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GaN$_y$As$_{1-x-y}$Bi$_x$ Alloy Lattice Matched to GaAs with 1.3 µm Photoluminescence Emission

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GaN$_y$As$_{1-x-y}$Bi$_x$ alloy was grown by molecular beam epitaxy. The lattice matching between the GaN$_y$As$_{1-x-y}$Bi$_x$ epilayer and the GaAs substrate was achieved by adjusting the N composition used in this experiment. Photoluminescence (PL) at the wavelength of 1.3 µm was observed at room temperature for the GaN$_y$As$_{1-x-y}$Bi$_x$ epilayer lattice matched to the GaAs substrate. The temperature coefficient of the PL peak energy for this GaN$_y$As$_{1-x-y}$Bi$_x$ epilayer in the temperature range of 150–300 K was 0.14 meV/K which was much smaller than the temperature dependence of the band gap of GaInAsP alloy. [DOI: 10.1143/JJAP.43.L1350]

KEYWORDS: GaN$_y$As$_{1-x-y}$Bi$_x$, PL emission, lattice matching, MBE growth, temperature dependence

Temperature-insensitive-wavelength laser diodes (LDs) are very important in wavelength-division-multiplexing (WDM) optical fiber communication systems. For LDs with a lasing wavelength that fluctuates with ambient temperature, such as the one fabricated from InGaAsP, the use of a massive Peltier device for temperature control is indispensable in WDM optical fiber systems. The required use of a Peltier device seriously hinders the application of WDM systems due to high cost and energy consumption. Semiconductor materials with a temperature-independent band gap are then strongly required to fabricate temperature-insensitive-wavelength LDs. Semimetallic components incorporated into semiconductor alloys have been proposed to have temperature-insensitive band gaps.[1,2] For instance, Bi-incorporated III-V semiconductor alloys, such as GaAs$_{1-x}$Bi$_x$, have been reported to have a temperature-insensitive band gap based on the studies of photoluminescence (PL) measurement and photoreflectance spectroscopy.[3–5] The incorporation of Bi into GaAs also resulted in a reduced band gap, as did the incorporation of N into GaAs. However, GaAs$_{1-x}$Bi$_x$ is not appropriate for the fabrication of LDs for WDM systems because it is not lattice matched to a GaAs substrate and a GaAs$_{1-x}$Bi$_x$ alloy with a band gap that covers the optical fiber communication waveband seems very difficult to produce and hence has not been obtained yet. For the consideration of lattice matching and band gap adjustment, GaAs$_{1-x}$Bi$_x$ incorporated with N, GaN$_y$As$_{1-x-y}$Bi$_x$, is a promising material for the possible realization of a laser diode for WDM fiber communication systems because the matching of its lattice constant to that of the GaAs substrate might be achieved as well as temperature-insensitive emission in a suitable wavelength region, *e.g.* 1.3 µm.

GaAs$_{1-x}$Bi$_x$ has been successfully grown first by metal-organic vapor phase epitaxy (MOVPE)[3] and recently by molecular beam epitaxy (MBE).[6,7] Because a nitrogen source is easily available from rf plasma-activated N$_2$ gas in MBE at a low substrate temperature, which is required for the incorporation of Bi, MBE has an advantage over MOVPE for the realization of GaN$_y$As$_{1-x-y}$Bi$_x$. Recently, we have grown GaN$_y$As$_{1-x-y}$Bi$_x$ successfully for the first time by MBE using activated nitrogen generated from rf plasma as a nitrogen source.[8] The incorporation of Bi and N was confirmed by Rutherford backscattering spectroscopy (RBS) and secondary ion mass spectroscopy (SIMS), respectively.[8,9] For the fabrication of laser diodes for optical fiber communication, it is very important to grow a GaN$_y$As$_{1-x-y}$Bi$_x$ epilayer lattice matched to the GaAs substrate and to realize an emission at a suitable wavelength, as mentioned above. In this work, GaN$_y$As$_{1-x-y}$Bi$_x$ alloy lattice matched to a GaAs substrate has been grown for the first time by selecting the N composition. PL emission at the wavelength of 1.3 µm obtained from the GaN$_y$As$_{1-x-y}$Bi$_x$ epilayer lattice matched to the GaAs substrate is demonstrated. Also, the temperature dependence of the PL peak energy in the temperature range of 150–300 K is reported.

