

Large and composition-dependent band gap bowing in $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys

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Abstract

We present theoretical and experimental results for the band gap of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys, showing significantly larger bowing than has been commonly assumed. We highlight the importance of properly including strain in the experimental analysis. Using X-ray diffraction (XRD) and Rutherford backscattering spectrometry the layers in our study were determined to be pseudomorphically strained. The In content determined by XRD depends strongly on the assumptions made about the strain in the InGaN layers. Strain also affects the band structure and hence the transition energies measured by optical-transmission spectroscopy. An analysis of the experimental results produces a bowing parameter $b \approx 3.8$ eV at $x = 0.1$. First-principles calculations, based on pseudopotential–density–functional theory, produce values of the bowing parameter in agreement with the experimental determination, and also indicate a strong dependence of the bowing parameter on composition. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Great progress has recently been made in research and fabrication of optoelectronic devices based on nitride semiconductors. One of the attractive features of the nitride semiconductors is that their band gaps, in principle, span most of the visible spectrum, into the ultraviolet; the band gaps of InN, GaN, and AlN are, respectively, 1.89, 3.44, and 6.28 eV (at 300 K) [1]. Appropriate alloying should allow formation of alloys with band gaps intermediate to those of the binary compounds. This feature is widely used in band-structure engineering of nitride-based devices; for instance, most light emitters contain an active region consisting of an InGaN layer with band gap lower than that of GaN.

Accurate knowledge of the band gap as a function of alloy composition is essential for interpretation of optical experiments, as well as for design of new device structures. One issue that complicates an assessment of the band gap, in the case of nitride alloys, is the presence of strain. The lattice mismatch between GaN

($a_{\text{GaN}} = 3.189 \text{ \AA}$) and InN ($a_{\text{InN}} = 3.54 \text{ \AA}$) is more than 10%. Epitaxial growth of InGaN on GaN will therefore lead to strains in the InGaN layer. As long as the InGaN thickness is less than the *critical layer thickness*, the InGaN is pseudomorphically strained: its in-plane lattice constant matches that of the GaN, and lattice relaxation occurs in the perpendicular direction. When the critical-layer thickness is exceeded, strain relaxation occurs through the introduction of extended defects, and the magnitude of the strain will be less than in the pseudomorphic case.

The presence of strain needs to be properly taken into account when analyzing experimental results for InGaN layers. The effects of strain enter in two major ways: in the determination of the lattice constant, and in measured transition energies. The lattice constant is commonly determined from X-ray diffraction (XRD); as we will see in Section 2, significant errors occur when the presence of strain is not properly taken into account, resulting in a systematic overestimation of the In content. Strain also has an important effect on the band structure: the hydrostatic component of the strain affects the band gap, and the biaxial component causes a splitting of the valence-band states. These effects need to be taken into consideration when interpreting mea-

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sured transition energies. Measurements on thin InGaN layers may, in addition, reveal quantum–confinement effects; the layers discussed in the present work, however, are thick enough not to give rise to any quantum confinement.

The band gap of the relaxed unstrained alloy is usually expressed as:

$$E_g(\text{In}_x\text{Ga}_{1-x}\text{N}) = xE_g(\text{InN}) + (1-x)E_g(\text{GaN}) - bx(1-x) \quad (1)$$

where b is the bowing parameter. Previous experimental [2] and theoretical [3] studies reported a bowing parameter $b \approx 1$ eV for $\text{In}_x\text{Ga}_{1-x}\text{N}$. In Section 3 we derive the bowing of the band gap from optical transmission measurements for $\text{In}_x\text{Ga}_{1-x}\text{N}$ with $x < 0.12$. We find a bowing parameter $b \approx 3.8$ eV at $x = 0.1$. We also perform first-principles calculations (Section 4) for $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys, producing values for the bowing parameter in good agreement with experiment; these values also show a marked dependence on composition. In Section 5 we will discuss the consequences of our findings.

