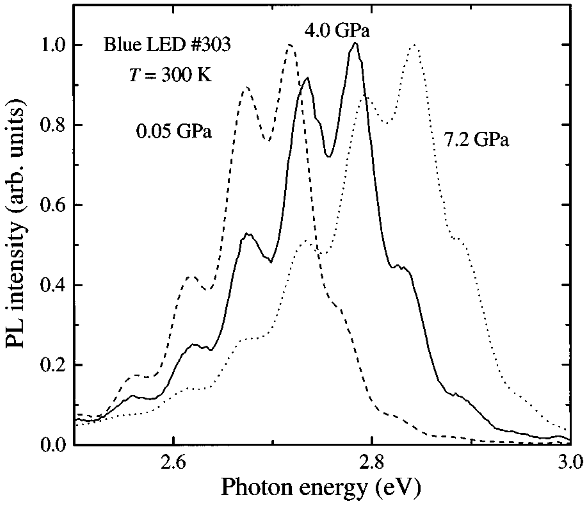

FIG. 2. Normalized PL spectra of Nichia NSPB-500 blue SQW LED measured at different pressures. Undulations are due to Fabry–Perot resonances.

These results are much smaller than the best available values for the pressure coefficients of the band gaps of GaN (40 meV/GPa from experiment)[14] and InN (33 meV/GPa from theory).[15] In order to ascertain why, let us estimate to what extent quantum confinement effects can contribute to the influence of pressure on the PL peak of the SQW active layer. In general, the pressure-induced increase in the band gap tends to flatten the band minima, thus increasing the effective mass and lowering the confined energy levels, which in turn leads to a slight decrease in the pressure coefficient of the QW emission relative to that of the corresponding bulk alloy. This effect has, for example, been observed previously in GaAs/AlGaAs QWs.[16] Its magnitude can be estimated from the first-order $\mathbf{k}\cdot\mathbf{p}$ theory, in which the relative change in the effective mass is proportional to the relative change in the band gap. Accordingly, the pressure coefficient of the confined state energy in an InGaN/AlGaN QW should be ~2 meV/GPa in the conduction band, and much less in the valence band. Clearly, this does not represent a very important contribution to the overall pressure coefficient of the luminescence peak.

Another possible origin of the observed low pressure

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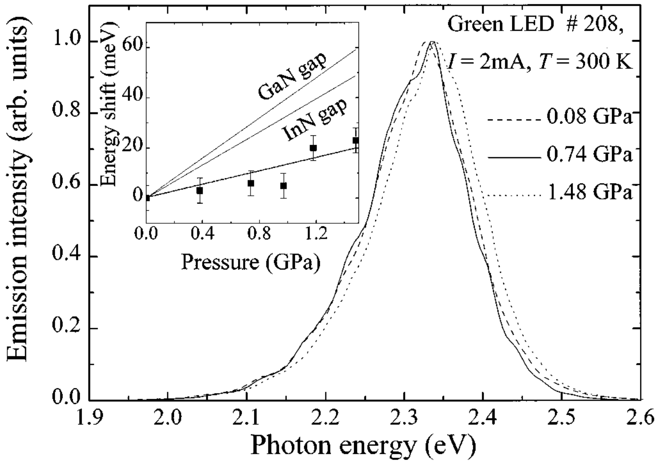

FIG. 4. Electroluminescence (EL) spectra of green SQW LED measured at various pressures. Insert shows peak position of the EL as a function of pressure.

coefficients is the influence of substrate on the pressure behavior of a heterostructure. However, experimental evidence shows that bulk GaN crystals and epitaxial layers of GaN on sapphire both behave very similarly under applied hydrostatic pressure (cf. the case of ''yellow luminescence'' in Ref. 14). Thus, since the observed pressure coefficients of the QW emission peaks are two to three times smaller than those of the band gaps of the corresponding bulk materials, we are led to the conclusion that the QW emission is associated with strongly localized states.

Let us assess this result in terms of the proposed models of luminescence in InGaN/AlGaN QW LEDs. Considering the model based on highly localized excitons,[7–9] the most familiar example is the nitrogen related luminescence in GaAs. In this material, nitrogen at an As site forms an isoelectronic center which can bind electrons via a short range potential. High pressure experiments[17] showed that the pressure coefficient of this emission can be much lower than that of the bulk GaAs band gap. Although strongly localized excitons of this type usually produce sharp emission lines, the broadening seen in the present samples might arise from the effects of alloy fluctuations on the exciton localization in the InGaN/AlGaN QWs.

Small pressure coefficients are also expected if the recombination takes place between uncorrelated electrons and holes trapped in band-tail states that may arise from In content fluctuations and/or defect states.[6] The model of tail-related transitions has been successfully used to explain the light emission properties of amorphous silicon,[18] including the effects of applied pressure.[19] Band-tail states become increasingly deep as they extend into the forbidden gap, and deep electronic states are known to have pressure coefficients determined by an average over the whole Brillouin zone. These average coefficients will be much lower than that of the Γ-point direct band gap (cf. Ref. 15), in accordance with the present results for the QW emission. It is important to note that this model can also account for the anomalous temperature shift of the QW peaks observed in GaN/InGaN/AlGaN SQW LEDs.[6]

Considering the third model based on recombination within quantum dots,[8,11] it was demonstrated by Li *et al.*[20] that the pressure coefficient of the luminescence from InAs quantum dots embedded in GaAs is not substantially different from the pressure coefficient of the bulk InAs band gap. Comparing InAs and InGaN, one should remember that the exciton radius becomes approximately 5 times smaller for InGaN in comparison with InAs (~30 Å versus ~150 Å). The difference in the exciton radii may be partially responsible for the different pressure behavior. Nevertheless, if we assume that the observed recombination occurs inside quantum dots whose electronic levels are sufficiently unmixed by disorder so that they behave like normal band-edge states, we cannot account for the small magnitude of the measured pressure coefficients for any possible fixed value of local In composition. Hence, a distribution of quantum dot compositions and sizes would have to be invoked, and this would give rise to a significant density of localized band-tail states.

In conclusion, we have measured the pressure dependence of the photoluminescence and electroluminescence from two different types of GaN/InGaN/AlGaN light emitting diodes. Unusually low pressure coefficients were found indicating the involvement of highly localized states in the process of radiative recombination.

The UNM authors (P.P., P.G.E., and M.O.) acknowledge support from ARPA through the Optoelectronic Materials Center. The SUNY/Buffalo authors (V.I. and B.A.W.) acknowledge partial support from the Xerox Research Foundation.

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