Bowing of the band gap pressure coefficient in $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys

G. Franssen,$^{1, a}$ I. Gorczyca, $^1$ T. Suski, $^1$ A. Kamińska, $^2$ J. Pereiro, $^3$ E. Muñoz, $^3$ E. Iliopoulos, $^4$ A. Georgakilas, $^4$ S. B. Che, $^5$ Y. Ishitani, $^5$ A. Yoshikawa, $^5$ N. E. Christensen, $^6$ and A. Svane$^6$

$^1$Institute of High Pressure Physics “Unipress,” Polish Academy of Sciences, Sokolowska 29/37, 01-142 Warsaw, Poland
$^2$Institute of Physics, Polish Academy of Sciences, Aleja Lotników 32/46, 02-668 Warsaw, Poland
$^3$ISOM, Universidad Politecnica de Madrid, Ciudad Universitaria, 28040 Madrid, Spain
$^4$FORTH, Institute of Electronic Structure and Lasers, P.O. Box 1527, 71110 Heraklion-Crete, Greece
$^5$Department of Physics, University of Crete, P.O. Box 2208, 71003 Heraklion-Crete, Greece
$^6$Department of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark

(Received 9 November 2007; accepted 21 November 2007; published online 8 February 2008)

The hydrostatic pressure dependence of photoluminescence, $dE_{PL}/dp$, of $\text{In}_x\text{Ga}_{1-x}\text{N}$ epilayers has been measured in the full composition range $0<x<1$. Furthermore, ab initio calculations of the band gap pressure coefficient $dE_G/dp$ were performed. Both the experimental $dE_{PL}/dp$ values and calculated $dE_G/dp$ results show pronounced bowing and we find that the pressure coefficients have a nearly constant value of about 25 meV/GPa for epilayers with $x>0.4$ and a relatively steep dependence for $x<0.4$. On the basis of the agreement of the observed PL pressure coefficient with our calculations, we confirm that band-to-band recombination processes are responsible for PL emission and that no localized states are involved. Moreover, the good agreement between the experimentally determined $dE_{PL}/dp$ and the theoretical curve of $dE_G/dp$ indicates that the hydrostatic pressure dependence of PL measurements can be used to quantify changes of the band gap of the InGaN ternary alloy under pressure, demonstrating that the disorder-related Stokes shift in InGaN does not induce a significant difference between $dE_{PL}/dp$ and $dE_G/dp$. This information is highly relevant for the correct analysis of pressure measurements. [DOI: 10.1063/1.2837072]

I. INTRODUCTION

The $\text{In}_x\text{Ga}_{1-x}\text{N}$ semiconductor alloy is of considerable importance for short and medium wavelength optoelectronics and photonics. InGaN is used for the construction of green-blue-violet light emitting diodes and blue-violet laser diodes. Furthermore, InGaN-based solar cells as well as detectors containing InGaN and operating in the short wavelength range have been constructed in several laboratories. In spite of very advanced optoelectronic applications, mechanisms of radiative and nonradiative recombination in InGaN are still under debate. The discussion concentrates mainly on the Ga-rich range of InGaN ternary alloys. The pressure studies to be presented here, performed for $\text{In}_x\text{Ga}_{1-x}\text{N}$ in the entire range $0<x<1$, can shed some light on the microscopic origin of recombination effects in InGaN alloys, enabling efficient light emission in a longer wavelength region, e.g., in the green range of the spectrum.

Usually, measurements of the photoluminescence (PL) energy $E_{PL}$ under pressure are applied to determine $dE_G/dp$. Bulk crystals, thick epitaxial layers, or quantum structures are employed for such studies. However, there are particular effects that can lead to incorrect conclusions. We mention here three such situations. The first one concerns the involvement of a localized impurity/defect state in optical transitions responsible for PL. When the initial state of the optical transition is of localized nature, i.e., composed of wave functions from the entire Brillouin zone, its shift with pressure is much smaller than the upward shift of the conduction band minimum (CBM). Particularly in the case of a localized donor state we see that $dE_{PL}/dp \ll dE_G/dp$. A second situation, in which $dE_{PL}/dp \ll dE_G/dp$, occurs for quantum structures built from wurtzite semiconductors from the nitride or ZnO family. In this case, pressure-induced changes of the internal electric field (caused by spontaneous and piezoelectric polarizations) cause a strong compensation of the opening of the band gap via the so-called quantum confined Stark effect. This mechanism was intensively studied during the last decade. Third, a lowering of $dE_{PL}/dp$ with respect to $dE_G/dp$ occurs in the case of InN with large electron concentrations because of band filling effects in combination with the increase of the electron effective mass $m^*$ with pressure. This effect is only observable in InN because it has a narrow band gap and therefore a low, pressure-sensitive $m^*$.

