

Band gaps of the dilute quaternary alloys $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ and $\text{Ga}_{1-y}\text{In}_y\text{N}_x\text{As}_{1-x}$

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We report strong band gap photoluminescence at room temperature in dilute quaternary $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ alloys ($x < 1.6\%$, $y < 2.6\%$) grown by molecular beam epitaxy. The band gap of the alloy can be approximated by the band gap of GaAs minus the reduction in gap associated with the effects of N and Bi alloying individually. A one-parameter method for fitting the composition dependence of the band gaps of dilute quaternary semiconductor alloys is proposed which is in excellent agreement with data for $\text{Ga}_{1-y}\text{In}_y\text{N}_x\text{As}_{1-x}$. © 2005 American Institute of Physics.
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Isoelectronic co-doping has been proposed as a way to alleviate the degradation in electronic properties associated with nitrogen in the “abnormal” dilute alloy $\text{Ga}_{1-y}\text{In}_y\text{N}_x\text{As}_{1-x}$. It has been suggested that co-alloying GaAs with Bi and N may lead to increased solubility and improved transport properties.^{1,2} Since Bi is a large atom and N is small, the combination causes strain compensation, which might in principle extend to the atomic level if the Bi and N are correlated and therefore could lead to improved transport properties. Some progress has been made in exploring the co-doping concept. It has been shown that the presence of a Bi surfactant during growth leads to an increase in N content³ and dilute GaAs bismide-nitride alloys have been grown.^{4,5} However, there have been no reports on their electronic and optical properties. In this paper we present photoluminescence and electroreflectance measurements of the optical band gap of dilute bismide-nitride alloys ($\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$) grown by molecular beam epitaxy. The strong room temperature photoluminescence is surprising, given that the low growth temperature is outside the normal range of growth for good quality GaAs.

Four $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ samples with different compositions were grown by MBE in a VG-V80H system with elemental sources for Ga, In, and Bi, a two-zone cracker source for As_2 , and a helical radio frequency plasma source for nitrogen. The plasma source is equipped with a baffle to suppress the ion flux. High purity N_2 (99.999%) was fed into the plasma source via a leak valve in a gas system that was differentially pumped with a turbopump. The plasma source was operated at 180 MHz with a net power of 100 W and a background nitrogen pressure in the growth chamber in the

10^{-6} Torr range during growth. Since Bi has a strong tendency to surface segregate, the growths were performed at low temperature (365–380 °C) and at a low As_2 overpressure, such that the Ga/ As_2 flux ratio was approximately equal to one, in order to incorporate Bi. For all growths the Bi beam equivalent pressures were on the order of 10^{-7} Torr and the Ga and As_2 pressures were on the order of 10^{-6} Torr as measured by a retractable ion gauge. The substrate temperature was measured by band gap thermometry while the 200–300 nm thick $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ layers were deposited at approximately 1 $\mu\text{m}/\text{h}$ on GaAs (100) substrates, with no cap layer or postgrowth annealing.

The Bi and N concentrations were measured by Rutherford backscattering (RBS) and elastic recoil detection (ERD) respectively, as discussed elsewhere.⁵ We also determined the N concentration by x-ray diffraction from Vegard’s Law using the RBS measurements of the Bi concentration. In this analysis we used a theoretical estimate for the lattice constant of GaBi (0.632 nm),² which is in excellent agreement with an experimental estimate (0.633 nm) extrapolated from low Bi concentration samples.⁶ ERD gives slightly higher N concentrations than the x-ray diffraction possibly due to the presence of interstitial nitrogen. In this paper we use the N concentrations determined by x-ray diffraction. Although there was no intentional variation in source fluxes, the RBS results show a ~20% reduction in Bi incorporation as a function of time during growth. The N and Bi are assumed to incorporate substitutionally on As sites. Room temperature photoluminescence was measured with a CW 808 nm laser diode excitation source with an incident power density of

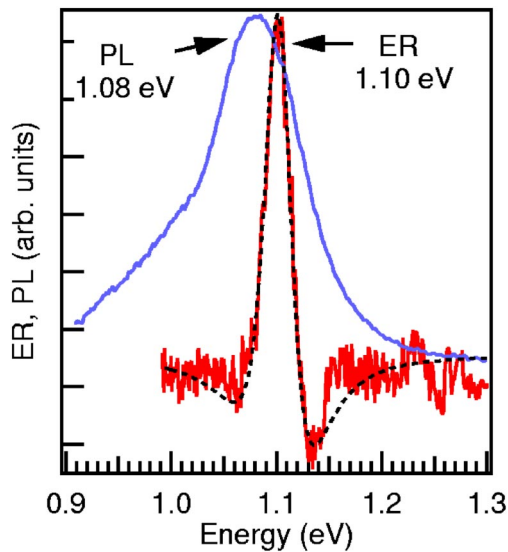


FIG. 1. Room temperature photoluminescence and electroreflectance spectra for $\text{GaN}_{0.0085}\text{As}_{0.9775}\text{Bi}_{0.014}$ showing the optical band gap. The dotted line is a fit to the electroreflectance spectrum as discussed in Ref. 7.

