

Spectroscopic ellipsometry study on the dielectric functions of GaPN alloys

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Received 24 May 2003, revised 6 June 2003, accepted 5 August 2003

Published online 23 October 2003

PACS 61.10.Nz, 71.20.Nr, 78.20.Ci, 78.66.Fd

We have determined the complex dielectric functions of GaP_{1-x}N_x alloys using spectroscopic ellipsometry to clarify the electronic structure. With increasing N concentration, the E_1 -gap peak height for both ϵ_1 and ϵ_2 decreases and the E_1 -gap energy shifts to higher energies, showing that the electronic state at the L point is considerably changed due to the N incorporation. In the lower energy range, a broad peak appears near the fundamental band gap energy of GaP. With increasing N concentration, this peak becomes broader and the peak height increases. This indicates that the band-edge formation in GaP_{1-x}N_x alloys is extremely unique compared to that in conventional semiconductor alloys.

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1 Introduction III–V–N alloys are promising materials for applications in optoelectronic and microwave devices fabricated on Si substrates because they can be lattice-matched to Si. For example, GaP_{1-x}N_x ($x = 0.02$) is lattice-matched to Si and can be grown without misfit dislocations [1]. Although several papers have reported that the band gap energy of GaPN alloys decreases with increasing N concentration in the dilute nitrogen range due to its huge band gap bowing [2, 3], the dielectric functions or optical constants of GaPN alloys have been little clarified so far [4]. In the present paper, we have measured the complex dielectric functions of GaP_{1-x}N_x alloys using spectroscopic ellipsometry to investigate in particular the fundamental absorption edge and higher energy band gaps.

2 Experimental procedures The samples used in this study were grown on GaP (100) substrates by low-pressure (60 T) metalorganic vapor phase epitaxy (MOVPE). Trimethylgallium, PH₃, and 1,1-dimethylhydrazine were used as the Ga, P, and N sources, respectively. Prior to the growth of a GaPN alloy layer, a 0.2- μ m-thick GaP layer was grown as a buffer layer. The epitaxial layer thickness was between 0.15 and 0.8 μ m. The N concentration was determined from (511) asymmetric X-ray diffraction taking into account the effect of the lattice mismatch between GaP_{1-x}N_x and GaP. The X-ray diffraction measurements confirmed that all the GaPN alloys were coherently grown on GaP. Owing to the optimization of the MOVPE growth, highly luminescent GaPN alloys have been successfully obtained with N concentration up to ~3.2% [2]. The optical properties of GaPN alloys were investigated using spectroscopic ellipsometer (Sopra, model GESP-5). The measurements were carried out in the wavelength range of 250–850 nm at room temperature. In this study, we assumed the oxide layer formed on the GaPN surface. The thickness of the oxide and GaPN layers was determined from curve fitting to the experimental data in the lower energy range. The complex dielectric functions of GaPN alloys were

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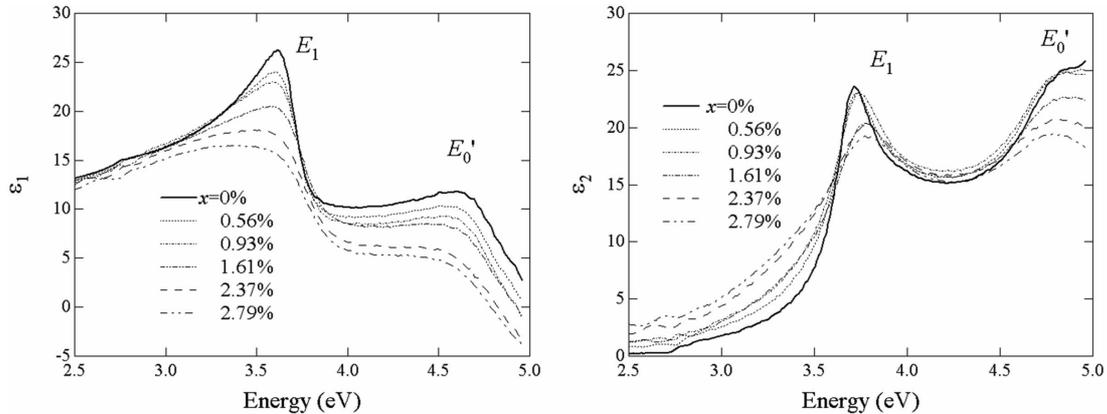


Fig. 1 Complex dielectric functions, ϵ_1 and ϵ_2 , of GaP_{1-x}N_x alloys ($x = 0$ –2.79%) in the higher energy range.

determined from the curve fit using model dielectric functions [4] in the lower energy range, and were numerically determined using the Newton–Raphson method in the higher energy range.

