

Epitaxial GaN_{1-y}As_y layers with high As content grown by metalorganic vapor phase epitaxy and their band gap energy

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GaN_{1-y}As_y epitaxial alloy samples with $[N] \gg [As]$ were grown by metalorganic vapor phase epitaxy. The range of As content achieved, up to $y = 0.067$, greatly extends the range of achievable As levels to values that are well within the miscibility gap of the GaN–GaAs system. The single-phase epitaxial nature of the alloy samples was confirmed by x-ray diffraction. The As-content dependence of the band gap was determined by optical absorption measurements. A highly-bowed bandgap was observed as a function of the As content, and a refined value of the bowing parameter of 16.9 ± 1.1 eV was determined. © 2004 American Institute of Physics. [DOI: 10.1063/1.1652232]

The GaN_{1-y}As_y alloy at high N content is an attractive material for extending the wavelength range of GaN-based blue-light-emitting devices toward the red/infrared region. These alloys have a narrower band gap at smaller strain than InGaN alloys when grown on a GaN layer, due to the large band gap bowing parameter, which is attributed to a large difference in the atomic radii of N and As.^{1,2} These GaN_{1-y}As_y-based light emitters could replace GaAs-based long wavelength devices, thus reducing the use of As-based substrates and materials, and allowing multiwavelength light-emitting devices to be integrated on a single substrate. This alloy system, however, also possesses a large miscibility gap.³ Although some GaN_{1-y}As_y alloys with high N contents have been grown,⁴ the realized As mole fraction (y) had been previously limited to $y \leq \sim 0.03$.^{5,6} Iwata *et al.* grew GaNAs alloys by gas source molecular beam epitaxy (MBE) over the composition range of $0 < y \leq 0.0094$ and determined a band gap bowing parameter.⁶ Gherasimova *et al.* also grew these alloys with As content up to 0.03 by metalorganic vapor phase epitaxy (MOVPE).⁵ Novikov *et al.* determined the MBE growth conditions to form the alloy over a limited range.⁴ An As content of $y \geq 0.07$ is, however, considered necessary for lasing wavelength of 650 nm in order to meet requirements for DVD applications. Moreover, the band gap of metastable GaN_{1-y}As_y, within the immiscible region has not been experimentally confirmed.

In this letter, we denote GaN_{1-y}As_y on the N-rich side of the composition regime as GaNAs and GaN_{1-y}As_y on the As-rich side as GaAsN for simplicity. We successfully grew the GaN_{1-y}As_y alloy with As content, y , over the range of

$0 < y \leq 0.067$. The optical band gap for the GaN_{1-y}As_y alloy was obtained from optical absorption experiments and its compositional dependence was determined.

GaNAs layers were grown to a thickness of 0.25–1 μm on GaN layers on sapphire substrates by low-pressure (76 Torr) MOVPE. The sources were trimethyl gallium (TMGa), ammonia (NH₃), and tertiarybutyl arsine (C₄H₉AsH₂, TBAs). The flow rates were 16.3–49.0 $\mu\text{mol}/\text{min}$ for TMGa, 0.071–0.214 mol/min for NH₃, and 26.3–937 $\mu\text{mol}/\text{min}$ for TBAs. The carrier gas was hydrogen (H₂). The growth temperature was 700–750 °C and the growth rate was 0.9–2.7 $\mu\text{m}/\text{h}$ for the GaNAs layers. The high As content materials were obtained through a combination of reduced growth temperatures, low V/III ratio, and increased As/N ratio within the reactor. The As content was dependent on the specific growth conditions employed and the optimal growth conditions were a function of the alloy composition. Details of the growth conditions are described elsewhere.⁷

The phase composition of the epitaxial layers was characterized by x-ray diffraction (XRD) measurements in a $\theta/2\theta$ diffraction geometry. The XRD measurements utilized Cu K α_1 radiation. Electron probe microanalysis (EPMA) was used to quantitatively determine the As content in the films. The surface morphology was observed with an atomic force microscope (AFM). The band gap was determined by optical absorption experiments based on transmission and reflectivity measurements⁸ with a xenon lamp. The samples exhibited no detectable photoluminescence.

