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Optical Investigation of GaNAs

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Abstract. A systematic study of the energy and time-resolved photolumienscence of GaInP/GaN_xAs_{1-x} double heterostructures has been performed for 0 x 1.3%. A large temperature-dependent optical-bowing coefficient (about 20–25 eV) is observed and the bandgap variation with temperature is found to depend on the nitrogen content. Finally, the minority-carrier lifetime is not simply related to the nitrogen content. Instead, the recombination rate is proportional to the majority-carrier concentration for x 0.3% and the carbon concentration for x 0.3%.

INTRODUCTION

Epitaxial GaAs, when alloyed with nitrogen, exhibits a *reduction* in the bandgap and lattice constant(1, 2). The bandgap reduction is surprising because GaN has a much larger bandgap than GaAs (3.4 eV vs. 1.4 eV at room temperature, respectively). Furthermore, these variations may be large enough to allow the GaN_xAs_{1-x} ternary to achieve, under different values of x, a bandgap of interest to the telecommunications industry (1.3 µm) as well as lattice constant equivalent to that of Silicon.

Of interest to the PV Program, this ternary can further be alloyed with indium to provide a 1-eV direct-gap $Ga_{0.92}In_{0.08}N_{0.03}As_{0.97}$ quaternary that is lattice-matched to GaAs. Incorporation of this material as a third junction under the currently successful GaInP/GaAs tandem cell has the potential to increase the calculated idealized AM1.5D conversion efficiency (at 500 suns) to more than 46 %, and more than 50 % with the incorporation of a junction in an underlying Ge substrate(3).

GaInNAs material grown to date exhibit very low diffusion lengths(4), a significant problem for application as a photovoltaic material. This study focuses on the optical and material qualities of GaN_xAs_{1-x} with x 1.3%, which is where much of this degradation occurs.

EXPERIMENTAL PROCEDURE

A series of GaN_xAs_{1-x} films were grown by atmospheric pressure metal organic vapor phase epitaxy (MOVPE) using trimethythylgallium, arsine, and dimethylhydrazine (DMHy) sources. The pressure reactor is a standard vertical tube reactor utilizing radio-frequency (RF) heating. The growth temperature was 650 C,

and the growth rate about 7 μm/hour. The nitrogen content was varied from x = 0 to 0.013 by varying the DMHy-to-total-group-V ratio. All films were grown on GaAs substrates.

The device structures were 1-μm-thick GaN_xAs_{1-x} double heterostructures (DH) with 0.1-μm-thick GaInP passivating layers. All DHs were doped n-type, using Si, with electron carrier concentrations ranging from 10^{16} to 10^{18} cm^{-3}. The majority-carrier concentrations were determined from capacitance-voltage measurements performed in an electrochemical cell from Bio-Rad.

The nitrogen content of the GaN_xAs_{1-x} films was determined from (004) reflection double-crystal x-ray diffraction (XRD) and secondary ion mass spectroscopy (SIMS) measurements. On samples where both measurements were performed, the XRD analysis was in agreement with the SIMS data provided the GaN_xAs_{1-x} layers were assumed to be coherently strained. From the XRD data, the lattice mismatch (Δa/a) was found to be 0.3% for the x = 0.013 sample. For comparison, Δa/a = 0.16% for AlAs on GaAs.

The optical characterization was performed by spectrally and temporally resolved photoluminescence measurements. The bandgaps were determined as a function of nitrogen concentration and sample temperature (10 K   T   300 K) using photoluminescence (PL) spectroscopy. The excitation source was a HeNe laser (632.8 nm; 18 mW; 250-μm spot size) and the PL was detected by a silicon charge-coupled device (CCD) array. The lifetimes were determined by the single-photon counting technique, also known as time-resolved photoluminescence (TRPL). The excitation source was a cavity-dumped dye laser (600 nm; 1-10 mW; 0.5–1-mm spot size), and the signal was detected by a micro-channel plate (MCP) photomultiplier detector.

