

## GaInNAs/GaAs: Novel III-V semiconductor

Masahiko Kondow<sup>a</sup>, Takeshi Kitatani,<sup>b</sup> Yoshiaki Yazawa,<sup>b</sup> and Makoto Okai<sup>b</sup>

<sup>a</sup> RWCP Optoelectronics Hitachi Laboratory,  
c/o Central Research Laboratory, Hitachi, Ltd.,  
1-280 Higashi-Koigakubo, Kokubunji, Tokyo 185, Japan,

<sup>b</sup> Central Research Laboratory, Hitachi, Ltd.,  
1-280 Higashi-Koigakubo, Kokubunji, Tokyo 185, Japan

The crystal growth of GaInNAs using gas-source molecular beam epitaxy is described. Transmission electron microscopic and photoluminescence examination showed that the crystalline and optical quality of GaInNAs is sufficient for practical application. The bandgap of the GaInNAs was experimentally found to decrease with increasing N content in the same way as in GaNAs, as expected. Lasing operation at 77 K demonstrated the applicability of GaInNAs to long-wavelength-range laser diodes. The use of GaInNAs is expected to greatly improve the high-temperature performance of laser diodes used in optical-fiber communications.

### 1. INTRODUCTION

In present optical-fiber communications, laser diodes are used in the 1.3- or 1.55- $\mu\text{m}$  wavelength ranges to minimize transmission loss at the optical fiber windows. These diodes consist mostly of GaInPAs alloy semiconductors formed on an InP substrate. Since the GaInPAs/InP laser diodes have a poor characteristic temperature ( $T_0$ ), thermoelectric coolers are required for practical use. Uncooled laser diodes that can perform well at high temperatures would be very useful. While  $T_0$  has been recently improved from 60 to 80 K by using an AlGaInAs alloy semiconductor formed on an InP substrate,<sup>1)</sup> this is still much lower than that of 0.98- $\mu\text{m}$ -range GaInAs laser diodes formed on a GaAs substrate, whose  $T_0$  is over 150 K. The low  $T_0$  of lasers formed on an InP substrate is mainly due to poor electron confinement.

We previously proposed a novel material: GaInNAs.<sup>2)</sup> Adding In to GaAs, i.e., making a GaInAs alloy semiconductor, increases the lattice constant, and adding N to GaAs, i.e., making a GaNAs alloy semiconductor, decreases the lattice constant. GaInNAs can therefore be lattice matched to GaAs by adjusting the In and N contents. Adding In to GaAs decreases the bandgap. In the same way, adding N to GaAs also decreases the bandgap.<sup>3,4)</sup> Note that this bandgap dependence on alloy

composition differs from the conventional GaPAs alloy semiconductor: increasing the P content decreases the lattice constant and increases the bandgap. Since GaInAs and GaNAs are both direct-transition-type semiconductors, GaInNAs is expected to become a light-emitting material and to have a bandgap energy suitable for long-wavelength-range laser diodes, i.e., less than 1 eV. Combining GaInNAs with materials, such as GaAs, AlGaAs and GaInP, that can be formed on a GaAs substrate provides type-I hetero-interfaces that have ideal band lineups for laser diodes.<sup>2)</sup> Large band discontinuity energy in a conduction band ( $\Delta E_c$ ) of more than 500 meV can thus be achieved. This is sufficient to completely prevent electrons from overflowing from the well layer to the barrier layer. The band discontinuity energy in the valence band ( $\Delta E_v$ ) is also sufficient for confining holes. Therefore, uncooled laser diodes that perform well at high temperatures appear to be attainable if GaInNAs is used. In this case, the  $T_0$  will be increased to the intrinsic value for a laser diode, i.e., over 150 K.

Mixed group-V nitride alloy semiconductors are novel materials that were not created until later than 1992. Their bandgaps are theoretically predicted to have huge bandgap bowing.<sup>5,6)</sup> Such extraordinary bandgap dependence on alloy composition can significantly increase our freedom in designing semiconductor devices.<sup>2)</sup> However, reports so far on the crystal growth of mixed group-V nitride alloy

semiconductors have been limited to GaNP<sup>6,7)</sup> and GaNAs.<sup>3,4)</sup>

In this report, the crystal growth of GaInNAs is described. The crystalline and optical quality of the GaInNAs was examined by transmission electron microscopy and photoluminescence. The bandgap of GaInNAs was experimentally found to decrease with increasing N content in the same way as in GaNAs. Finally, to demonstrate the applicability of GaInNAs to long-wavelength range laser diodes, lasing operation at 77 K is presented.