In this work, we are interested in studies of the pressure dependence of the band gap in the entire range of ternary $\text{In}_x\text{Ga}_{1-x}\text{N}$ ($0<x<1$). Large Stokes shifts between $E_G$ (from absorption/transmission measurements) and $E_{PL}$ have been attributed to the presence of In-rich fluctuations in the InGaN region. PL probes these regions of locally reduced band gap of the alloy. Therefore, one may speculate that the pressure...
dependence of $E_{\text{pl}}$ is sensitive to effects caused by In segregation. Investigation of this possibility is important for the interpretation of PL measurements on InGaN under hydrostatic pressure. From the experimental point of view, corroboration of the usefulness of PL measurements for the determination of $dE_G/dp$, measurements of transmission/absorption of light or photocconductivity can be applied. Such experiments are technically more challenging than PL studies. Another method, used in the present work, to examine this involves theoretical predictions of the behavior of $dE_G/dp$ calculated for InGaN alloys. Uniform and nonuniform arrangements of In cations in the GaN matrix are investigated in the modeling procedure in order to examine possible atom-distribution related effects. Theoretically calculated values of $dE_G/dp$ will be compared with the measured $dE_{\text{pl}}/dp$.

The paper is organized as follows: after Sec. II, which contains descriptions of calculation procedures and experimental methods, in Sec. III theoretical and experimental results are presented. Section IV contains a discussion and our main conclusions.

II. METHODS

A. Theoretical procedures

The electronic structures of In$_x$Ga$_{1-x}$N alloys have been analyzed by ab initio calculations in a supercell geometry. The indium concentrations, $x=$0.031, 0.062, 0.124, 0.25, 0.50, and 0.75, were realized by substituting 1, 2, 4, 8, 16, and 24 Ga atoms, respectively, by In in a 64-atom supercell.

The calculations were performed in two steps using different approaches based on the local density approximation (LDA) to the density functional theory, with the Perdew-Zunger parametrization of the Ceperley-Alder exchange-correlation. We applied two computational schemes. The first one used pseudopotentials as implemented in the Vienna Ab initio Simulation Package (VASP). This code is well suited for calculations of the atomic relaxations in the whole supercell by minimizing the Hellman-Feynman forces. A cutoff energy of 30 Ry for the atomic relaxations in the whole supercell by minimizing the Hellman-Feynman forces. A cutoff energy of 30 Ry for the plane wave basis set was sufficient to obtain converged results. The $k$-space integrations were performed by summing over a $3 \times 3 \times 3$ mesh of Monkhorst-Pack special points.

For each value of $x$ and a given configuration of indium atoms, the relaxed atom positions were determined. Then the In$_x$Ga$_{1-x}$N band structure was obtained by the second approach—the linear-muffin-tin-orbital (LMTO) method. A full-potential (FP) version of the LMTO was applied. The semi-core cation $d$ states were included as local orbitals. In fact, this was the main reason for choosing this method, because a proper inclusion of the coupling between the anion $p$ and cation-semicore $d$ is important for the accuracy of the calculated pressure coefficients (see below). So-called “empty spheres” $(E)$ were included for the accuracy of interpolation of the charge density between the muffin-tin spheres at the sites of real atoms. No $E$-site orbitals were included. Although the LDA underestimates the band gaps of semiconductors, the pressure coefficients of the gaps are usually considered to be well described within this approximation.

B. Experimental details

Pressure-dependent PL studies of In$_x$Ga$_{1-x}$N were performed on a range of samples from different laboratories: Universidad Politecnica de Madrid, Cornell University, FORTH Research Center in Heraklion, Ritsumeikan University, and Chiba University. In contents and thicknesses of the samples are summarized in Table I. Pressure-dependent measurements of the samples from Ritsumeikan and Cornell were already reported in previous publications (as indicated in the table). Data for these samples are also displayed in Table I. The variety of laboratories makes the results of our studies more general, since production-source-dependent effects are eliminated. As will be demonstrated, the full set of experimental data is coherent and exhibits a systematic trend in In content dependence.