3 Results and discussion The complex dielectric functions, ϵ_1 and ϵ_2 , of GaP_{1-x}N_x alloys ($x = 0$ –2.79%) in the higher energy range are shown in Fig. 1. Two distinct peaks are observed at ~ 3.7 eV and ~ 4.7 eV. These two peaks correspond to E_1 and E'_0 gaps, respectively. The E_1 gap peak height for both ϵ_1 and ϵ_2 is found to decrease with increasing N concentration, indicating that the optical transition probability at the E_1 gap decreases and that the electronic state at the L point is considerably changed. In addition, as can be seen from the broadening of the E_1 gap peak, alloy fluctuations much affect the transition energy at only a few percent of N concentration.

Figure 2 shows the E_1 gap energy and its broadening parameter of GaP_{1-x}N_x alloys estimated from the complex dielectric functions using model dielectric functions [4]. We treated the E_1 transition as a two-dimensional M_0 critical point. With increasing N concentration, the E_1 gap energy shifts to higher energies. Since the GaP_{1-x}N_x layers used in this study were coherently grown on GaP, the change in the band gap energy is affected by the strain. Calculation based on the deformation potentials theory predicts the E_1 gap shifts to lower energies under the tensile strain. However, the E_1 gap of GaP_{1-x}N_x alloy is observed to shift to higher energies in spite of the tensile strain, which indicates that this shift is not due to the strain but mainly due to the intrinsic alloy effect. Assuming that the E_1 gap energy of GaP_{1-x}N_x at $x = 1$ are equal to the E_1 gap energy of cubic GaN [5], the E_1 gap energy is expressed as

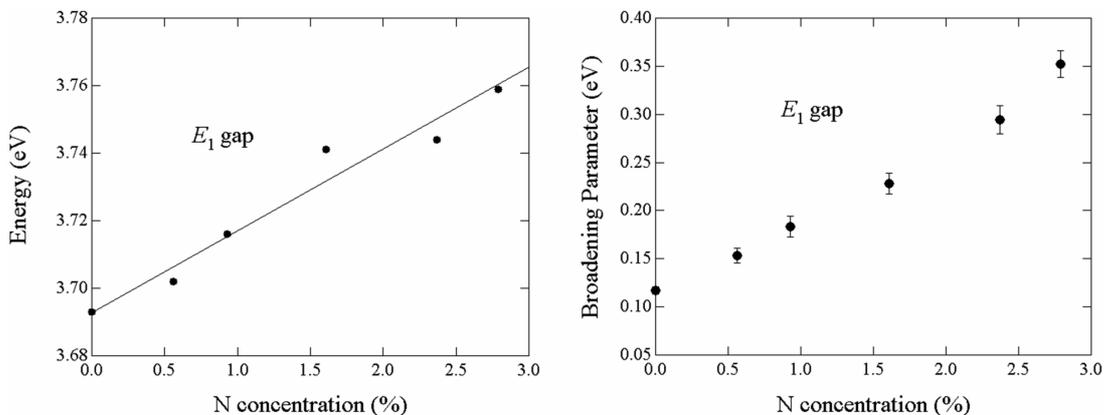


Fig. 2 Band gap energy and broadening parameter of the E_1 transition of GaP_{1-x}N_x alloys.

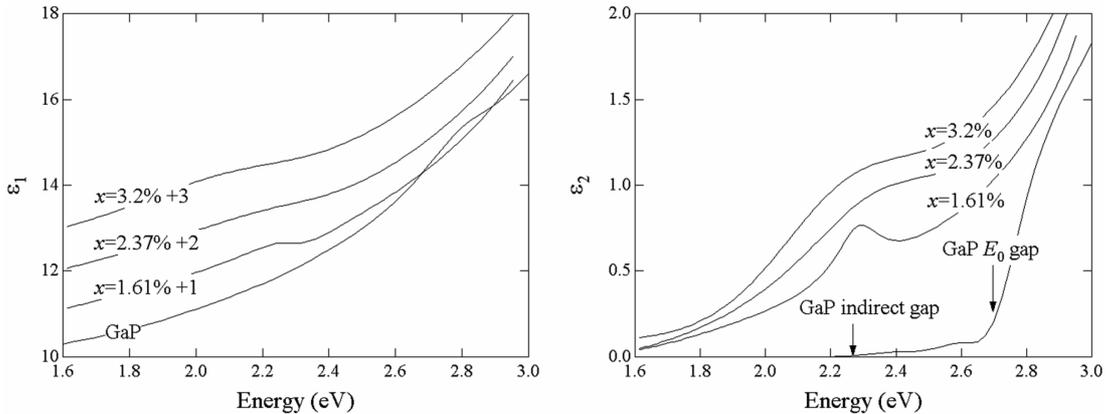


Fig. 3 Complex dielectric functions near the fundamental absorption edge of $\text{GaP}_{1-x}\text{N}_x$ alloys.