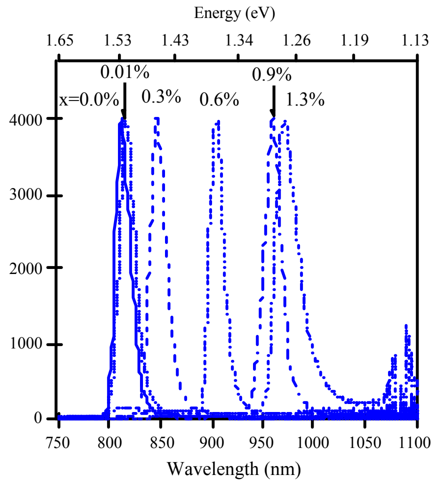
RESULTS AND DISCUSSION

Photoluminescence of GaNAs

Figures 1 and 2 show the steady-state photoluminescence spectra at 10 K and 300 K, respectively, as a function of the nitrogen content. Evident in these spectra is the strong redshift associated with the addition of nitrogen. There is also a corresponding increase in the FWHM between the GaAs and $GaN_{0.013}As_{0.987}$ sample, from 31 to 33 meV at 10 K and from 68 to 85 meV at 300 K. Figure 3 shows the PL peak energy as a function of nitrogen content for both temperatures. Assuming a linear relationship between this energy and the nitrogen content, x, results in a slope of –26 and –21 eV over the linear region (x   1%) for the 10 K and 300 K data, respectively.

The dependence of the bandgap, E_g, on the nitrogen composition can be analyzed using a mixed-alloy type of relationship

$$E_g(x) = xE_g(GaN) + (1-x)E_g(GaAs) - bx(1-x), \qquad (1)$$



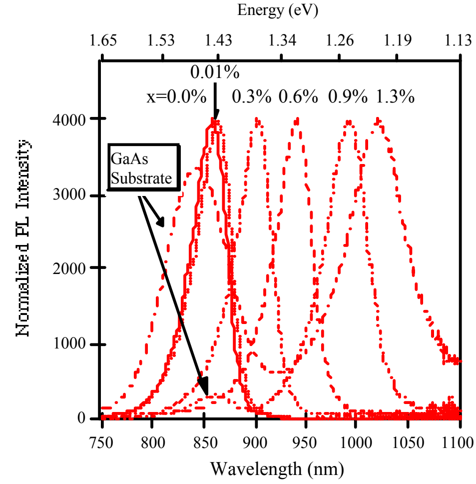


FIGURE 1. GaN_xAs_{1-x} photoluminescence spectra at 10 K.

FIGURE 2. GaN_xAs_{1-x} photoluminescence spectra at 300 K.

where $E_g(GaN)$ is 3.5 and 3.4 eV for 10 and 300 K, respectively. Fitting of this expression to the PL peak energy, which will track with the bandgap energy, results in linear appearing fits with an optical-bowing coefficient, b, equal to 24 and 21 eV for the 10 K and 300 K data, respectively. Solving for b on a point-by-point basis from the change in PL peak energy with respect to the unalloyed GaAs peak results in the b values listed in Table 1.

The particularly strong dependence of the bandgap on nitrogen content is in agreement with other experimental(1, 2) and theoretical(5) work. The x=0.009% sample, where there is a real redshift in the PL spectra and b approaches 100 eV, is anomalous and may be due to transitions involving a shallow N-related impurity band. For comparison, the b value for the AlGaAs system is 1eV.

The temperature dependence of the PL Peak is shown in Figure 4 and is analyzed using the expression by O'Donnell and Chen(6)

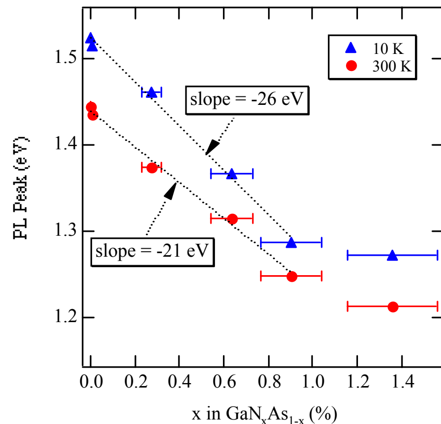


FIGURE 3. PL peak energy of GaN_xAs_{1-x} as a function of the nitrogen concentration.

TABLE 1. Optical bowing coefficient from the data of Figure 3 and Equation 1.

x (%)	b @ 10 K	b @ 300 K
0.009	95 (± 50) eV	95 (±50) eV
0.3	25 (±5)	28 (±5)
0.6	27	16
0.9	28	24
1.3	21	19

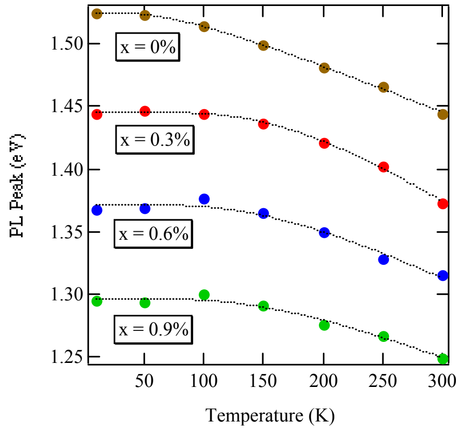


FIGURE 4. PL peak energy of GaN_xAs_{1-x} as a function of the temperature.