All samples were grown by means of molecular-beam epitaxy on sapphire substrates, employing either an InN or a GaN buffer layer. The In contents reported in Table I were determined by means of x-ray diffraction. In the performed optical experiments, PL was excited by either the 325 nm line of a He-Cd laser (for $x<0.25$) or the 514.5 nm line of an argon laser (for $x>0.25$) and dispersed by a Spex 500 M monochromator. For detection purposes a GaAs-based photomultiplier tube with photon counting unit (for $x<0.25$) or a Ge-based photodiode (for $x>0.25$) were used. Hydrostatic pressures up to 10 GPa were applied by a diamond anvil cell (DAC) with argon as a pressure-transmitting medium, while

---

**TABLE I. List of investigated In$_x$Ga$_{1-x}$N samples with In content $x$, thickness, and growth source.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>In content</th>
<th>Thickness (µm)</th>
<th>Grower</th>
</tr>
</thead>
<tbody>
<tr>
<td>R335</td>
<td>0.13</td>
<td>1</td>
<td>Madrid</td>
</tr>
<tr>
<td>R331</td>
<td>0.20</td>
<td>1</td>
<td>Madrid</td>
</tr>
<tr>
<td>U368</td>
<td>0.72</td>
<td>0.41</td>
<td>Chiba</td>
</tr>
<tr>
<td>U366</td>
<td>0.72</td>
<td>0.45</td>
<td>Chiba</td>
</tr>
<tr>
<td>G925</td>
<td>0.37</td>
<td>1</td>
<td>FORTH</td>
</tr>
<tr>
<td>G935</td>
<td>0.17</td>
<td>1</td>
<td>FORTH</td>
</tr>
<tr>
<td>R594</td>
<td>0.58</td>
<td>0.35</td>
<td>Ritsumeikan</td>
</tr>
<tr>
<td>R824</td>
<td>0.71</td>
<td>0.19</td>
<td>Ritsumeikan</td>
</tr>
<tr>
<td>R810</td>
<td>0.80</td>
<td>0.2</td>
<td>Ritsumeikan</td>
</tr>
<tr>
<td>R808</td>
<td>0.90</td>
<td>0.2</td>
<td>Ritsumeikan</td>
</tr>
<tr>
<td>GS1366</td>
<td>0.89</td>
<td>0.25</td>
<td>Cornell</td>
</tr>
<tr>
<td>GS1586</td>
<td>1</td>
<td>7.5</td>
<td>Cornell</td>
</tr>
</tbody>
</table>

---

$a$Samples were examined in the context of the present work.

$^b$Results were taken from Ref. 22.

$^c$Results were taken from Ref. 8.

Theoretical calculations were performed for different configurations of In atoms inside the supercell, keeping the same overall concentration. No significant differences with regard to the resulting band gap pressure coefficients were found (see Sec. III), which indicates that clustering of In atoms does not influence the pressure behavior of the band gap. The calculations differ from Ref. 5 by the choice of a larger supercell (64 atoms instead of 32) and by detailed treatment of the lattice relaxation (not only the first neighbors, but all the atoms in the cell are relaxed). Also, the range of concentrations considered in this work is larger.
the pressure was calibrated by means of the R1-line of a ruby crystal. Pressure dependences of PL spectra were measured at a temperature of 80 K.

### III. RESULTS

Normalized low-pressure PL spectra of the investigated samples, recorded at 80 K, are displayed in Fig. 1. The main trend is a redshift of the PL peak as the In content increases, which agrees with the expected lowering of the band gap energy. By “low-pressure” we denote the lowest hydrostatic pressure that could be realized experimentally inside the closed DAC. This pressure is occasionally slightly but not significantly above ambient pressure. This is due to the fact that samples are sometimes damaged on the full release of hydrostatic pressure at the end of the pressure cycle, which thwarts performing the PL measurement at ambient pressure. Using In$_{x}$Ga$_{1-x}$N samples with very different In contents, we are able to map the behavior of $dE_{PL}/dp$ across the full range of ternary alloys from GaN to InN. Please note that the PL spectrum of the In$_{x}$Ga$_{1-x}$N sample with $x=0.13$ has a slightly lower PL peak energy than the sample with $x=0.17$, which is partly due to the fact that these PL spectra were recorded at different pressures (see figure caption). For the same reason there is a small difference between the peak energies of U366 and U368, for both of which $x=0.72$.

