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InGaN/GaN quantum wells studied by high pressure, variable temperature, and excitation power spectroscopy

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The energies of photo- and electroluminescence transitions in $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$ quantum wells exhibit a characteristic ''blueshift'' with increasing pumping power. This effect has been attributed either to band-tail filling, or to screening of piezoelectric fields. We have studied the pressure and temperature behavior of radiative recombination in $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$/GaN quantum wells with $x=0.06$, 0.10, and 0.15. We find that, although the recombination has primarily a band-to-band character, the excitation-power induced blueshift can be attributed uniquely to piezoelectric screening. Calculations of the piezoelectric field in pseudomorphic $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$ layers agree very well with the observed Stokes redshift of the photoluminescence. The observed pressure coefficients of the photoluminescence (25–37 meV/GPa) are surprisingly low, and, so far, their magnitude can only be partially explained. © *1998 American Institute of Physics.* [S0003-6951(98)01045-6]

$\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$ is presently the only material used commercially as an active layer in high brightness optoelectronic devices emitting in the green-to-UV spectral region.[1,2] However, difficult technological problems arise in the use of this material system for quantum well (QW) device structures. First, InN and GaN are far from being lattice matched (11% difference in lattice constant). Second, the low miscibility of these compounds leads to large fluctuations of the indium content, and/or to phase separation in alloys.[3,4] Emission from the $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$ QWs is frequently characterized by large Stokes shift between the emission and absorption energies,[5] and also by large pumping power induced blueshift of the electroluminescence (EL) and the photoluminescence (PL) peaks.[6] So far, these puzzling phenomena have been interpreted in terms of models involving strong localization of carriers, combined with the effects of phase separation, indium concentration fluctuations, and band tailing.[3–8] Here we report a study of $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$/GaN QWs in which the PL and EL transitions exhibit large Stokes shifts and large excitation-power induced blueshifts, but there are no apparent band-tailing effects. We demonstrate that an explanation based on strain induced piezoelectric fields is adequate to account for the observed behavior.

The $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$ QW structure studied in this work was grown by metalorganic chemical vapor deposition (MOCVD) on a sapphire substrate, on top of a 1.85 μm thick GaN layer. Three pairs of the quantum wells were grown. The first pair had a thickness of 35 Å and an indium content of 0.06; the second had $d=45$ Å and $x=0.1$, and the third $d=53$ Å, $x=0.15$. They were sandwiched between 200 Å thick GaN barriers. These parameters were determined by the combined measurements of secondary electron mass spectroscopy, Rutherford backscattering, and high resolution transmission electron microscopy (HRTEM).[9] Preliminary results of stress analysis (HRTEM) indicate that the $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{N}$ layers are fully strained.[9] Detailed results of the structural analysis of this sample will be published elsewhere.[9] PL spectra were recorded using a 3/4 m double monochromator with a GaAs photomultiplier. Photoluminescence was excited by 325 nm He–Cd or the 350 nm Kr-ion line. Incident powers were in the 5–25 mW range, focused into a 10 μm diam spot. A Diamond anvil cell operated at low temperature was used for high pressure experiments.

Figure 1(a) shows the PL spectra measured for our sample at 4 K using different excitation powers, as described in the caption. Luminescence peaks from each of the three pairs of quantum wells (labeled α, β, and γ) can be distinguished. Note that the energies of these peaks lie below that of the PL in bulk InGaN.[10] All three peaks exhibit remarkably small linewidths, the broadest being 110 meV for the QW with 15% indium concentration.[11] The splitting seen in the $\mathrm{In}_{0.12}\mathrm{Ga}_{0.88}\mathrm{N}$ PL peak is attributed to a slight variation of the indium content in this pair of quantum wells. When the excitation power is increased, the PL peaks shift toward higher energies, changing the overall visual color of the emission from the green to blue. Figures 1(b) and 1(c) show that the peak positions depend logarithmically on the excitation power, but the intensities vary linearly with the excitation power.

