

## Large band gap bowing of $\text{In}_x\text{Ga}_{1-x}\text{N}$ alloys

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Band gap measurements have been performed on strained  $\text{In}_x\text{Ga}_{1-x}\text{N}$  epilayers with  $x \leq 0.12$ . The experimental data indicate that the bowing of the band gap is much larger than commonly assumed. We have performed first-principles calculations for the band gap as a function of alloy composition and find that the bowing is strongly composition dependent. At  $x = 0.125$  the calculated bowing parameter is  $b = 3.5$  eV, in good agreement with the experimental values. © 1998 American Institute of Physics. [S0003-6951(98)02321-3]

The development of blue light-emitting diodes<sup>1</sup> and laser diodes<sup>2</sup> has focused a great deal of research activity on GaN-based III-V nitrides. The band gaps of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloys cover a wide spectral range, from red (InN) to UV (GaN), making this alloy system ideal for optoelectronic applications.<sup>3</sup> It has recently been reported that thick ( $> 1000$  Å)  $\text{In}_x\text{Ga}_{1-x}\text{N}$  epilayers grown on GaN on a sapphire substrate are pseudomorphically strained for  $x \leq 0.2$ .<sup>4,5</sup> In this letter, we report the results of experimental and theoretical studies of the band gaps of strained  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloys. From the experimental data, a bowing parameter of 3.8 eV is derived for relaxed  $\text{In}_x\text{Ga}_{1-x}\text{N}$  with  $x = 0.10$ .

Wurtzite GaN and InN have direct band gap minima at 3.4<sup>6</sup> and 1.8 eV,<sup>7</sup> respectively, at room temperature. The band gap of an  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloy is usually described by

$$E_{\text{InGa}}(x) = (1-x)E_{\text{GaN}} + xE_{\text{InN}} - bx(1-x), \quad (1)$$

where  $b$  is a concentration-independent bowing parameter. Wright and Nelson<sup>8</sup> used first-principles calculations to derive a bowing parameter of  $b = 1.02$  eV for  $\text{In}_x\text{Ga}_{1-x}\text{N}$ . This value was obtained from Eq. (1), with the calculated band gaps of GaN, InN, and  $\text{In}_{0.5}\text{Ga}_{0.5}\text{N}$ .

In this letter, the bowing of the band gap is derived from optical transmission measurements for  $\text{In}_x\text{Ga}_{1-x}\text{N}$  with  $x \leq 0.12$ .  $\text{In}_x\text{Ga}_{1-x}\text{N}$  epilayers were grown by metalorganic chemical vapor deposition to a thickness of approximately  $0.25 \mu\text{m}$  on a  $1 \mu\text{m}$  layer of GaN on a sapphire substrate. As reported by Romano *et al.*,<sup>4,9</sup> 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 is identical to the in-plane lattice constant of the underlying GaN. Pseudomorphically strained  $\text{In}_x\text{Ga}_{1-x}\text{N}$  has also been reported by Takeuchi *et al.*<sup>5</sup> Typically, x-ray diffraction (XRD) is used to measure the lattice constant along the  $c$  axis. The InN concentration is then determined by linear interpolation between the lattice constants of InN and GaN (Vegard's law). Since the  $\text{In}_x\text{Ga}_{1-x}\text{N}$  layers experience biaxial compression, however, the lattice constant along the  $c$  axis is elongated, resulting in a systematic overestimation of the InN concentration.<sup>5,9</sup>

The band gap minima of the  $\text{In}_x\text{Ga}_{1-x}\text{N}$  epilayers were determined by optical transmission spectroscopy (Fig. 1). The InN fractions  $x$  are plotted as a function of the band gap

energies in Fig. 2, where  $x$  was determined by Rutherford backscattering spectrometry (RBS), which determines the InN fraction with an accuracy of  $\pm 0.005$ . A linear least-squares fit to the band gap data yields

$$E = 3.42 - 3.93x, \quad (x \leq 0.12) \quad (2)$$

where  $E$  is in units of eV, as shown in Fig. 2. Alternatively,  $x$  may be determined by XRD, with the assumption of pseudomorphic strain and a Poisson's ratio of 0.20.<sup>10</sup> This latter method yields the same results as those obtained by RBS to within experimental error. Our measured values of the band gap are somewhat higher than those previously obtained by photoluminescence (PL) spectroscopy.<sup>5</sup> This 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.<sup>11</sup>

We emphasize that Eq. (2) applies only 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. The shift of excitonic transition energies in GaN is given by<sup>12</sup>

$$\Delta E = -9.3\epsilon_{\parallel}, \quad (3)$$

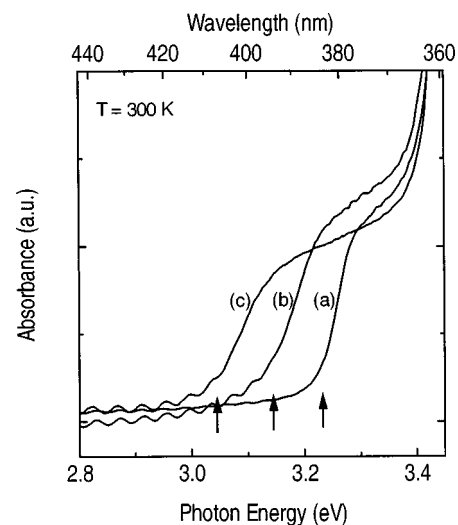


FIG. 1. Optical absorption spectra of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  epilayers for (a)  $x = 0.054$ , (b)  $x = 0.07$ , and (c)  $x = 0.10$ , at room temperature. The InN fraction was determined by RBS. The absorption thresholds are indicated by arrows. The absorption for photon energies greater than 3.4 eV is due to the GaN layer.