The GaNAs layers possessed a yellow hue and had specular surfaces. AFM measurements determined a typical root mean square surface roughness of 0.637 nm for a 10-nm-thick GaN_{0.98}As_{0.02} layer measured over a $2 \times 2 \mu\text{m}^2$ area. While the morphology undoubtedly has an increased roughness with thickness, these materials could be used in

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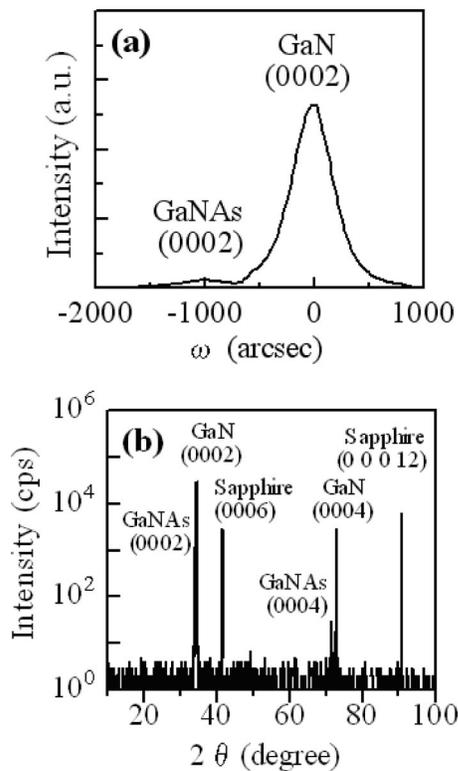


FIG. 1. $\theta/2\theta$ XRD patterns of the $\text{GaN}_{0.936}\text{As}_{0.064}$ sample (a) around the GaN (0002) peak and (b) in the wide range of 2θ .

quantum well applications where the interface morphology in thin layers (~ 10 nm) is critically important.

$\theta/2\theta$ XRD spectra of a $\text{GaN}_{0.936}\text{As}_{0.064}$ sample are shown in Fig. 1. The GaNAs (0002) peak is clearly observed on the low-angle side of the underlying GaN (0002) peak in the XRD spectrum obtained for each sample, shown in Fig. 1(a) for $\text{GaN}_{0.936}\text{As}_{0.064}$. The GaNAs (0002) peak positions are consistent with the EPMA-determined compositions, assuming a lattice constant for hexagonal (*h*-)GaAs based on the known Ga–N and Ga–As bond lengths in cubic GaAs and the *h*-GaN lattice constant. The GaNAs layers are assumed to be totally relaxed. Within the limit of detection of the XRD measurement, only peaks related to the hexagonal form of GaN(As) and to sapphire were detected over the wide range of 2θ shown in Fig. 1(b). No peaks attributable to GaAsN or cubic (*c*-)GaAs phases were observed. No separation into GaNAs and GaAsN phases was observed in the XRD measurements over the range of As content investigated ($0 < y < 0.0669 \pm 0.0054$). Our highest alloy composition measured was greater than that in previous reports.⁶ No statistically significant fluctuation of the As content was detected in EPMA over 20 spots with $50 \mu\text{m}$ separation on each sample. Each spot had resolution of $\sim 0.25 \mu\text{m}$ for both lateral (horizontal) and vertical (depth) directions.

Both absorption and reflectivity measurements were used to determine the optical gap of the alloy samples. Typical results for optical absorption experiments on the GaNAs samples are shown in Fig. 2. The absorption coefficient, α , was obtained from reflectivity and transmission measurements that are shown in the inset. Reflectance (*R*) and transmittance (*T*) spectra had interference fringes because of the large difference in refractive index between the GaN(As)

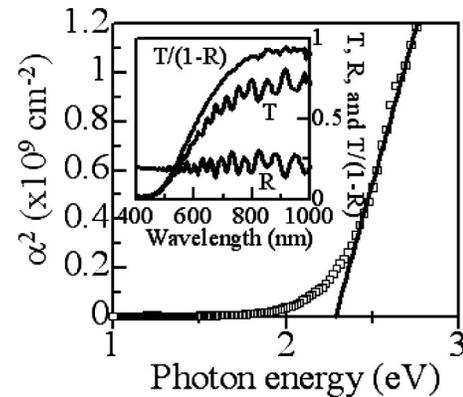


FIG. 2. Typical results for optical absorption measurements on $\text{GaN}_{1-y}\text{As}_y$ samples. The absorption coefficient α is calculated from results for reflectivity (*R*) and transmission (*T*) measurements that are shown in the inset. In this sample, $y = 0.0669 \pm 0.0054$ (EPMA) and its optical band gap was found to be 2.28 ± 0.09 eV.

layers and sapphire substrates. These interference effects can be accounted for through an iterative procedure⁸ based on fitting the reduced data, $T/1 - R$. The absorption coefficient was determined from the fitted imaginary part of the complex index of refraction. As shown in Fig. 2, α^2 possessed good linearity to the photon energy and α rose sharply up to more than 10^4 cm^{-1} , indicating that these GaNAs alloys have a direct energy gap. The optical band gap was obtained from the *x*-axis intercept calculated from a fit of the linear relationship to a plot of α^2 as a function of the photon energy. Figure 2 presents the results for the GaNAs sample with the highest As content of $y = 0.067$ and the band gap of this sample was estimated to be 2.28 ± 0.09 eV.