The effects of increasing temperature on the PL spectra are displayed in Fig. 2. The inset shows the peak position

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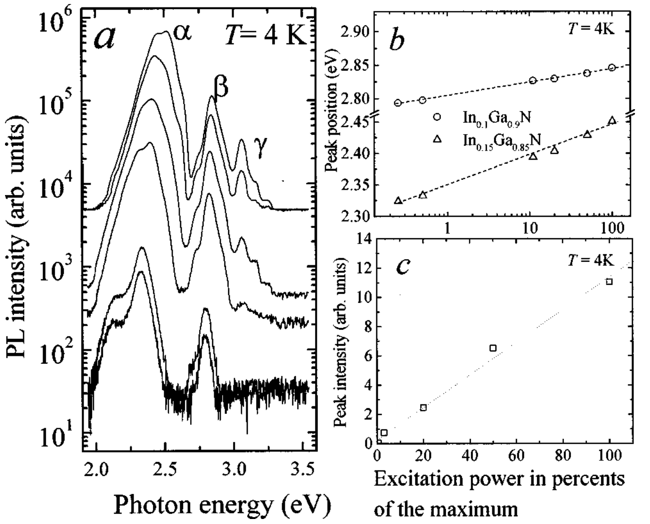

FIG. 1. (a) Photoluminescence spectra measured for excitation powers (from bottom to top) of 0.01, 0.025, 0.05, 0.3, 2.1, 5.0, and 10.0 kW/cm^2. Peaks α, β, and γ originate in the $In_{0.15}Ga_{0.85}N$, $In_{0.1}Ga_{0.9}N$, and $In_{0.06}Ga_{0.94}N$ QWs, respectively. (b) and (c) Excitation power dependence of the peak positions and intensities, respectively.

versus temperature for the $In_{0.15}Ga_{0.85}N$ QW emission for both quantum wells, separately. The observed dependence is similar to that of the energy gap in GaN,[12] and can be described well by the Varshni function, $E=E_0-\gamma T^2/(T+\beta)$, with γ and β equal to 9.4×10^{-4} eV/K and 770 K, respectively. The relatively large scatter of the peak positions can be explained by changes in the power density of the laser beam. This, in turn, is due to a slight defocusing of the beam during the temperature sweep.

Figures 3(a) and 3(b) show the influence of applied hydrostatic pressures on the PL spectra (recorded at 8 K). All three peaks shift to higher energy with increasing compression. The linear pressure coefficients are 37, 30, and 25 meV/GPa for the QWs with x equal to 0.06, 0.1, and 0.15, respectively. These values are similar to those observed previously in commercially manufactured (Nichia Chemicals) InGaN single QWs,[8] and are much smaller than the pressure shifts predicted for bulk $In_xGa_{1-x}N$ (40–33 meV/GPa for $x=0$ to $x=1$).[13]

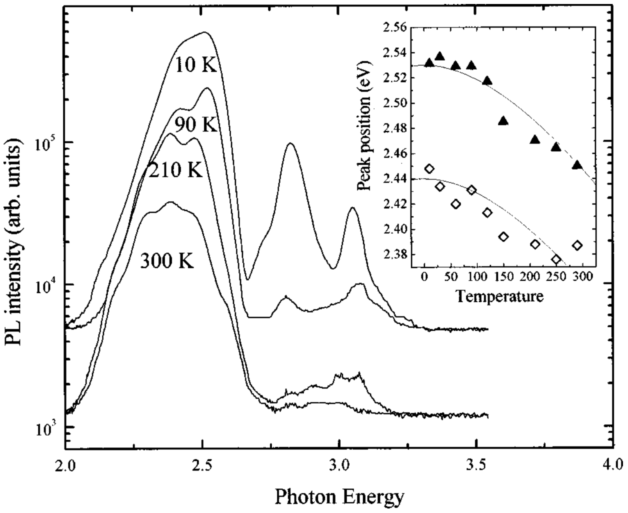

FIG. 2. Temperature dependence of the PL spectra. The inset pertains to splitted peak α in Fig. 1(a), from the $In_{0.15}Ga_{0.85}N$ QW.