2. Effects of strain

2.1. Effect of strain on determination of the InN fraction

In the pseudomorphic case (when the layer thickness is less than the critical-layer thickness), the in-plane strain is given by:

$$\epsilon_{\parallel} = \frac{a_s}{a_{\text{InGaN}}} - 1, \quad (2)$$

where a_s is the in-plane lattice constant of the layer to which the InGaN layer is pseudo-morphically matched. The lattice constant of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloy is given to high accuracy by Vegard's law, i.e. by linear interpolation between the binary compounds:

$$a_{\text{InGaN}} = xa_{\text{InN}} + (1-x)a_{\text{GaN}}. \quad (3)$$

The validity of Vegard's law will be discussed below. The strain in the perpendicular direction is given:

$$\epsilon_{\perp} = -D\epsilon_{\parallel}, \text{ with } D = 2\frac{c_{13}}{c_{33}}. \quad (4)$$

c_{13} and c_{33} are the elastic constants of the overlayer. The elastic constants of the InGaN alloy can be obtained by linear interpolation between the binary compounds. The published elastic constants for GaN and InN exhibit wide variation; a critical discussion has been given by Wright [4]; Ref. [4] also contains first-principles values for these constants. We feel that the first-principles results provide reliable and consistent values for the elastic constants.

We deliberately use the notation D for the quantity in Eq. (4); this parameter is some times called 'Poisson's ratio'. This nomenclature is potentially confusing: Poisson's ratio ν is defined as the ratio of transverse to axial strain, usually assuming application of a *uniaxial* stress. In hexagonal crystals this leads to:

$$\nu = \frac{c_{13}}{c_{11} + c_{12}}. \quad (5)$$

It is possible to consider the ratio of transverse to axial strain when a *biaxial* stress is present, as is the case here. However, that obviously leads to a different value, as shown in Eq. (4). In cubic materials, where $c_{11} = c_{33}$ and $c_{12} = c_{13}$, D and ν are related in a simple fashion:

$$D = \frac{2\nu}{1-\nu} \text{ or } \nu = \frac{D}{2+D}. \quad (6)$$

This relationship does not strictly hold in hexagonal crystals, although it is still a reasonable approximation since $c_{11} \approx c_{33}$ and $c_{12} \approx c_{13}$ in the nitrides.

The In composition of an $\text{In}_x\text{Ga}_{1-x}\text{N}$ overlayer is commonly determined by XRD, in which the lattice parameter c of the alloy is measured; we call this measured value c_m . In the absence of strain in the overlayer, the measured value c_m corresponds to the true lattice constant of the unstrained alloy, c_{InGaN} , which can be related to the alloy composition using Vegard's law:

$$c_{\text{InGaN}} = xc_{\text{InN}} + (1-x)c_{\text{GaN}}, \quad (7)$$

from which x can be determined by:

$$x = \frac{c_m - c_{\text{GaN}}}{c_{\text{InN}} - c_{\text{GaN}}}. \quad (8)$$

If, however, the InGaN layer is pseudomorphically strained, then the measured lattice constant c_m corresponds to the *strained* c which can be determined from Eq. (4) by:

$$\frac{c_m}{c_{\text{InGaN}}} - 1 = -D \left(\frac{a_s}{a_{\text{InGaN}}} - 1 \right) \quad (9)$$

where c_{InGaN} and a_{InGaN} are the lattice constants of an unstrained layer. Vegard's law (Eqs. (3) and (7)) holds for these unstrained lattice constants, and Eq. (9) can therefore be solved for the alloy composition. It is instructive to assess the effect of strain on this determination of the alloy composition by making a few approximations; we can rewrite Eq. (9) as

$$c_{\text{InGaN}} = \frac{c_m + Da_s(c_{\text{InGaN}}/a_{\text{InGaN}})}{1+D} \quad (10)$$

The measured c_m then produces a value for c_{InGaN} in the unstrained alloy, for which Vegard's law is valid, leading to a determination of x using Eq. (7). The quantities D and $c_{\text{InGaN}}/a_{\text{InGaN}}$ should be evaluated at

the appropriate composition x — but since their variation over the alloy range is relatively small, it is a reasonable approximation to set them equal to the value in GaN. If strain is neglected, the measured c_m would translate into an alloy composition x_u (for ‘unstrained’) given by Eq. (8). If strain is included, Eqs. (8) and (10), with the approximations above and setting $a_s = a_{\text{GaN}}$, produce a value for the alloy composition x_s . It is easy to see that

$$\frac{x_s}{x_u} = \frac{1}{1 + D}. \quad (11)$$

With the values for elastic constants from Ref. [4], the ratio in Eq. (11) is 0.66, i.e. proper inclusion of strain in the determination of the alloy composition leads to a value x_s which is smaller by a factor 0.66 than the value x_u which would be derived if strain effects were ignored.