The PL peak energies of the complete set of investigated InGaN samples are plotted in Fig. 2 as a function of In content. For the discussion of the Stokes shift between PL and absorption edge, also shown are results concerning the band gap energy as obtained from absorption measurements. A fit of the band gap energies (using a bowing parameter of 1.43 eV) is indicated by a dashed line. The values obtained for $dE_{PL}/dp$ on In content is displayed graphically. The error bars are based on the data scatter in combination with experimental uncertainties. The experimental point concerning GaN is taken from Ref. 18. Also shown is the theoretical

Hydrostatic pressure dependences of two selected samples, U366 and R335, are shown in Figs. 3(a) and 3(b), respectively. A blueshift of the PL peak with increasing pressure can be observed, in accordance with the opening of the band gap. Qualitatively similar results in terms of signal-to-noise ratio and range of applied pressures were obtained for the other investigated samples. Fabry-Perot oscillations, such as those observable for sample U366 in Fig. 3(a), were removed during analysis by means of Fourier filtering.

Dependences of PL peak energies on hydrostatic pressure are displayed for all investigated samples in Fig. 4. Also shown are linear fits of the PL pressure coefficient $dE_{PL}/dp$. The values obtained for $dE_{PL}/dp$ in the case of In$_{x}$Ga$_{1-x}$N samples U366 ($x=0.72$), U368 ($x=0.72$), G925 ($x=0.37$), R331 ($x=0.20$), G935 ($x=0.17$), and R335 ($x=0.13$) are, respectively, 23.2, 24.1, 26.0, 28.3, 32.6, and 33.0 meV/GPa. In Fig. 5, the dependence of the measured values of $dE_{PL}/dp$ on In content is displayed graphically. The error bars are based on the data scatter in combination with experimental uncertainties. The experimental point concerning GaN is taken from Ref. 18. Also shown is the theoretical

![Image 1](http://example.com/image1.png)

**FIG. 1.** (Color online) Normalized low-pressure spectra of the investigated In$_{x}$Ga$_{1-x}$N samples. In contents $x$ are indicated. Displayed PL spectra were recorded at ambient pressure, except in the case of samples G935 ($x=0.17$) and U368 ($x=0.72$), for which PL was recorded at pressures of 0.50 and 0.57 GPa, respectively.

**FIG. 2.** (Color online) PL peak energy at ambient pressure and 80 K of the In$_{x}$Ga$_{1-x}$N samples investigated in the present work. In contents $x$ are indicated. Also shown is the band gap energy dependence on In content as obtained via absorption measurements taken from Ref. 17. A fit of the band gap energies (using a bowing parameter of 1.43 eV) is indicated by a dashed line.

![Image 2](http://example.com/image2.png)

Hydrostatic pressure dependences of two selected samples, U366 and R335, are shown in Figs. 3(a) and 3(b), respectively. A blueshift of the PL peak with increasing pressure can be observed, in accordance with the opening of the band gap. Qualitatively similar results in terms of signal-to-noise ratio and range of applied pressures were obtained for the other investigated samples. Fabry-Perot oscillations, such as those observable for sample U366 in Fig. 3(a), were removed during analysis by means of Fourier filtering.

Dependences of PL peak energies on hydrostatic pressure are displayed for all investigated samples in Fig. 4. Also shown are linear fits of the PL pressure coefficient $dE_{PL}/dp$. The values obtained for $dE_{PL}/dp$ in the case of In$_{x}$Ga$_{1-x}$N samples U366 ($x=0.72$), U368 ($x=0.72$), G925 ($x=0.37$), R331 ($x=0.20$), G935 ($x=0.17$), and R335 ($x=0.13$) are, respectively, 23.2, 24.1, 26.0, 28.3, 32.6, and 33.0 meV/GPa. In Fig. 5, the dependence of the measured values of $dE_{PL}/dp$ on In content is displayed graphically. The error bars are based on the data scatter in combination with experimental uncertainties. The experimental point concerning GaN is taken from Ref. 18. Also shown is the theoretical

![Image 3](http://example.com/image3.png)

