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Effect of composition on the band gap of strained $In_xGa_{1-x}N$ alloys

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The band gap of pseudomorphically strained $In_xGa_{1-x}N$ alloys has been measured using optical absorption spectroscopy. X-ray diffraction measurements indicated that the in-plane lattice parameter of the $In_xGa_{1-x}N$ film equaled that of the underlying GaN layer. For strained $In_xGa_{1-x}N$, it was determined that the band gap shift versus composition is given by $dE_g/dx = -4.1$ eV for $x<0.12$. Our results contradict some recent reports that $In_xGa_{1-x}N$ has a relatively small bowing parameter. Possible reasons for the discrepancies are discussed. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1560563]

$In_xGa_{1-x}N$ alloys are preferred semiconductors for blue lasers and light-emitting diodes.[1] The emission and absorption wavelengths depend strongly on the composition x. The determination of optical properties as a function of composition is complicated by the presence of strain in $In_xGa_{1-x}N$ layers. X-ray diffraction measurements have shown that thick (200 nm) $In_xGa_{1-x}N$ layers on GaN can be pseudomorphic up to $x=0.114$.[2] For *relaxed* alloys, the band gap is described by

$$E(x)=(1-x)E_{\mathrm{GaN}}+xE_{\mathrm{InN}}-bx(1-x), \tag{1}$$

where b is the optical bowing parameter and E_{GaN} and E_{InN} are the band gaps of GaN and InN, respectively. Computational studies[3–5] have shown that b is strongly composition dependent. For a composition of $x=0.1$, the calculated bowing parameter is $b\sim 3.8$ eV,[3,4] in apparent agreement with experimental values.[3,6] The experimental studies were performed on pseudomorphic $In_xGa_{1-x}N$ layers on GaN. The band gap of relaxed $In_xGa_{1-x}N$ was inferred by subtracting the contribution due to biaxial strain. However, the results of these studies were contradicted by recent studies[7,8] which obtained much smaller band-gap shifts. In this article, we present experimental and theoretical work that supports the claim that $In_xGa_{1-x}N$ exhibits a large degree of band-gap bowing.

The samples used in this study were thick (225 nm) $In_xGa_{1-x}N$ epilayers grown by metalorganic chemical vapor deposition on 5 μm thick GaN on c-plane sapphire.[9] InN concentrations were determined by Rutherford backscattering spectrometry (RBS). Optical transmission spectra were obtained using a visible-UV spectrophotometer. The absorbance is defined as $\log_{10}(I_0/I)$, where I_0 and I are the transmitted reference and sample light intensities, respectively. Photoluminescence (PL) measurements were performed at room temperature with the 325 nm line of a 5 mW He–Cd laser as the excitation source. First-principles calculations of the band gap of wurtzite $In_xGa_{1-x}N$ were performed, using the pseudopotential-density-functional method described in Ref. 10.

To measure the strain in the $In_xGa_{1-x}N$ epilayers, triple-axis x-ray diffraction measurements were performed for the (204) reflection. The diffracted x-ray intensity is plotted in a reciprocal-space map for the $x=0.072$ sample (Fig. 1). The dimensionless variables a^* and c^* are the coordinates in reciprocal space, perpendicular and parallel to the c axis, respectively. For the (204) reflection, the lattice constants a and c are determined by

$$a^*=\frac{2\lambda}{\sqrt{3}a} \quad \text{and} \quad c^*=\frac{2\lambda}{c}, \tag{2}$$

where $\lambda=1.54$ Å is the x-ray wavelength. From Fig. 1, the in-plane a lattice parameter for the $In_xGa_{1-x}N$ film equals that of the underlying GaN layer to within 0.1%. The $In_xGa_{1-x}N$ films with $x=0.054$ and 0.100 were also observed to be completely pseudomorphically strained.

Optical absorbance spectra are shown in Fig. 2. The spectra were modeled by a modified Boltzman function:

$$\alpha(E)=\alpha_0\frac{1+B(E-E_g)}{1+\exp[(E_g-E)/\Delta E]}, \tag{3}$$

where α is the absorption coefficient (cm^{-1}), α_0 and B are adjustable parameters, E is the photon energy (eV), E_g is defined to be the optical band gap, and ΔE is a broadening parameter. The absorbance is equal to $\alpha d/\ln(10)$, where d is the layer thickness (cm). The B parameter is used to model the increase in absorption for photon energies greater than the band gap. The total absorption for the $In_xGa_{1-x}N$/GaN heterostructure is given by the sum of the $In_xGa_{1-x}N$ and GaN absorption coefficients:

$$\alpha(E)d=[\alpha(E)d]_{\mathrm{InGaN}}+[\alpha(E)d]_{\mathrm{GaN}}. \tag{4}$$