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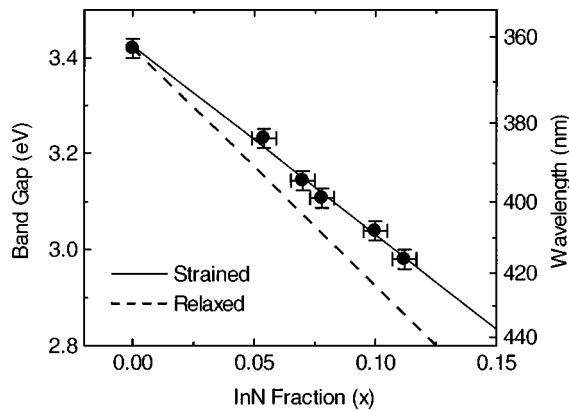


FIG. 2. Band gaps of strained  $\text{In}_x\text{Ga}_{1-x}\text{N}$  from optical transmission measurements. The solid line is a linear least-squares fit to the strained band gaps [Eq. (2)]. The dashed line is the band gap of *relaxed*  $\text{In}_x\text{Ga}_{1-x}\text{N}$ , obtained by subtracting the strain contribution, yielding Eq. (7).

where  $\Delta E$  is in units of eV and  $\epsilon_{\parallel}$  is the in-plane strain. The strain in  $\text{In}_x\text{Ga}_{1-x}\text{N}$  is imposed by lattice-matching to GaN:

$$\epsilon_{\parallel} = [a(\text{GaN}) - a(\text{In}_x\text{Ga}_{1-x}\text{N})]/a(\text{In}_x\text{Ga}_{1-x}\text{N}). \quad (4)$$

To first order Eq. (4) can be approximated as

$$\epsilon_{\parallel} = \frac{a(\text{GaN}) - a(\text{InN})}{a(\text{GaN})} x. \quad (5)$$

To estimate the band gap of relaxed  $\text{In}_x\text{Ga}_{1-x}\text{N}$ , we assume that Eq. (3) correctly describes the shift of the band gap for  $x \leq 0.12$ . Combining Eqs. (3) and (5) yields

$$\Delta E = 1.02x. \quad (6)$$

Subtracting this shift from the experimental data for the strained band gap [Eq. (2)] yields

$$E = 3.42 - 4.95x, \quad (7)$$

which is plotted as a dashed line in Fig. 2. Equation (7) 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 just described ignores the dependence of the materials parameters on InN concentration. However, more sophisticated calculations that take this dependence into account yield essentially the same result. For these calculations, we obtained the strain along the  $c$  axis by linear interpolation of the elastic constants for GaN and InN.<sup>10</sup> Once the strain is known, the deformation potentials for GaN<sup>12-14</sup> and InN<sup>14</sup> are used to determine the band gap shift due to strain. Subtracting this shift from the strained band gap [Eq. (2)], we obtain values which agree with Eq. (7) to within experimental uncertainty.

Since only a narrow range of compositions was studied, the bowing of the band gap was not directly observed. Nevertheless, the bowing parameter can be calculated by combining Eqs. (7) and (1), yielding a value of 3.8 eV at  $x = 0.1$ . To further analyze this problem, we have performed first-principles calculations of the band gap of  $\text{In}_x\text{Ga}_{1-x}\text{N}$  alloys with low In content using the pseudopotential-density-functional method described in Ref. 15. The effects of Ga and In  $d$  states were included through the nonlinear core correction. The lattice constant was consistent with Vegard's law, and full relaxation of the structure was allowed. Al-

though the calculations were performed for the zincblende phase, band gap bowing in the wurtzite phase is expected to be very similar.<sup>8</sup>

Strong deviations from the quadratic approximation [Eq. (1)] were found; i.e., the bowing parameter is strongly composition dependent. For  $x = 0.0625, 0.125,$  and  $0.25$ , we find  $b = 4.8, 3.5,$  and  $3.0$  eV. These results are in reasonable agreement with the relaxed band gap values that were derived experimentally. The large value and strong composition dependence of the bowing parameter are not surprising considering the large lattice mismatch of the binary compounds GaN and InN.<sup>16,17</sup> It is conceivable that the previous measurements<sup>11,18</sup> that yielded  $b = 1$  eV for  $x \sim 0.1$  were also performed on  $\text{In}_x\text{Ga}_{1-x}\text{N}$  layers that were pseudomorphic to GaN. In that case, XRD measurements of the lattice constant along the  $c$  axis would result in an overestimate of  $x$  and a corresponding underestimate of  $b$ .

In conclusion, using the correct values for the InN fraction, we have obtained experimental data for the band gap of strained  $\text{In}_x\text{Ga}_{1-x}\text{N}$  for  $x \leq 0.12$ . Our experimental and theoretical results suggest that the bowing parameter for  $\text{In}_x\text{Ga}_{1-x}\text{N}$  is approximately 3.8 eV at  $x = 0.1$ . First-principles calculations reveal a strong composition dependence of the bowing parameter due to the large size mismatch between the cations in the alloy.

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