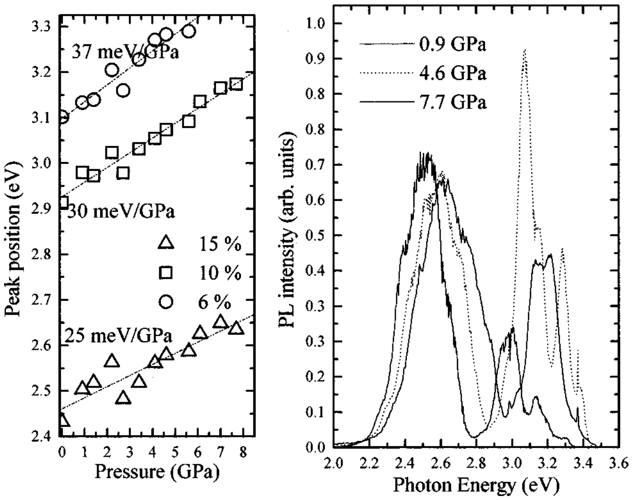

FIG. 3. (a) Effects of hydrostatic pressure on the PL spectra. (b) Peak energy vs applied pressure for the emission from three types of $In_xGa_{1-x}N$ QWs ($x=0.15$, 0.1, and 0.06) in our sample.

The observed temperature behavior of the PL closely resembles the normal dependence found in GaN. This result is unique for $In_xGa_{1-x}N$ QWs and epilayers, in which the effects of temperature on the emission peaks are usually the anomalous—blueshifts with increasing temperature or insensitivity to temperature.[7,14] The ''normal'' temperature dependence found here indicates that the transitions in our multi-QW sample probably have band-to-band character.

We have found that the PL peaks originating in QWs with higher In content have smaller pressure coefficients. Although the same trend is found in $In_xGa_{1-x}N$ alloys, it is much more pronounced in the QWs. It is clear that the experimental points for the PL peaks lie systematically below the predicted bulk band gap values.

Two factors partially explain this discrepancy. The first factor is the decrease of the electron confinement energy with pressure (due to variation of the effective mass); this was discussed in Ref. 8. The second factor relates to the compressibility of the $In_xGa_{1-x}N$ QWs, which is dominated (in plane) by the smaller compressibility of the thick (1.8 μm) GaN layer. This means that the effective pressure experienced by the $In_xGa_{1-x}N$ QWs is less than what is applied, leading to smaller pressure coefficients. However, these two effects decrease the pressure coefficient of the gap by around 6% for the well with the highest indium content, failing to explain the huge decrease of the pressure coefficients (35% in the case of $In_{15}Ga_{85}N$ QW).

If the $In_xGa_{1-x}N$ QW emission observed here has band-to-band character, its large Stokes shift and excitation-power-induced blueshift can be explained only by internal piezoelectric fields. In biaxially strained $In_xGa_{1-x}N/GaN$ layers, the mismatch strain induces a polarization field (allowed by the hexagonal lattice symmetry) along the growth direction.[15,16] This field tilts the potential profile, setting up triangular quantum wells for holes and electrons in the heterointerface regions of the barriers and wells, respectively. The energy of an optical transition is then reduced by the amount $eE_{pz}d$ (E_{pz} is the macroscopic piezoelectric field, e the electron charge, and d the QW thickness), producing a