2.2. Effect of strain on the band structure

Strain in the InGaN layer has the following effects on the band gap. The shift in the conduction band is expressed as:

$$\begin{aligned} \Delta E_c &= a_{c\parallel} 2\epsilon_{\parallel} + a_{c\perp} \epsilon_{\perp} \\ &= 2a_c \epsilon_{\parallel} \left(1 - \frac{c_{13}}{c_{33}} \right) \end{aligned} \quad (12)$$

where we have used Eq. (4) and assumed (in the absence of better information) that $a_{c\parallel} = a_{c\perp}$, i.e. the deformation potential a_c describing the response of the conduction band to strain does not depend on orientation.

For the valence bands, we focus on the heavy-hole band, which is the highest-energy band (i.e. the one leading to the lowest transition energy) under biaxial compressive strain:

$$\begin{aligned} \Delta E_{v,hh} &= 2(D_2 + D_4)\epsilon_{\parallel} + (D_1 + D_3)\epsilon_{\perp} \\ &= 2\epsilon_{\parallel} \left[-(D_2 + D_4) - (D_1 + D_3) \frac{c_{13}}{c_{33}} \right] \end{aligned} \quad (13)$$

The strain-induced shift in the band gap is therefore:

$$\begin{aligned} \Delta E_g &= \Delta E_c - \Delta E_{v,hh} \\ &= 2 \left[-(D'_2 + D_4) + (D'_1 + D_3) \frac{c_{13}}{c_{33}} \right] \epsilon_{\parallel} \end{aligned} \quad (14)$$

where we have set $D_1 - a_c = D'_1$ and $D_2 - a_c = D'_2$; the primed quantities indicate that changes in the valence-band positions are *referenced to the conduction band*. This eliminates the need for knowledge about the shift in the bands on an absolute energy scale. Even though the latter information is available (cf. absolute deformation potentials discussed in Ref. [5]), it is not required for the present study in which only transitions across the band gap are considered.

A variety of values for the deformation potentials D_i have been reported (Refs. [6–10]). Care has to be taken when using these values. In particular, values for D_1 and D_2 are often affected by the lack of a proper reference, as mentioned above. For instance, values of these quantities extracted from bulk calculations [9] are defined only to within an arbitrary constant.

We have evaluated the coefficient multiplying ϵ_{\parallel} in Eq. (14) in the case of GaN, using values of D_i reported in the references mentioned above, and Wright’s [4] value for c_{13}/c_{33} for GaN; even when limiting ourselves to cases where the reference for D_1 and D_2 is properly known, we find that the resulting coefficient varies over quite a wide range (from -7.1 to -12.2 eV). For $x = 0.1$, this translates into an uncertainty for the band gap shift of 0.05 eV, or an uncertainty in the bowing parameter of 0.6 eV. Given these uncertainties, we thought it more appropriate to use direct experimental information about the variation in the band gap due to strain. The variation of excitonic transition energies as a function of strain was studied in GaN by Shan et al. [11]; Fig. 3 of Ref. [11] yields for the change in the lowest transition energy:

$$\Delta E_g = -9.3\epsilon_{\parallel}. \quad (15)$$

We note that the coefficient in Eq. (15) falls right in the middle of the range of values obtained above by using explicit values for deformation potentials. Even though Eq. (15) was derived for GaN, we will apply it to $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys; this should be a reasonable approximation as long as x is small. Since ϵ_{\parallel} is negative for compressive strain, Eq. (15) indicates that strain shifts the band gap to higher values.