TABLE 2. $E_g(T)$ fitting parameters for the fits in Figure 4 using Equation 2.

x (%)	$E_g(0)$	S	$\langle \hbar\omega \rangle$
0	1.52 eV	2.3 (±0.3)	19 (±6) meV
0.3	1.45	4.7 (±1.4)	53 (±10)
0.6	1.37	3.1 (±1)	45 (±10)
0.9	1.29	2.6 (±1)	46 (±10)

$$E_g(T) = E_g(0) - S\langle \hbar\omega \rangle \left[\coth(\langle \hbar\omega \rangle / 2k_B T) - 1)\right], \quad (2)$$

where S is a coupling constant(7) and $\langle \hbar\omega \rangle$ is an average phonon energy. The results of the fits are compiled in Table 2. From these data, it can be seen that the temperature dependence of the bandgap energy changes when going from GaAs to GaN_xAs_{1-x}. This is most evident in the $\langle \hbar\omega \rangle$ fitting parameter. This may correspond to the presence of GaN-like modes (the observed Ga-N local vibrational mode is 58 meV)(8) playing a large role in the electron-phonon component of the change in bandgap over this temperature region. Also of note is the 10 meV blueshift that occurs for the x = 0.6% and 0.9% samples between 50 and 100 K. This may be due to a presence of ordering effects in this ternary(9) and suggests that improved characterization of the average bandgap may be achieved through various modulation techniques.

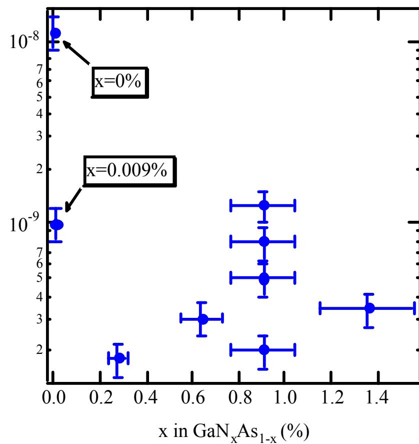


FIGURE 5. Lifetime of GaN_xAs_{1-x} as a function of the nitrogen concentration.

Time-Resolved Photoluminescence of GaNAs

The minority-carrier lifetime, as measured by TRPL, is shown as a function of nitrogen content in Figure 5. While the incorporation of nitrogen in GaAs does result in a reduction in the lifetime (τ), there is no clear functional dependence between τ and the relative percentage of nitrogen, x. Correspondingly, because the amount of strain is directly related to the nitrogen content, this also implies that lattice mismatch is not the source of the dominant recombination mechanism. In fact,

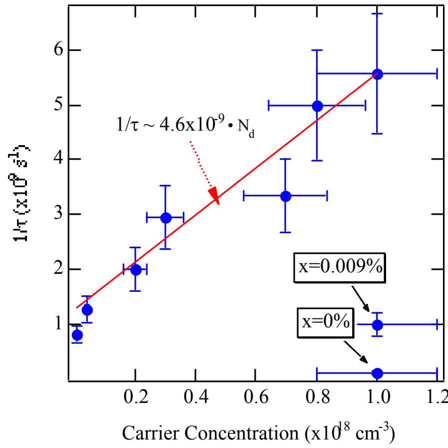


FIGURE 6. Recombination rate of GaN_xAs_{1-x} as a function of the majority-electron concentration.

comparison of the XRD and SIMS data imply that these films remain coherently strained. Closer analysis of the data does reveal a relationship between τ and the carrier concentration, N_d.

As can be seen in Figure 6, for 0.3% x 1.3%, the recombination rate, 1/τ, is proportional to the majority-electron concentration, independent of the nitrogen content. Specifically,

$$1/\tau = 1/\tau_0 + 4.6\text{x}10^{-9} \bullet N_d$$

where τ_0 = 1 ns. Assuming the relevant defect density is equal to N_d, this corresponds to a hole capture cross section, σ_p, of about $2\text{x}10^{-16}$ cm^{-2}. This type of relationship typically signifies radiative band-to-band transitions as the rate-limiting process. The difficulty with this supposition in this case is that the resulting volume capture rate ($4.9\text{x}10^{-9}$ cm^3/s) is not expected to be that different from the GaAs value ($2\text{x}10^{-10}$ cm^3/s)(10, 11). Thus, these lifetimes are considerably lower than expected for this type of transition.