800 W/cm^2 . The electroreflectance was measured as discussed earlier.⁷

The photoluminescence (PL) and electroreflectance (ER) data for one of the samples, $\text{GaN}_{0.0085}\text{As}_{0.9775}\text{Bi}_{0.014}$, are shown in Fig. 1. The band gap of the sample is 1.10 eV as measured by ER, in good agreement with the PL emission at 1.08 eV. Qualitatively, the photoluminescence is strong, especially given the absence of a capping layer and the fact that no attempt was made to optimize the growth conditions. Figure 2 presents the (004) x-ray diffraction pattern for this sample (upper pattern), as well as a dynamical simulation indicating that it is nearly lattice matched to GaAs. Previous RBS results⁵ for this sample showed that the Bi content was not uniform but increased with depth below the surface, which may account for the absence of pendellosung fringes in the experimental data. Experimental and simulated x-ray spectra are also presented for a second sample, $\text{GaN}_{0.0155}\text{As}_{0.9725}\text{Bi}_{0.012}$. The position of the diffracted peak corresponding to this layer indicates that it is under tensile

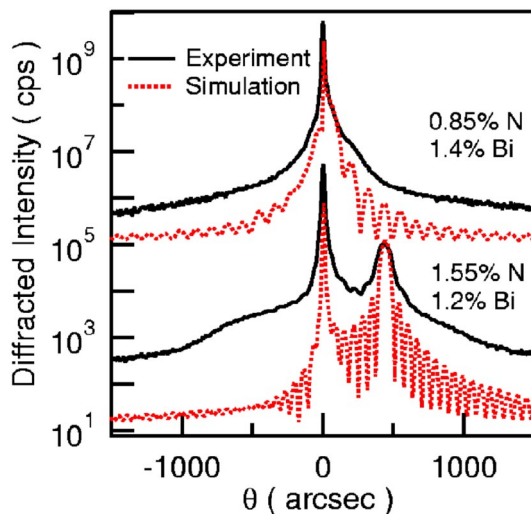


FIG. 2. Experimental and simulated (004) x-ray diffraction patterns for two $\text{GaN}_x\text{As}_{1-x}\text{Bi}_y$ samples of different compositions (data offset for clarity).

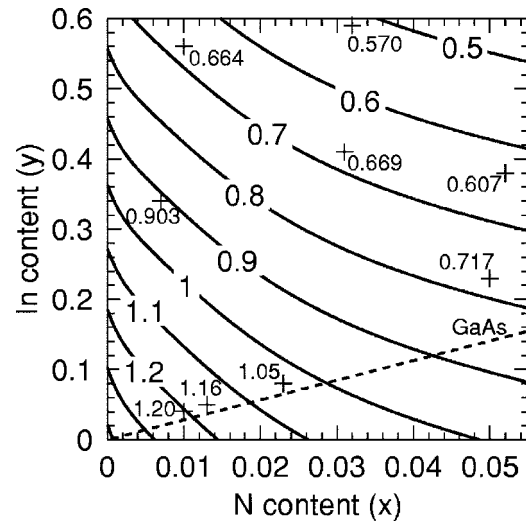


FIG. 3. Band gap map for strained $\text{Ga}_{1-y}\text{In}_y\text{N}_x\text{As}_{1-x}$ on GaAs substrates calculated from Eq. (1) with $\gamma = -0.47 \pm 0.10 \text{ eV}^{-1}$. Contour labels are in eV. Experimental data points (+ symbols) were gathered by Duboz (Ref. 10) with labels in eV. Compositions that are lattice matched to GaAs fall on the dashed line.

strain relative to the GaAs substrate, consistent with the higher nitrogen content of this sample.

Conventional fits to the composition dependence of the band gaps of ternary III-V semiconductor alloys,⁸ with quadratic bowing parameters, do not accurately describe the bandgap of the dilute nitride alloy $\text{GaN}_x\text{As}_{1-x}$ as a function of N content.⁹ Although band gaps can be calculated from underlying physical properties by theoretical methods such as the band-anticrossing model,¹⁰ tight binding theory¹¹ or density functional theory,¹² these methods typically involve multiple parameters and relatively complex computations that are inconvenient or not sufficiently accurate for device design. As a simple fitting procedure we propose the following mathematical expression with one adjustable parameter, which parameterizes the bandgap of the dilute nitride quaternary alloys as a function of composition in an intuitive way

$$E_{aN}(x,y) = E_{\text{GaAs}} - \Delta_N(x) - \Delta_a(y) - \gamma \Delta_N(x) \Delta_a(y). \quad (1)$$

In this expression $E_{aN}(x,y)$ is the band gap of the quaternary alloy $\text{Ga}_{1-y}\text{In}_y\text{N}_x\text{As}_{1-x}$ ($a=\text{In}$) or $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ ($a=\text{Bi}$), E_{GaAs} is the band gap of GaAs, and $\Delta_N(x)$ is the reduction in the band gap of GaAs associated with N alloying for concentration x . Similarly $\Delta_{\text{In}}(y)$ [or $\Delta_{\text{Bi}}(y)$] represents the change in band gap associated with In (or Bi) alloying of GaAs, and γ is an adjustable coupling parameter used to match the experimental data.