Limiting ourselves to small values of x (i.e. low In content), Eq. (2) can be approximated as

$$\epsilon_{\parallel} \approx \frac{a_{\text{GaN}} - a_{\text{InGaN}}}{a_{\text{GaN}}} x. \quad (16)$$

Combining Eq. (16) with Eq. (15) then yields

$$\Delta E_g = 1.02x. \quad (17)$$

3. Experimental results

$\text{In}_x\text{Ga}_{1-x}\text{N}$ epilayers were grown by metal–organic chemical vapor deposition (MOCVD) to a thickness of ca. 225 nm on a 1 μm layer of GaN on a sapphire substrate. As reported by Romano et al. [12], the $\text{In}_x\text{Ga}_{1-x}\text{N}$ epilayers used in this study are strained such that the measured value of the in-plane lattice constant (3.191 Å) is almost identical to the in-plane lattice constant of the underlying GaN (3.189 Å). Pseudomorphically strained $\text{In}_x\text{Ga}_{1-x}\text{N}$ has also been reported by Takeuchi et al. [13]. Since it is known that the $\text{In}_x\text{Ga}_{1-x}\text{N}$ layers are under biaxial compression,

care has to be taken when using the XRD values to determine the InN concentration in the alloy, as explained in Section 2. To confirm the approach, Rutherford backscattering spectrometry (RBS) was used for an independent determination of the alloy composition. Values of x determined from XRD, taking strain into account, agree with RBS values to within the experimental accuracy (± 0.005). The experimental analysis also confirms the validity of Vegard's law, and produces a value of D (Eq. (4)), namely $D = 0.439$, in good agreement with the value calculated in Ref. [4].

The band gap minima of the $\text{In}_x\text{Ga}_{1-x}\text{N}$ epilayers were determined by optical transmission spectroscopy [14]. The band gap energies are plotted as a function of the InN fraction x (as determined by RBS) in Fig. 1. A linear least-squares fit to the band gap data yields

$$E = 3.42 - 3.93x \quad (18)$$

for $x \leq 0.12$ and with E in units of eV. Our measured values of the band gap are somewhat higher than those previously obtained by photoluminescence (PL) spectroscopy [13]; the difference is not surprising, since the PL peak energies of thick $\text{In}_x\text{Ga}_{1-x}\text{N}$ layers are typically lower than the band gap energies.

Eq. (18) applies to strained $\text{In}_x\text{Ga}_{1-x}\text{N}$. To determine the band gap for relaxed $\text{In}_x\text{Ga}_{1-x}\text{N}$, the shift of the band gap due to strain must be considered. As discussed in Section 2, we can use Eq. (17) to describe the strain-induced band gap shift for $x \leq 0.12$. Combining Eq. (17) and Eq. (18) yields

$$E = 3.42 - 4.95x \quad (19)$$

which is plotted as a dashed line in Fig. 1. Eq. (19) represents a linear approximation of the relaxed $\text{In}_x\text{Ga}_{1-x}\text{N}$ band gap for $x \leq 0.12$. The approach described here ignores the dependence of the materials parameters on InN concentration. We have also carried

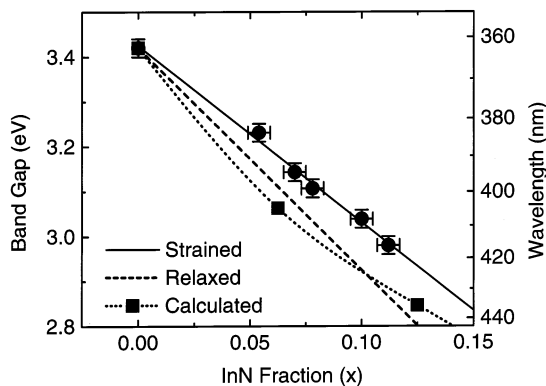


Fig. 1. Band gaps of strained $\text{In}_x\text{Ga}_{1-x}\text{N}$ from optical transmission measurements. The solid line is a linear least-squares fit to the strained band gaps (Eq. (18)). The dashed line is the band gap of relaxed $\text{In}_x\text{Ga}_{1-x}\text{N}$, obtained by subtracting the strain contribution, yielding Eq. (19). The dotted line is a fit to (relaxed) band gap values based on first-principles calculations of the bowing parameter.

out more sophisticated calculations that take this dependence into account. The results agree with Eq. (19) to within experimental uncertainty.