## 2. CRYSTAL GROWTH OF GaInNAs

The GaInNAs was grown using gas-source molecular beam epitaxy in which a nitrogen radical was used as the nitrogen source. We think that the successful growth of the GaInNAs is due to the growth method, which has been developed on the basis of our proposed growth method for GaNAs.<sup>3)</sup> This method produces more reactive-N-source supply and fewer reactions between the sources. Metal Ga, metal In, arsine gas, and nitrogen gas were used as precursors. The Ga and In flux were derived from conventional thermal effusion cells. The N-radical flux was produced by rf discharge in the N radical cell. The As<sub>2</sub> flux was obtained by cracking arsine at 900°C. The substrate was (100)-oriented Si-doped n-type GaAs. After thermal cleaning of the substrate surface at 580°C, the epitaxial layers were grown at 500°C. The growth conditions were as follows: growth rate—38 nm/min for GaInNAs and 30 nm/min for GaAs, AsH<sub>3</sub> flow rate—6 sccm, N<sub>2</sub> flow rate—0.04 sccm, rf power—380 W, and distance from the radical-cell exit plate to the substrate—15 cm.

Nitrogen was added to GaInAs to form GaInNAs so that the red shift in the bandgap could be definitely confirmed. A GaInNAs/GaAs double-hetero (DH) structure was fabricated to observe the photoluminescence. Since GaInNAs needs to be compressively strained to obtain a type-I hetero-interface between GaInNAs and GaAs,<sup>2)</sup> the GaInNAs layer used in this study was compressively strained about 1.5%, resulting in about twice the lattice deformation in the growth direction due to elastic deformation, i.e., about 3%. Thus, a large In content of 25% and a small N content of 0.5% were selected for the GaInNAs layer. The GaInNAs layer was made about 20-nm thick to prevent misfit dislocation generation.

## 3. RESULTS AND DISCUSSION

The surface morphology of the GaInNAs was smooth and mirror-like, exactly like that of a GaAs homo-epitaxial layer. The In and N contents of the grown GaInNAs were estimated by measuring the (400) X-ray diffraction of GaInAs and GaNAs epitaxial layers that were grown under the same growth conditions as the GaInNAs except for the absence of the N or In supply. The layer thickness of the GaNAs layer, which had a small tensile strain, was 450 nm, while the layer thickness of the GaInAs layer, which had a large compressive strain, was reduced to about 20 nm to prevent misfit dislocation generation. The surface morphology of these epitaxial layers was also smooth and mirror-like. The measured lattice mismatch was +3.24% for GaInAs and -0.19% for GaNAs. Assuming elastic deformation and Vegard's law, the In and N contents were estimated at 23% and 0.5%, respectively. These values agree well with the intended values, as described above. Although it is also possible to estimate the N content directly by measuring the lattice constant difference between the GaInNAs and GaInAs, the result has a large experimental error due to the broad and weak X-ray diffraction peaks for the thin GaInNAs and GaInAs layers. The N content estimated by this method was also consistent with the above value evaluated using GaNAs diffraction within experimental error.

Figure 1 shows a cross-sectional transmission electron microscopic (TEM) image of the GaInNAs/GaAs DH structure. The thickness of the GaInNAs was measured to be 19 nm. Both the upper

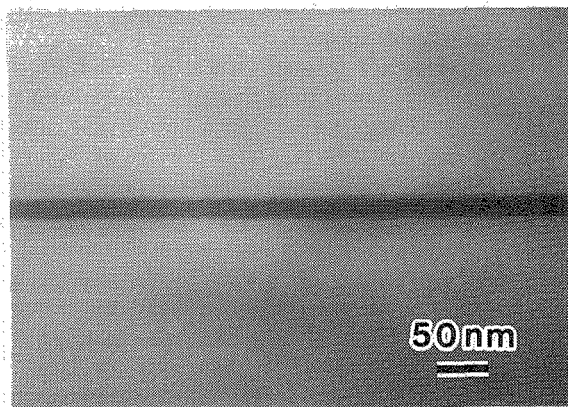


Fig.1 Cross-sectional TEM image of GaInNAs/GaAs DH structure.

and lower hetero-interfaces between the GaInNAs and the GaAs are sharp and smooth. No dislocations are observed, not only in Fig. 1, but also in low-magnification TEM images. The crystalline quality of the GaInNAs/GaAs DH structure was equal to that of a conventional GaInAs/GaAs DH structure.