If $\gamma=0$, then in the case of In and N alloying for example, the band gap of the quaternary alloy GaInNAs will be equal to the band gap of GaAs minus the sum of the reductions associated with In and N alloying measured independently in the corresponding ternary alloys. Similarly, if $\gamma>0$, then the effect of the two alloying elements will be greater than the sum of the two elements separately. A feature of Eq. (1) is that it maintains the same shape for the concentration dependence of the band gap as the ternary compound if the concentration of one of the elements is held fixed. The Δ -functions are determined from fits to the experimentally determined composition dependence of the band gaps of the ternary alloys.

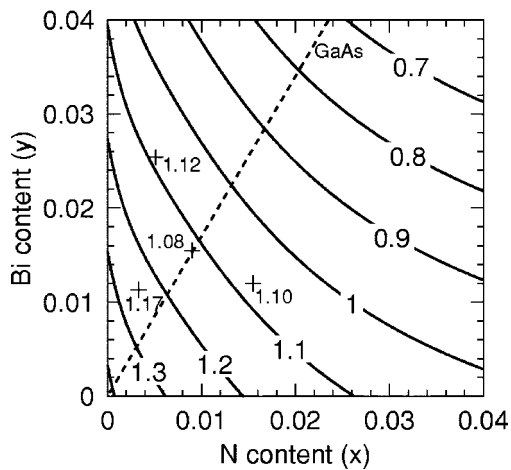


FIG. 4. Band gap map for strained $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ on GaAs substrate using Eq. (1) with $\gamma=0.7\pm 0.7\text{ eV}^{-1}$. Contours and experimental data points (+ symbols) are labeled in eV. The lattice matched condition to GaAs is shown by the dashed line.

In the contour plot in Fig. 3 we show a best fit of Eq. (1) to a set of data on the band gap of GaInNAs compiled by Duboz *et al.*¹⁰ The fit is excellent, with a standard deviation of 28 meV for the 9 data points. In this fit, the coupling parameter $\gamma=-0.47\pm 0.10\text{ eV}^{-1}$, which means that the effect on the band gap of co-alloying with In and N is less than the sum of the two elements separately, as has been observed previously.¹⁰ The uncertainty in γ was estimated from the variation in γ required to degrade the standard deviation by $\sim 30\%$ which was visible by eye. We determined $\Delta_{\text{In}}(y)$ from a conventional parabolic fit to the band gap of $\text{Ga}_{1-y}\text{In}_y\text{As}$ with a bowing parameter of 0.477 eV. This band gap was corrected to take into account the strain required to lattice match to GaAs using the Pikus and Bir Hamiltonian method.^{13,14} In the case of the $\text{GaN}_x\text{As}_{1-x}$ alloys we used the composition dependent bowing parameter expression given in Eq. (4) of Tisch *et al.*⁹ for samples strained to match GaAs.

In Fig. 4 we show the corresponding best-fit contour plot for the band gap of $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$, fitted to four experimental data points. In this fit the band gap of $\text{GaAs}_{1-y}\text{Bi}_y$ is assumed to vary linearly with Bi content, with a slope of 83 meV/% as reported earlier.⁵ The standard deviation between the data and the fit in this plot is 47 meV and the coupling parameter $\gamma=0.7\pm 0.7\text{ eV}^{-1}$. The positive value of the coupling constant means that the combination of Bi and N has a larger effect on the band gap than the sum of the two elements individually, however the accuracy with which we can determine γ is only marginally adequate to determine its sign in this case. A positive correlation effect plus the giant band gap bowing for both N and Bi alloying means that long

wavelength devices can be grown lattice matched to GaAs with relatively low concentrations of Bi and N.

A positive coupling parameter for co-alloying with Bi and N was previously predicted theoretically by Janotti *et al.*,² although they used a rather different form for the composition dependence which does not translate into the coupling parameter in Eq. (1). Their theoretically predicted bandgap for a sample with 2% Bi and 2% N is 1.22 eV at 0 K, somewhat larger than the 0.95 eV predicted for room temperature in Fig. 4. The $\sim 300\text{ K}$ temperature difference should account for almost half of the difference between the two values.

In summary, the dilute nitride-bismide alloy $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$, grown by MBE on GaAs substrates, shows strong band gap photoluminescence at room temperature. We fit the composition dependence of the band gap of the quaternary alloy with a parameterization scheme based on the band gaps of the corresponding ternary alloys, and a single adjustable parameter. This parameterization scheme is in excellent agreement with experimental data on the $\text{Ga}_{1-y}\text{In}_y\text{N}_x\text{As}_{1-x}$ dilute nitride alloys, and predicts optical emission at $1.55\text{ }\mu\text{m}$ for a $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ alloy lattice matched to GaAs, with $x=2\%$ and $y=3.5\%$.

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