GaN$_y$As$_{1-x-y}$Bi$_x$ alloy was grown on a (100)-oriented GaAs substrate by MBE using solid Ga, Bi, As sources and nitrogen radicals generated from N$_2$ gas in rf plasma. The substrates were ramped to ~600°C for 10 min to remove the native surface oxide layer before growth. The growth rate of GaN$_y$As$_{1-x-y}$Bi$_x$ was approximately 500 nm/h. The substrate temperature was measured using an infrared (IR) pyrometer with an accuracy of ~2°C. The N$_2$ flow rate was measured and controlled with using a flowmeter. Before the growth of the GaN$_y$As$_{1-x-y}$Bi$_x$ epilayers, 100 nm-thick GaAs buffer layers were grown at 500°C. GaN$_y$As$_{1-x-y}$Bi$_x$ epilayers with a thickness of 150–250 nm were grown at substrate temperatures ranging from 350 to 400°C. A 50 nm-thick GaAs layer was grown on the GaN$_y$As$_{1-x-y}$Bi$_x$ layer as a cap layer at 500°C. The detailed growth conditions can be found in our previous papers.[6,8,9] A (2×1) streaky pattern was observed in *in situ* reflection high-energy electron diffraction (RHEED) observation during the growth of GaN$_y$As$_{1-x-y}$Bi$_x$, which indicated a smooth growing surface. The grown GaN$_y$As$_{1-x-y}$Bi$_x$ epilayers showed a mirror surface without any Bi droplets even at a growth temperature as low as 350°C.

Figure 1 shows the diffraction patterns of GaN$_y$As$_{1-x-y}$Bi$_x$ epilayers grown with different N$_2$ flow rates for N plasma, obtained in the θ-2θ scan of X-ray diffraction (XRD) analysis. Figure 2 shows the lattice constants of GaN$_y$As$_{1-x-y}$Bi$_x$ obtained from Fig. 1 plotted against N$_2$ flow rates. The Ga, Bi, and As fluxes and the plasma power were maintained constant during the growth. The growth temperature was 370°C for all samples. When the N$_2$ flow rate was low, the diffraction peak of GaN$_y$As$_{1-x-y}$Bi$_x$ was observed at a 2θ value lower than that of GaAs. The 2θ value of GaN$_y$As$_{1-x-y}$Bi$_x$ increased with increasing N$_2$ flow rate for N plasma, as shown in Fig. 1, which indicates a decrease in the lattice constant due to an increase in the GaN molar

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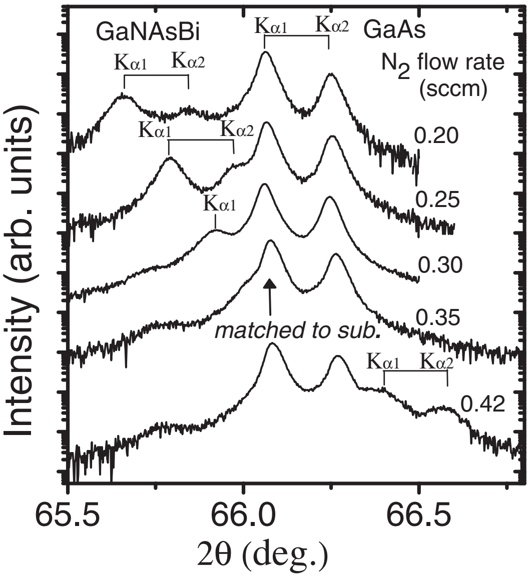

Fig. 1. XRD curve of $GaN_yAs_{1-x-y}Bi_x$ grown with different N_2 flow rates at 370°C.

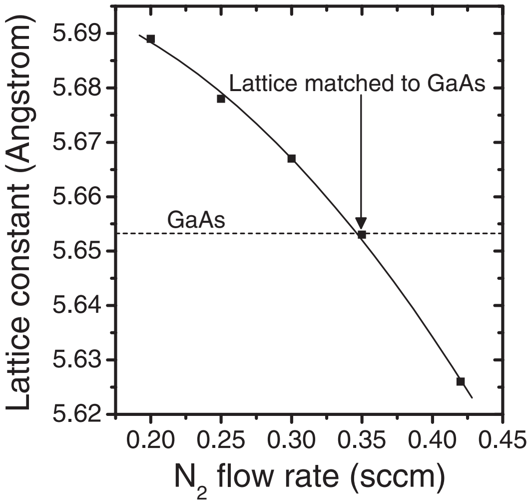

Fig. 2. The lattice constant of $GaN_yAs_{1-x-y}Bi_x$ changes with N_2 flow rate.