$E_1 = 3.693 + 2.404x + 0.834x^2$ eV. Thus, the bowing parameter of E_1 gap ($b_1 = 0.834$ eV) is found to be much smaller than that of E_g ($b_g = 14.2$ eV). The broadening parameter of the E_1 -gap transition increases with increasing N concentration, as shown in Fig. 2. This suggests that the electronic state at the L point is perturbed by the N incorporation.

Figure 3 shows the complex dielectric functions of $\text{GaP}_{1-x}\text{N}_x$ alloys ($x = 0\text{--}3.2\%$) in the lower energy range. In $\text{GaP}_{1-x}\text{N}_x$ alloys, a broad absorption peak is observed near the fundamental band gap energy of GaP, which is in agreement with the result obtained from photoluminescence excitation spectroscopy [3], and shows that the electronic structure of $\text{GaP}_{1-x}\text{N}_x$ alloys is extremely unique compared to that of conventional semiconductor alloys. With increasing N concentration, this absorption peak becomes broader and the peak intensity increases. In addition, the E_0 gap-related structure (2.76 eV for GaP) becomes obscure with increasing N concentration, indicating the N incorporation smears the Γ -point conduction-band edge which may be consumed to form the lower-energy states.

From the complex dielectric functions in the lower energy range, the absorption coefficients of $\text{GaP}_{1-x}\text{N}_x$ alloys at the photoluminescence peak energy were estimated to be $6\text{--}8 \times 10^3 \text{ cm}^{-1}$. This value is larger than that of indirect gap ($\sim 10^2 \text{ cm}^{-1}$) but smaller than that of direct gap ($> 10^4 \text{ cm}^{-1}$). This intermediate character contradicts the report that the transition type of $\text{GaP}_{1-x}\text{N}_x$ alloys changes from indirect to direct [6].

Figure 4 schematically shows the evolution of the absorption peak in $\text{GaP}_{1-x}\text{N}_x$ alloys. At lower nitrogen concentrations, the absorption peak appears near the A line which is formed by an isolated N atom. With increasing N concentration, the absorption peak becomes broader and the peak intensity increases. Further increase in N concentration combines the absorption peak with the fundamental band gap E_g and the E_0 gap, which becomes obscure. Thus, the electronic structure of $\text{GaP}_{1-x}\text{N}_x$ alloys is extremely unique compared to that of conventional semiconductor alloys.

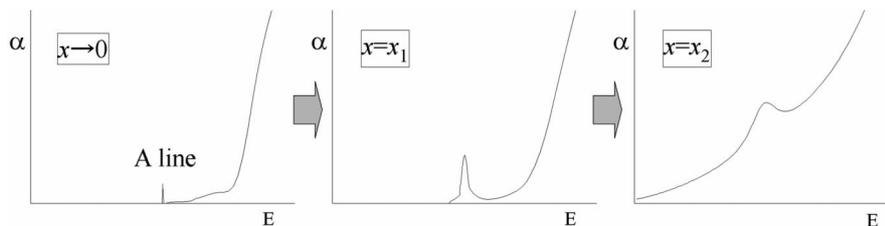


Fig. 4 Schematic view of the evolution of the absorption peak in $\text{GaP}_{1-x}\text{N}_x$ alloys.

4 Conclusions We determined the complex dielectric functions, ε_1 and ε_2 , of GaP_{1-x}N_x alloys ($x = 0-3.2\%$) using spectroscopic ellipsometry. In higher energy range, the two peaks corresponding to E_1 and E'_0 gap are clearly observed. With increasing N concentration, the E_1 gap-peak height for both ε_1 and ε_2 decreases and the E_1 gap shifts to higher energies, which indicates that the electronic state at the L point is significantly changed due to the N incorporation. In lower energy range, a broad absorption peak is observed near the fundamental band gap energy of GaP. This absorption peak becomes broader and the peak intensity becomes stronger with increasing N concentration. Thus, the electronic structure and the mechanism of the band edge formation of GaPN alloys are found to be considerably different from those of conventional semiconductor alloys.

References

- [1] H. Yonezu, *Semicond. Sci. Technol.* **17**, 762 (2002).
- [2] S. Miyoshi, H. Yaguchi, K. Onabe, R. Ito, and Y. Shiraki, *Appl. Phys. Lett.* **63**, 3506 (1993).
- [3] H. Yaguchi, S. Miyoshi, G. Biwa, M. Kibune, K. Onabe, Y. Shiraki, and R. Ito, *J. Cryst. Growth* **170**, 353 (1997).
- [4] G. Leibiger, V. Gottschalch, M. Schubert, G. Benndorf, and R. Schwave, *Phys. Rev. B* **65**, 245207 (2002).
- [5] S. Adachi, *Phys. Rev. B* **35**, 7454 (1987).
- [6] S. Logothetides, J. Petalas, M. Cardona and T. D. Moustakas, *Mater. Sci. Eng. B* **29**, 65 (1995).
- [7] L. Bellaiche, S. Wei, and A. Zunger, *Phys. Rev. B* **56**, 10233 (1997).