Figure 2 shows the photoluminescence (PL) spectrum of the GaInNAs/GaAs DH structure observed at 77 K. The specimen used in this measurement had a GaInAs cap reference layer with the same In content above the GaInNAs/GaAs DH structure. The peak at 1.168 eV was PL from the GaInNAs, while the peak at 1.243 eV was due to the GaInAs cap layer. The integral PL intensity of the GaInNAs was as strong as that of GaInAs with the same DH structure. The half-width of the peak was 21 meV, which is somewhat large in comparison with conventional III-V semiconductors. This broadening may be a consequence of fluctuations in the N content in the GaInNAs rather than crystalline defects, because the integral PL intensity of the GaInNAs is on the same level as that of GaInAs, and because the bandgap dependence on the alloy composition for mixed group-V nitride alloy semiconductors is a few times larger than that for conventional III-V semiconductors. Note that the GaInNAs has no accompanying peak (down to 0.8 eV). In the reports concerning GaNAs PL, intense deep-level luminescence caused by crystalline defects

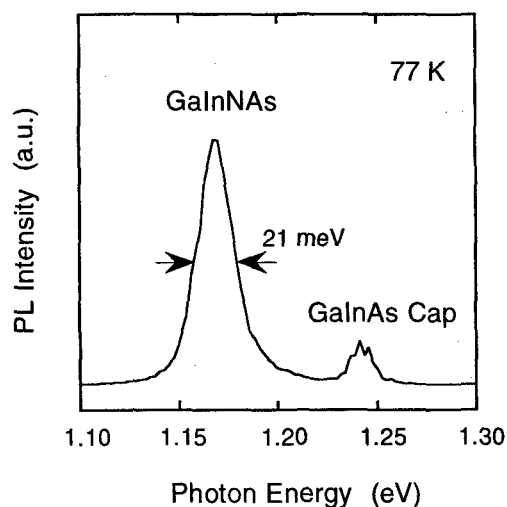


Fig. 2 PL spectrum of GaInNAs/GaAs DH structure.

was always observed.<sup>4)</sup> Therefore, the optical quality of the present GaInNAs DH structure appears to be excellent, and may have reached the level at which it can be applied in laser diodes.

We will now discuss the red shift in the bandgap. In Fig. 2, the difference in the PL peak energy between the GaInNAs and GaInAs was 75 meV. Since the GaInNAs was thick enough to neglect the quantum size effect, this 75 meV can be considered to be the red shift of the bandgap. Under strain-free conditions, the red shift in the bandgap for this GaInNAs was calculated to rise to 80 meV based on the deformation potential parameters for GaAs.<sup>8)</sup> As a result, the slope was estimated to be 160 meV/at.% N. This value agrees very well with that for the strain-free GaNAs, i.e., 156 meV/at.% N.<sup>3)</sup> Thus, the bandgap of GaInNAs decreases with increasing N content in the same way as in GaNAs, as expected.

To demonstrate the applicability of GaInNAs, we fabricated a conventional laser diode using GaInNAs in the active layer. It was a gain-guided type with a broad-area stripe (40 x 800 μm), as shown in Fig. 3. Al<sub>0.3</sub>Ga<sub>0.7</sub>As and GaAs were used as the cladding layers and wave guide layers, respectively. The GaInNAs active layer was thinned down to 7 nm to obtain the quantum size effect. The growth conditions of the GaInNAs were the same as those for the sample in Figs. 1 and 2. Transmission

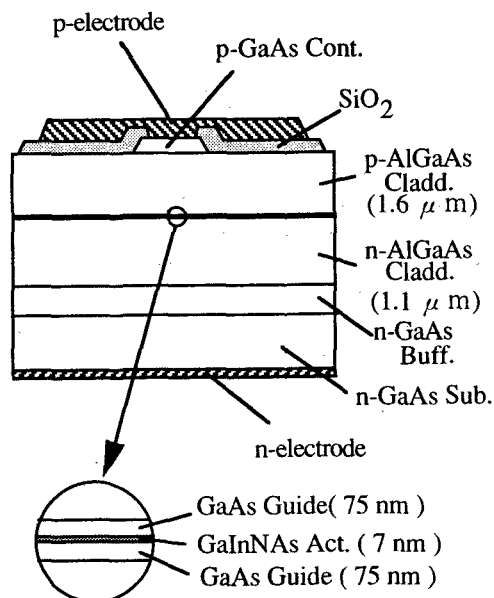


Fig. 3 Schematic structure of GaInNAs laser diode.