For GaN, $\alpha_0=1.3\times10^5$ cm^{-1} (Ref. 11). Since only the absorption onset is observed for the thick GaN layer, it is not necessary to consider the absorption above the band gap, so

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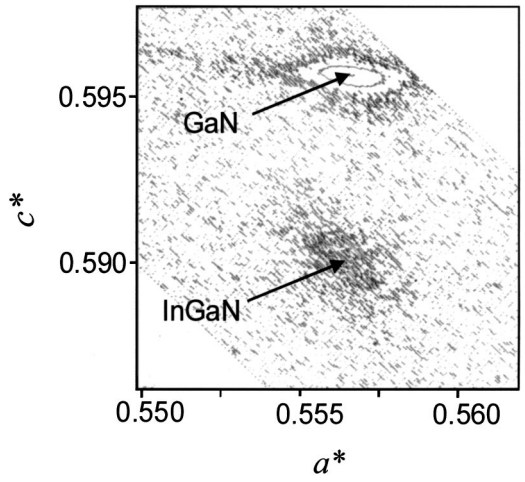

FIG. 1. Reciprocal-space map of x-ray diffraction intensity, in the vicinity of the (204) reflection, for the $In_xGa_{1-x}N$/GaN sample.

a value of $B=0$ was used. For all spectra, the fits yielded a GaN band gap of $E_g=3.47\pm0.01$ eV. A value of $B=2.24$ eV^{-1}, obtained by fitting the absorption data above the band gap, was used to model all the measured $In_xGa_{1-x}N$ spectra. The parameters obtained by the fits are listed in Table I. The $In_xGa_{1-x}N$ band gaps (E_g) are plotted as a function of composition x in Fig. 3. A linear fit to the data yields

$$E_g(\text{eV})=3.47\pm0.02-(4.1\pm0.2)x \quad (x\leqslant 0.12). \tag{5}$$

The slope of -4.1 eV is in agreement with the value obtained by McCluskey *et al.*[3] (-3.9 eV). Equation (5) describes the band gap for pseudomorphically strained $In_xGa_{1-x}N$.

To provide a comparison between theory and experiment, *ab initio* calculations were performed to determine the band gap of wurtzite $In_xGa_{1-x}N$. First, the bowing parameter b was calculated for *relaxed* alloys. Values of $b=5.0$ and 3.5 eV were calculated for $x=0.0625$ and 0.125, respectively, in good agreement with the calculated values for zincblende $In_xGa_{1-x}N$.[3] Then, calculations were performed for *strained* alloys, in which the a lattice parameter was constrained to equal the calculated value for GaN. This pseudomorphic strain resulted in a band-gap shift δE, which was described by

$$\delta E=-8.6\epsilon_{\|}, \tag{6}$$

where $\epsilon_{\|}$ is the in-plane strain. This result is close to the experimental[12] result $\delta E=-9.3\epsilon_{\|}$ which was used in Ref. 3 to relate the band gap of strained and relaxed alloys. Subtracting the shift [Eq. (6)] from Eq. (5) yields the band gap for *relaxed* $In_xGa_{1-x}N$:

$$E(\text{eV})=3.47\pm0.02-(5.0\pm0.2)x \quad (x\leqslant 0.12). \tag{7}$$

The shift of -5.0 eV is significantly larger in magnitude than that reported by Pereira *et al.*[7] (-3.6 eV).

It should be noted that recent studies have reported an InN band gap of $E_{\text{InN}}=0.8$ eV,[13,14] much lower than the previously accepted value of 1.89 eV.[15] This obviously affects the value of the bowing parameter that would be extracted from experimental band-gap measurements. From Eq. (1), we see that lowering the InN band gap from 1.89 eV to 0.8 eV results in a reduction of the bowing parameter by 1.09 eV/$(1-x)$, i.e. roughly 1.1 eV for small x.

After removing the strain-induced shift of the band gap, our measurements at $x=0.1$ yield $b\sim3.8$ eV using $E_{\text{InN}}=1.89$ eV, or $b\sim2.6$ eV using $E_{\text{InN}}=0.8$ eV. These values are still significantly larger than $b\sim1.4$ eV recently reported by Wu *et al.*[8] It should be noted that in the work of Wu *et al.*, the experimental band gaps for Ga-rich InGaN were taken

TABLE I. Band gap (E_g) and broadening parameter (ΔE) for $In_xGa_{1-x}N$ samples.