**FIG. 3.** (Color online) Hydrostatic pressure dependences of PL spectra of (a) sample U366 ($x=0.72$) and (b) sample R335 ($x=0.18$).
of hydrostatic pressure show a very weak pressure shift of the PL bands of $-6-8 \text{ meV/GPa}$, which is very low both in comparison with the pressure-induced band gap shift as determined by absorption measurements ($\sim 30 \text{ meV/GPa}$) (Ref. 19) and compared to the present theoretical and experimental results (Fig. 5). This was interpreted as evidence of a localized donor state in the radiative recombination mechanism of In-rich InGaN. However, studies of the pressure dependence of the PL energy performed by our group on In$_{x}$Ga$_{1-x}$N alloy samples (of higher structural quality) with $0.6 < x < 1.0$ (also included in Fig. 5 of the present work) led to the contradictory conclusion that band-to-band transitions determine the nature of radiative recombination in InGaN alloys.22 As a small but relevant digression, please note the difference between the value of $dE_{\text{PL}}/dp$ for InN in Ref. 22 (21.4 meV/GPa) and the present work (27.4 meV/GPa). This value was corrected in regard to the recent finding that the value of $dE_{\text{PL}}/dp$ is significantly lowered with respect to $dE_{\text{PL}}/dp$ in InN in the presence of large electron concentrations.8 As mentioned in the Introduction, this effect is related to band filling effects in combination with the increase of the electron effective mass $m^*$ with pressure. In view of their larger band gap energies, this effect can be expected to be much less pronounced in ternary InGaN alloys. In fact, it was demonstrated to be absent in the case of In$_{0.5}$Ga$_{0.5}$N.23

Furthermore, the agreement in Fig. 5 between the presented experimental results concerning $dE_{\text{PL}}/dp$ and the theoretical curve of $dE_{G}/dp$ produced via an $ab$ initio approach implies that the hydrostatic pressure dependence of PL measurements can be used to quantify changes of the band gap of the InGaN ternary alloy under pressure. The disorder-related Stokes shift in InGaN, clearly observable in Fig. 2, is not large enough to cause a significant difference between $dE_{\text{PL}}/dp$ and $dE_{G}/dp$. It should be added here that the reported experimental errors on $dE_{\text{PL}}/dp$ are typical and cannot be expected to be improved much. This information is relevant for the correct analysis of pressure measurements. Indeed, as was mentioned in Sec. I, in the case of InGaN there exist several mechanisms which significantly reduce $dE_{\text{PL}}/dp$ with respect to $dE_{G}/dp$. We conclude that the disorder-related Stokes shift is not one of those.

Next, we discuss the nature of the observed dependence of $dE_{G}/dp$ on In content in InGaN. To begin with, the observed strong bowing of $dE_{G}/dp$ versus In content can be attributed to either the absolute volume deformation potential of the band gap, $dE_{G}/d \ln V$, where $V$ represents the volume, or to the bulk modulus $B$, which is defined as $dp/d \ln V$. The calculated values of the bulk moduli are 198 GPa for GaN and 148 GPa for InN with their pressure derivatives equal to 4.0 and 4.3, respectively. The values of the bulk moduli change linearly between GaN and InN. Similar results were obtained recently by pseudopotential calculations [24 $B(\text{GaN}) = 200.6 \text{ GPa}$, $B(\text{InN}) = 145.6 \text{ GPa}$, and also linear dependence on In composition].

In Fig. 6 we plot the deformation potential of the band gap $a_G = dE_{G}/d \ln V$ as a function of indium composition $x$. We can see that the $a_G$ curve essentially consists of two approximately linear sections, one at low $x$ with a large slope...
value in the case of recombination via localized donor states confirm the band-to-band character of radiative recombination in InGaN alloys.

Furthermore, the good agreement between the experimentally determined $dE_{\rm PL}/dp$ of In$_{1-x}$Ga$_x$N and the theoretical curve of $dE_{\rm G}/dp$ versus $x$ indicates that the hydrostatic pressure dependence of PL measurements can be used to quantify changes of the band gap of the InGaN ternary alloy under pressure, demonstrating that the disorder-related Stokes shift in InGaN is not sufficient to cause a significant difference between $dE_{\rm PL}/dp$ and $dE_{\rm G}/dp$.

This information is highly relevant for the correct analysis of pressure measurements.

V. SUMMARY

Hydrostatic pressure-dependent measurements of the PL of In$_{1-x}$Ga$_x$N epilayers for the whole range of ternary alloys from GaN to InN were reported in conjunction with theoretical calculations of the InGaN band gap energy changes under pressure. Both experimental and theoretical results show pronounced bowing of the pressure coefficient, with a nearly constant value of about 25 meV/GPa for In$_{1-x}$Ga$_x$N epilayers with $x>0.4$ and a relatively steep dependence for $x<0.4$. As argued before in Ref. 22, the high values of the observed $dE_{\rm PL}/dp$ with respect to the expected significantly lower

ACKNOWLEDGMENTS

The work at UNIPRESS in Warsaw was partially supported by Project Nos. 1 P03B 021 29 and 1 P03B 037 29 of the Polish Ministry of Higher Education and Science.


22G. Franssen, A. Kamińska, T. Suski, I. Gorczyca, N. E. Christensen, A.