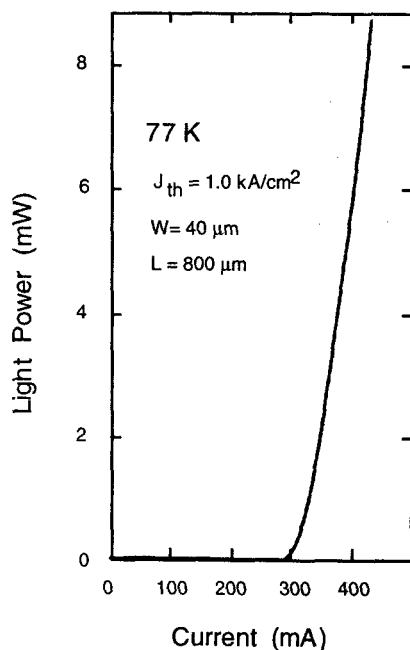


Fig. 4 Light output power vs. injected current characteristics under pulsed operation at 77 K.

electron microscopic observation revealed the absence of dislocations in the DH wafer from which the laser diode was fabricated. Photoluminescence was observed at room temperature from the DH wafer. The PL peak wavelength was  $1.135 \text{ } \mu\text{m}$  ( $1.093 \text{ eV}$ ).

Lasing was achieved at 77 K, but not at room temperature. Fig. 4 shows light output power vs. injected current characteristics under pulsed operation (5 kHz, 0.4% duty cycle). The threshold current was 320 mA, corresponding to a threshold current density of  $1.0 \text{ kA/cm}^2$ . We fabricated a GaInAs laser diode with the same structure as the GaInNAs laser diode for reference. Its threshold current density was  $0.14 \text{ kA/cm}^2$ , i.e.,  $1/7$  of that for the GaInNAs laser diode.

#### 4. CONCLUSION

In conclusion, the crystal growth of GaInNAs was described. GaInNAs/GaAs DH structures were fabricated on GaAs substrates by gas-source molecular beam epitaxy. The crystalline and optical quality of the GaInNAs was found to be fairly good by TEM and PL. The decreasing rate of the bandgap was estimated to be  $160 \text{ meV/at.}\% \text{ N}$ . Thus, a red shift in the bandgap of GaInNAs was confirmed to have the same N dependence as in GaNAs, as was expected. Finally, to demonstrate the applicability of GaInNAs to long-wavelength-range laser diodes, lasing operation at 77 K was presented. The use of GaInNAs will greatly improve the high-temperature performance of laser diodes used in optical-fiber communications.

#### REFERENCES

1. C. -E. Zah, R. Bhat, B. N. Pathak, F. Favier, W. Lin, M. C. Wang, N. C. Andreadakis, D. M. Hwang, M. A. Koza, T. -P Lee, Z. Wang, D. Darby, D. Flanders, and J. J. Hsieh, *IEEE J. Quantum Electron.* **30** (1994) 511.
2. M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Watahiki, and Y. Yazawa, *Extd. Abstr. '95 Int. Conf. Solid State Devices and Materials, Osaka, 1995*, p. 1016.
3. M. Kondow, K. Uomi, K. Hosomi, and T. Mozume, *Jpn. J. Appl. Phys.* **33** (1994) L1056.
4. M. Sato and M. Weyers, *Proc. 19th Int. Symp. GaAs and Related Compound Semiconductors, Karuizawa, 1992*, Inst. Phys. Conf. Ser. Vol. 129 (Institute of Physics, Ltd., Bristol and Philadelphia, 1993) p. 555.
5. S. Sakai, Y. Ueta, and Y. Terauchi, *Jpn. J. Appl. Phys.* **32** (1993) 4413.
6. J. N. Baillargeon, K. Y. Cheng, G. E. Hofler, P. J. Pearch, and C. Heigh, *Appl. Phys. Lett.* **60** (1992) 2540.
7. S. Miyoshi, H. Yaguchi, K. Onabe, R. Ito, and Y. Shiraki, *Appl. Phys. Lett.* **63** (1993) 3506.
8. A. Gavini and M. Cardona, *Phys. Rev.* **B1** (1970) 672.