The range of alloy compositions studied experimentally does not allow a direct determination of the bowing of the band gap. Nevertheless, the bowing parameter can be estimated by combining Eq. (1) and Eq. (19), yielding a value of 3.8 eV at $x = 0.1$. To further analyze this problem, we have carried out first-principles calculations as described in the next section.

4. First-principles calculations

We have performed first-principles calculations of the band gap of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys using the pseudopotential–density–functional method described in Ref. [15]. Relaxation of the lattice parameters confirmed the validity of Vegard's law; atomic relaxation was fully allowed. The effects of Ga and In d states were included through the nonlinear core correction [15], and the calculations were performed for the zinc-blende phase; band gap bowing in the wurtzite phase is expected to be very similar [3]. We found strong deviations from the quadratic approximation (Eq. (1)), i.e. the bowing parameter is strongly composition-dependent. For $x = 0.0625, 0.125,$ and 0.25 , we obtained $b = 4.8, 3.5,$ and 3.0 eV. These results are in good agreement with the relaxed band gap values that were derived experimentally; Fig. 1 displays a fit to our calculated points (where we have used linear interpolation of the experimental band gaps to shift the LDA gaps).

The bowing parameter $b = 1.02$ eV reported by Wright and Nelson [3] was based on first-principles calculations for zinc-blende GaN, InN, and a 'special quasi-random structure' for $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$. A smaller value for b at $x = 0.5$ than what we have found for small values of x is consistent with the strong composition dependence of b . Still, our calculations produce values for b larger than 1.0 eV over the whole range of alloy compositions.

5. Discussion

The large value and strong composition dependence of the bowing parameter can be attributed to the large lattice mismatch between GaN and InN (or size mismatch between the Ga and In atoms); similar effects have been observed in other alloy systems [16]. Indeed, given that this mismatch is so large, a bowing parameter of 1.0 eV would be uncharacteristically small. Still, the band gap bowing reported here is larger than what has been commonly assumed for $\text{In}_x\text{Ga}_{1-x}\text{N}$. For instance, Nakamura [2] reported band gap energies for $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys grown by MOCVD on GaN films

on sapphire substrates. The band gap values for $0.07 < x < 0.33$ were found to be consistent with a bowing parameter of 1.00 eV. While no details were provided about thickness or strain situation of the films, it is conceivable that the films considered by Nakamura were actually pseudomorphic to GaN; as discussed above, the In mole fraction determined by XRD would then be overestimated. Re-calculating the In composition using the assumption of pseudomorphic strain actually transforms the values of Ref. [2] into a band gap versus composition curve in good agreement with our present results [12].

Some previous experimental work also indicated the presence of large bowing, though it was not always properly interpreted. Matsuoka et al. measured the band gap in InGaN films grown by MOCVD on sapphire substrates [17]. They found a strong decrease in band gap with In composition. No details were given about the strain situation or thickness of the films. If we assume the films to be unstrained, the data reported in Ref. [17] would correspond to a bowing parameter b of at least 3.0 eV at low x . If the films are actually strained b would be even larger.

Takouchi et al. [13] measured the band gap of strained InGaN alloys with PL spectroscopy. Effects of strain were properly included in the determination of the In composition, and their band gap values are in good agreement with ours. Takeuchi et al. did not, however, attempt to assess the effects of strain on the measured band gaps.

We noted that our first-principles values for b are in good agreement with experiment. Still, we have reason to believe that our calculations overestimate the magnitude of the bowing parameter. The band gap in a true random alloy would then be larger than what is observed experimentally here, and this raises the interesting possibility of an additional lowering of the band gap due to alloy ordering effects. Chemical ordering in wurtzite InGaN layers was observed by diffraction analysis in transmission electron microscopy and in XRD [18,19]. Short-range order has already been shown to have a significant effect on bowing in $\text{In}_x\text{Ga}_{1-x}\text{N}$, in empirical pseudopotential calculations

by Bellaiche and Zunger [20]. The issue of ordering should be explored in detail in future work.

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