The As-content dependence of the optical band gap for GaNAs alloy shown in Fig. 3 can be compared to previous reports of the bowing parameter, which had been obtained over a greatly reduced range of As content. Our data agree well with these previous estimates.⁶ The bowing parameter, *B*, is defined as follows:

$$E_g^{\text{GaNAs}}(y) = y \cdot E_g^{\text{GaAs}} + (1 - y)E_g^{\text{GaN}} - y(1 - y)B, \quad (1)$$

where $E_g^{\text{GaNAs}}(y)$ is the band gap of $\text{GaN}_{1-y}\text{As}_y$. For expediency, we used the *c*-GaAs band gap of 1.429 eV for E_g^{GaAs} since the *h*-GaAs band gap is unknown. E_g^{GaN} is the *h*-GaN

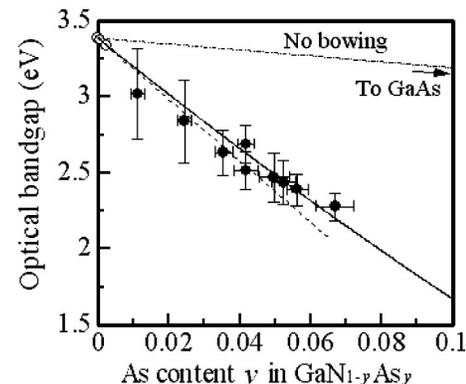


FIG. 3. As-content dependence of the optical band gap within the GaNAs alloy. The open circles and dashed line represent data of Iwata *et al.* (Ref. 6) which yielded a bowing parameter value of 19.58 eV. The solid line and closed circles are the results of the present study which has an improved bowing parameter value of 16.9 ± 1.2 eV.

band gap of 3.39 eV. The band gap values for GaNAs alloys with low As content have large errors in Fig. 3. The uncertainty in these measurements of low As content samples arises, in part, from strong optical absorption from the underlying thicker GaN layer which interfered with determination of the absorption edge of the top GaNAs layer. The high As content measurements have, however, a greater impact on determination of the specific bowing parameter. Our measurements, over a broader composition range, allow more exact determination of the bowing parameter, important in device design. The GaNAs bowing parameter was found to be 16.9 ± 1.2 eV. This value is slightly smaller than the value of 19.58 eV that had been estimated from the GaNAs samples over a much smaller As content range.⁶ The uncertainty in the previously determined value was not reported. The value of the bowing parameter determined in this study also agrees with the values determined from *c*-GaAsN samples on the As-rich side.^{1,2} It should be noted that in Fig. 3, only the gradients in the optical gap should be compared since Iwata *et al.* estimated their bowing parameter⁶ from photoluminescence (PL) peaks at 77 K, and the absolute values of the band gap cannot be determined from those measurements.

In summary, GaNAs epitaxial layers with high As content were successfully grown by MOVPE. While the compo-

sition of the alloys was well within the miscibility gap of the GaN–GaAs phase stability region, no phase separation into GaNAs and GaAsN phases was observed in $\theta/2\theta$ XRD measurements. As-mole fractions up to 0.067 were demonstrated in this study. The optical band gap of the GaNAs alloy was determined through optical absorption measurements. A refined value of the bowing parameter was found to be 16.9 ± 1.1 eV.

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- ¹M. Kondow, K. Uomi, A. Niwa, and T. Kitatani, *Jpn. J. Appl. Phys., Part 1* **35**, 1273 (1996).
- ²S. Sakai, Y. Ueta, and Y. Terauchi, *Jpn. J. Appl. Phys., Part 1* **32**, 4413 (1993).
- ³J. Neugebauer and C. G. Van de Walle, *Phys. Rev. B* **51**, 10568 (1995).
- ⁴S. V. Novikov, A. J. Winsor, A. Bell, I. Harrison, T. Li, R. P. Campion, C. R. Staddon, C. S. Davis, F. A. Ponce, and C. T. Foxon, *J. Cryst. Growth* **240**, 423 (2002).
- ⁵M. Gherasimova, B. Gaffey, P. Mitev, L. J. Guido, K. L. Chang, K. C. Hsieh, S. Mitha, and J. Spear, *MRS Internet J. Nitride Semicond. Res.* **4S1**, G3.44 (1999).
- ⁶K. Iwata, H. Asahi, K. Asami, R. Kuroiwa, and S. Gonda, *Jpn. J. Appl. Phys., Part 1* **37**, 1436 (1998).
- ⁷A. Kimura, H. F. Tang, and T. F. Kuech, *J. Cryst. Growth* (in press).
- ⁸Y. Hishikawa, N. Nakamura, S. Tsuda, S. Nakano, Y. Kishi, and Y. Kuwano, *Jpn. J. Appl. Phys., Part 1* **30**, 1008 (1991).