Sample	x	E_g(eV)	ΔE (eV)
B267	0.054	3.251	0.021
B287	0.072	3.164	0.033
B313E	0.078	3.114	0.036
B314	0.100	3.075	0.027
B313C	0.112	3.005	0.032

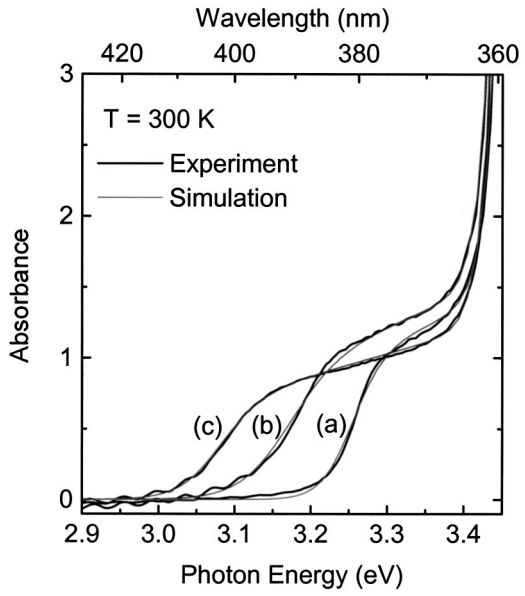

FIG. 2. Optical absorbance spectra of $In_xGa_{1-x}N$/GaN samples, for (a) $x=0.054$, (b) $x=0.072$, and (c) $x=0.100$. Simulated spectra [Eqs. (3) and (4)] are shown.

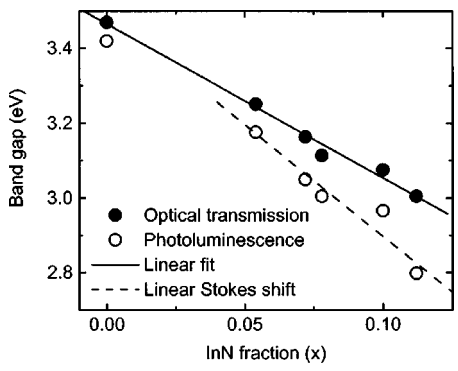

FIG. 3. Band-gap and PL energies as a function of composition. The solid line is a linear fit to the data. The dashed line is a plot of the linear Stokes shift model (proposed by O'Donnell *et al.*, Ref. 17).

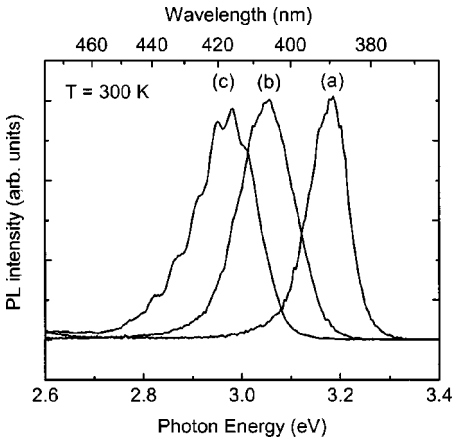

FIG. 4. PL spectra of $In_xGa_{1-x}N$/GaN samples, for (a) $x=0.054$, (b) $x=0.072$, and (c) $x=0.100$.

from two studies. The first study was that of Pereira *et al.*[7] As we have argued in this article, we believe that Pereira *et al.*[7] underestimated the bowing parameter. The second study was that of Shan *et al.*[16] However, the band gaps reported in that work were for pseudomorphic, not relaxed, alloys. Furthermore, the strain state of the InGaN alloys on the In-rich side was not discussed in Ref. 8. For these reasons, it is quite possible that the bowing parameter reported by Wu *et al.*[8] was too low, at least for small values of *x*.

In order to verify the optical quality of our samples, PL spectra were obtained from the $In_xGa_{1-x}N$ epilayers (Fig. 4). As *x* increases, the peak shifts to lower energies and broadens slightly. The peak positions were determined by Gaussian fits, and are plotted in Fig. 3. The difference between the band gap and PL energy (Stokes shift) increases with *x*. The dashed line in Fig. 3 assumes a Stokes shift that varies linearly with *x*, in the range of compositions studied, as proposed by O'Donnell *et al.*[17] Our data are in good agreement with this ''linear Stokes shift'' model, which was obtained for a large number of samples from a variety of laboratories.[17] If our samples were of poor quality with large compositional inhomogeneities, then we would expect a larger Stokes shift than what was observed.

In summary, we have verified the pseudomorphic strain of $In_xGa_{1-x}N$ on GaN, accurately modeled the band-gap absorption profiles, performed PL spectroscopy, and performed first-principles calculations. The results of these studies provide further confirmation of the work of McCluskey *et al.*[3] The different results obtained by Pereira *et al.*[7] may be due to the very broad band-gap absorption thresholds observed in their optical transmission spectra. Such broad thresholds may have resulted from inhomogeneous composition and/or strain in their samples.[18]

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