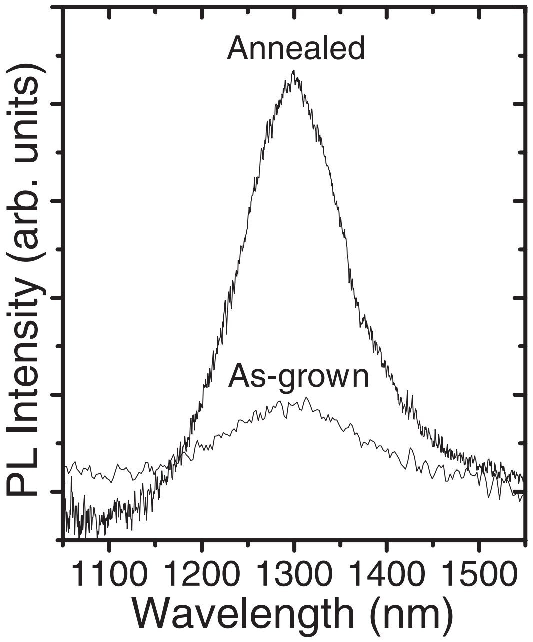

Fig. 3. PL spectra of as-grown and annealed $GaN_yAs_{1-x-y}Bi_x$ epilayers.

fraction in the epilayer, as can be seen in Fig. 2. With a suitable N_2 flow rate, the diffraction peak of $GaN_yAs_{1-x-y}Bi_x$ overlapped with the diffraction peak of GaAs and a $GaN_yAs_{1-x-y}Bi_x$ epilayer lattice matched to the GaAs substrate was realized, as illustrated in Figs. 1 and 2. With a further increase in the N_2 flow rate, the lattice constant of $GaN_yAs_{1-x-y}Bi_x$ became smaller than that of GaAs and the diffraction peak of $GaN_yAs_{1-x-y}Bi_x$ was observed at a 2θ value higher than that of GaAs.

The GaBi content, as determined by RBS, was the same value of ~3.0% for all the samples detailed in Fig. 1. That is to say, the Bi incorporation was not influenced by changes in the N_2 flow rate when the Ga, Bi, As fluxes and the growth temperature were maintained constant. The GaBi molar fractions in the $GaN_yAs_{1-x-y}Bi_x$ epilayers can be modulated by changing the growth conditions such as Bi flux and growth temperature. $GaN_yAs_{1-x-y}Bi_x$ epilayers lattice matched to GaAs substrates with different GaBi molar fractions have also been obtained.

The PL measurements on $GaN_yAs_{1-x-y}Bi_x$ were preformed using an Ar^+ laser for excitation with an excitation intensity of $5\,W/cm^2$. An InGaAs photomultiplier cooled to −80°C was used as a detector. Figure 3 shows the room-temperature PL spectra of as-grown and annealed $GaN_yAs_{1-x-y}Bi_x$ epilayers lattice matched to GaAs substrates shown in Fig. 1. An emission was observed at a wavelength of ~1300 nm. If Vegard's law and the no-strain condition are assumed for the $GaN_yAs_{1-x-y}Bi_x$ epilayer, the N composition is estimated to ~2% from the XRD pattern. The reduction in the PL peak energy of $GaN_yAs_{1-x-y}Bi_x$ induced by the introduction of N was then estimated to be ~130 meV%N on the basis of the PL peak energy difference between $GaN_yAs_{1-x-y}Bi_x$ and $GaAs_{1-x}Bi_x$ with the same Bi content. To obtain a more precise redshift coefficient of the PL peak energy of $GaN_yAs_{1-x-y}Bi_x$ caused by the incorporation of N, we are currently performing characterization to determine the N content more precisely. The PL emission for the as-grown sample was weak and the full width at half maximum (FWHM) of the emission was as wide as 120 meV. The intensity of the PL emission was lower than that of $GaAs_{1-x}Bi_x$ with the same GaBi molar fraction. This indicates that the number of nonradiative recombination centers in $GaAs_{1-x}Bi_x$ was increased by the incorporation of nitrogen. The reduction in the luminescence efficiency caused by the incorporation of N has always been observed in GaNAs and GaInNAs alloys. Spruytte *et al.* have suggested that the nonradiative recombination centers originating from interstitial nitrogen are responsible for the low luminescence efficiency of GaNAs.[10)] We believe that the low PL intensity of $GaN_yAs_{1-x-y}Bi_x$ can be attributed to the same reason as in GaNAs.