The lifetime of lowest nitrogen containing DHs do not correlate directly with the carrier concentration. Furthermore, as can be seen in Figure 7, at a constant carrier concentration of 10^{18} cm^{-3}, the recombination rate for x 0.3% is not proportional to the nitrogen concentration. Instead, for x 0.3%, the recombination rate is found to be proportional to the carbon concentration (Figure 8). The resulting volume capture rate of $9\text{x}10^{-8}$ cm^3/s, corresponds to a hole capture cross section of about $5\text{x}10^{-15}$ cm^{-2}.

It is possible that there are Si-, C-, and/or N-related complexes that are creating

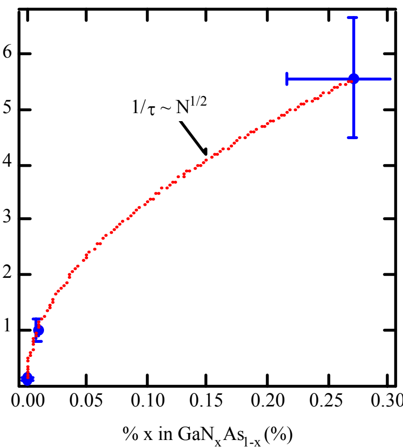


FIGURE 7. Recombination rate of GaN_xAs_{1-x} as a function of the nitrogen concentration.

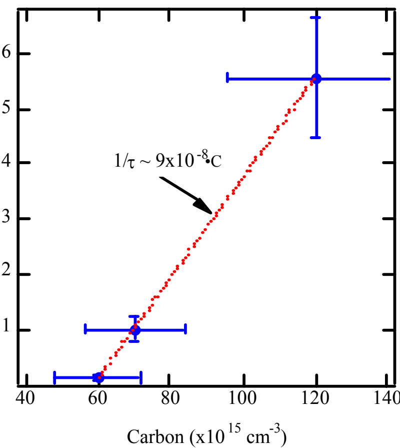


FIGURE 8. Recombination rate of GaN_xAs_{1-x} as a function of the carbon concentration.

the dominant recombination centers. One possibility is a Si-C defect. For example, at low x, and thus low C concentration, the density of Si-C defects in the highly doped material could be controlled by the C content. At higher values of x, there may be a sufficiently large C concentration that the defect density is then controlled by the Si content. The actual defect density may be some fraction of the total Si or C concentration, thus changing the previously calculated σ values. In any case, these possibilities need to be investigated further.

CONCLUSION

From the PL data, the bandgap of GaN_xAs_{1-x} (0   x   1.3%) has been tracked as a function of nitrogen concentration. The resulting bowing coefficient is on the order of 20–25 eV. The temperature dependence of the bandgap was also determined over the range 10 K   T   300 K, where there is a quantitative difference between GaAs and the nitrogen-containing compounds.

Finally, the lifetime is not simply related to the nitrogen content. The recombination rate for n-type (10^{18} cm^{-3}) samples with a low Nitrogen concentration (x   0.3%) is proportional to the sample's carbon content. The recombination rate for samples with a higher nitrogen concentration (0.3   %   x   1.3%) is proportional to the majority-electron concentration, independent of the nitrogen content.

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REFERENCES

1. Kondow, M., *et al.*, Jpn. J. Appl. Phys., 1994. **33**(Part 2, No. 8A): p. L1056-L1058.
2. Weyers, M., M. Sato, and H. Ando, Jpn. J. Appl. Phys., 1992. **31**(Part 2, No. 7A): p. L853-L855.
3. Kurtz, S.R., D. Myers, and J.M. Olson. in *26th IEEE Photovoltaic Specialists Conference*. 1997. Anaheim, CA.
4. Geisz, J.F., *et al.*, J. Cryst. Growth, 1998. **175**.
5. Wei, S.-H. and A. Zunger, Phys. Rev. Lett., 1996. **76**(4): p. 664-667.
6. O'Donnell, K.P. and X. Chen, Appl. Phys. Lett., 1991. **58**(25): p. 2924-2926.
7. Huang, K. and A. Rhys, Proc. R. Soc. A, 1950. **204**: p. 406-423.
8. Alt, H.C., B. Wiedemann, and K. Bethge, Mat. Sci. Forum, 1997. **258-263**: p. 867-872.
9. DeLong, M.C., *et al.*, J. Appl. Phys., 1993. **73**(10): p. 5163-5172.
10. Casey Jr, H.C. and F. Stern, J. Appl. Phys., 1976. **47**(2): p. 631-643.
11. Hall, R.N., Proc. Inst. Elect. Eng., 1960. **106B**(Suppl. 17): p. 923-931.