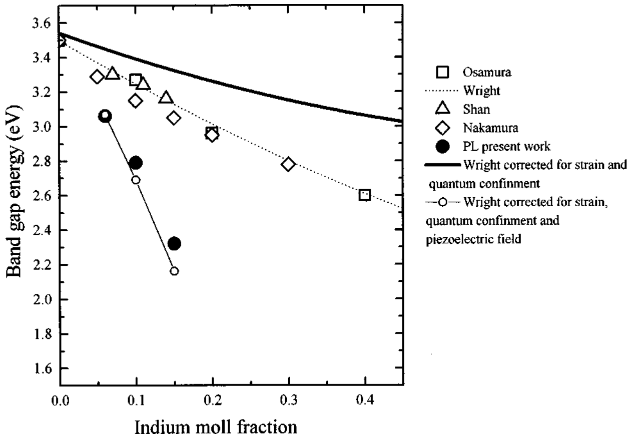

FIG. 4. Comparison of the literature values of the energy gap of unstrained $In_xGa_{1-x}N$, with the energy gap corrected for strain and quantum confinement and with energies of photoluminescence peaks observed in this letter. The small circles show predicted values of recombination energies by including the piezoelectric field. The calculation takes into account the real thicknesses of the wells determined from HRTEM. See Osamura, Ref. 10, Wright, Ref. 20, Shan, Ref. 22, and Nakamura, Ref. 21.

redshift, or effective Stokes shift, in the corresponding PL peak.

This phenomenon has been observed in many strained-layer piezoelectric systems, such as (111) oriented GaAs[17] QWs, and CdS/CdSe superlattices.[18] Its fingerprint is a blueshift with increasing excitation power of the PL peak energy due to screening of E_{pz} by the photopumped carrier density. Here, we make the assumption that our layers are pseudomorphically strained. Evidence for the presence of high strain (up to 2%) in $In_xGa_{1-x}N$ QWs has recently been reported.[19] In order to determine the Stokes shift of the photoluminescence, we have to know the composition dependence of the $In_xGa_{1-x}N$ energy gap. After analyzing the existing literature data, we decided that the most coherent set of data are in the papers of Wright *et al.*,[20] Osamura *et al.*,[10] Nakamura *et al.*,[21] and Shan *et al.*[22] (bowing parameter -1 eV). We believe that the papers indicating the larger bowing parameter (-3.5 eV)[23,19,24] have a weaker experimental basis. Especially important here is the fact that the data of Shan *et al.* and Osamura *et al.* are obtained via absorption measurements which should not be influenced that much by the existence of electric fields or indium concentration fluctuations. To correct the energy gap for strain we use the same procedure as described in Ref. 24. The piezoelectric field is computed using the equation[18]

$$E_{\mathrm{pz}} = -\frac{2\epsilon_{xx}}{\epsilon_0 \epsilon} \cdot \left[\frac{c_{13} e_{33}}{c_{33}} - e_{31} \right], \tag{1}$$

where $\epsilon_{xx} = \epsilon_{yy}$ is the in-plane strain, c_{ij} are the elastic constants, e_{ij} are the piezoelectric constants (referred to hexagonal principal axes), ϵ is the c-axis static dielectric constant, and ϵ_0 is the permittivity of free space. The following parameters were adopted for these calculations: for GaN, $C_{13} = 106$ GPa,[25] $C_{33} = 398$ GPa,[25] $e_{33} = 0.79$ C/m^2,[26] $e_{31} = -0.49$ C/m^2,[26] and $\epsilon = 10.3$;[26] for InN, $C_{13} = 94$ GPa,[27] $C_{33} = 200$ GPa,[27] $e_{33} = 0.97$ C/m^2,[26] $e_{31} = -0.57$ C/m^2, and $\epsilon = 14.6$.[26]

We find that the calculated piezoelectric fields are extremely high ($>10^6$ V/cm). Figure 4 shows an excellent agreement between the observed Stokes shifts and the piezoelectric voltage calculated using Eq. (1), indicating again that the piezoelectric effect plays an important role in determining recombination energies in this structure.

In conclusion, the PL peaks measured in the present $GaN/In_xGa_{1-x}N$ ($x = 0.08$, 0.1, and 0.12) QWs exhibit normal temperature behavior. This fact, together with the observation of very good agreement between the calculated values of the piezoelectric field and observed Stokes shift of the PL peaks, rules out strong localization as the primary cause of the large PL Stokes shifts in our sample. The reduction of the pressure coefficients is much larger than expected from the mechanical properties of the $GaN/In_xGa_{1-x}N$ system and still requires additional explanation.

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