It has been shown that annealing significantly improves the luminescence efficiency of GaNAs and GaInNAs alloys.[10–12)] To obtain higher PL intensity from $GaN_yAs_{1-x-y}Bi_x$, we have attempted postgrowth annealing on $GaN_yAs_{1-x-y}Bi_x$. The annealing was carried out in the growth chamber at 550°C for 1 h immediately after the growth of the GaAs cap layer. The As flux irradiated to the sample was maintained constant throughout the annealing process. The annealed sample showed a PL intensity approximately 5 times higher than that of the as-grown sample, as can be seen in Fig. 3. It turns out that postgrowth annealing is very effective in decreasing the number of nonradiative recombination centers in $GaN_yAs_{1-x-y}Bi_x$. The annealing probably removed or at least reduced the amount of interstitial nitrogen, as in the case of GaNAs.10) An obvious blue shift of the emission, which is always reported to occur upon the annealing of GaNAs and GaInNAs, was not observed in our experiment. The FWHM of the PL emission for the annealed sample was also improved to 100 meV. This FWHM is not narrow, but is comparable to the reported ones for GaNAs and $GaAs_{1-x}Bi_x$ with the same GaBi molar fraction.3,10) Considering that both GaNAs and GaAsBi are metastable alloys, the wide FWHM is probably due to the microphase separation in $GaN_yAs_{1-x-y}Bi_x$. Further improvement in both PL intensity and FWHM is possible by optimizing the growth process and postgrowth annealing conditions.

Figure 4(a) shows the PL spectra of the $GaN_yAs_{1-x-y}Bi_x$ sample mentioned above measured in the temperature range of 150–300 K. The change in PL peak energy with temperature is very small, as can be seen in Fig. 4(a). The PL peak energy as a function of measured temperature is shown in Fig. 4(b). The temperature coefficient of the PL peak energy in the temperature range of 150–300 K, as determined from Fig. 4(b), is ~0.14 meV/K. The temperature coefficient of the PL peak energy for $GaN_yAs_{1-x-y}Bi_x$ is very close to that for $GaAs_{1-x}Bi_x$ with the same GaBi molar fraction. For comparison, the band gap variation with temperature for $In_{1-x}Ga_xAs_yP_{1-y}$ ($x = 0.32$, $y = 0.65$) alloy with a band gap near 1300 nm13) is also shown in Fig. 4(b). It is clear that the temperature dependence of the PL peak energy for $GaN_yAs_{1-x-y}Bi_x$ is much weaker than the temperature dependence of the band gap for $In_{1-x}Ga_xAs_yP_{1-y}$. The weak temperature dependence of the PL peak energy of $GaN_yAs_{1-x-y}Bi_x$ we observed is highly consistent with the observation of the MOVPE-grown $GaAs_{1-x}Bi_x$ reported by Oe *et al.*3–5)

In summary, we have grown a $GaN_yAs_{1-x-y}Bi_x$ epilayer lattice matched to a GaAs substrate by adjusting the N composition. Photoluminescence emission at the wavelength of 1.3 μm was obtained from the $GaN_yAs_{1-x-y}Bi_x$ epilayer lattice matched to a GaAs substrate grown at a substrate temperature of 370°C. The PL intensity was increased by postgrowth annealing at 550°C. The temperature dependence of the PL peak energy for this sample was ~0.14 meV/K in the temperature range from 150 to 300 K. The temperature insensitivity of the PL peak energy of $GaN_yAs_{1-x-y}Bi_x$ strongly supports the proposal that the incorporation of semimetallic components such as GaBi into semiconductor alloys realizes alloys with temperature-insensitive band gaps. $GaN_yAs_{1-x-y}Bi_x$ is a material that is very promising for the realization of a laser diode with a temperature-insensitive emission in the wavelength region suitable for WDM communication systems.

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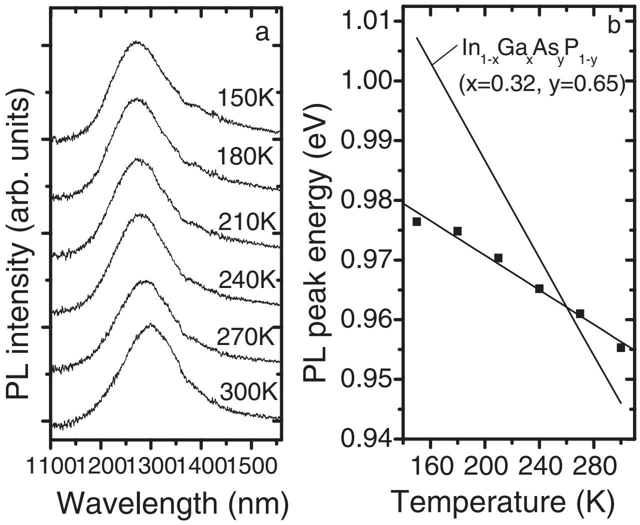

Fig. 4. (a) PL spectra of $GaN_yAs_{1-x-y}Bi_x$ measured at 150–300 K. (b) PL peak energy of $GaN_yAs_{1-x-y}Bi_x$ and the band gap of $In_{0.68}Ga_{0.32}As_{0.65}P_{0.35}$ as functions of measured temperature.

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