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High nitrogen composition GaAsN by atmospheric pressure metalorganic vapor-phase epitaxy

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Abstract

Highly luminescent $GaAs_{1-x}N_x$ alloys were successfully grown by atmospheric pressure metalorganic vapor-phase epitaxy (MOVPE). The nitrogen composition x of as high as 5.6% was obtained using trimethylgallium (TMGa), tertiarybutylarsine (TBAs) and dimethylhydrazine (DMHy) precursors. In-situ and post-growth rapid thermal annealing was performed to enhance the optical quality of the material. Intense low temperature photoluminescence was obtained from GaAsN down to 0.9 eV (1.38 μm). © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The large band gap bowing of the $GaAs_{1-x}N_x$ makes it a promising candidate for a wide range of semiconductor applications. Ga(In)NAs can be used as an active material in long-wavelength laser diodes on GaAs having improved high-temperature performance [1]. Moreover, adding a GaInNAs junction to a multi-junction solar cell is expected to improve the conversion efficiency of the device [2]. GaAsN containing up to 4% nitrogen has been grown by metalorganic vapor-phase epitaxy (MOVPE) on GaAs using dimethylhydrazine as the nitrogen source [3–5]. The optical quality of GaAsN has been found to decrease with increasing N composition, but can be improved with post-growth treatments [4,6].

In the present study, the growth conditions of GaAsN grown by atmospheric pressure MOVPE has been optimized for high nitrogen composition of up to 5.6%. The effects of in-situ and post-growth rapid thermal annealing on the optical quality of the material were studied. GaAsN/GaAs quantum-well (QW) structures showed intense luminescence at low temperatures.

2. Experimental procedure

MOVPE growth was carried out in a horizontal atmospheric pressure reactor having a cross-sectional area of 3 cm^2. Palladium-purified hydrogen was used as carrier gas. Trimethylgallium (TMGa), tertiarybutylarsine (TBAs) and dimethylhydrazine (DMHy) were used as sources for gallium,

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arsenic and nitrogen, respectively. $GaAs_{1-x}N_x$/GaAs multi quantum-well (MQW) structures and $GaAs_{1-x}N_x$ bulk epilayers were grown at the temperature range of 490°C–600°C on semi-insulating GaAs (1 0 0) substrates. All the temperatures mentioned here are thermocouple readings. The V/III and the DMHy/V ratios were varied from 12 to 34 and from 0.5 to 0.94, respectively. The growth rate of the GaAsN layers was 1.1 μm/h and the total gas flow in the reactor was kept constant (the gas velocity was about 0.3 m/s). The structures were grown on a 100 nm thick GaAs buffer layer. The nitrogen composition x in $GaAs_{1-x}N_x$ was varied from 0.1% up to 5.6%, as determined by simulations of the measured double-crystal X-ray rocking curves.

In-situ and post-growth rapid thermal annealing of the structures was performed under excess As ambient in the MOVPE reactor. The in-situ annealing was done directly after the growth of the structure by heating the sample to the annealing temperature. Thus, it gives a possibility to continue the crystal growth after the annealing of the GaAsN layer. In the post-growth annealing the sample was unloaded from the reactor after the growth and reloaded for the annealing. The optical properties of the structures were characterized by photoluminescence (PL) measurements mostly at the temperature of 9 K. The 488 nm line of an argon ion laser was used for excitation. The excitation power of 20 mW was focused to a spot having a diameter of 0.1 mm. The luminescence was dispersed with a 0.5 m monochromator and detected by a liquid-nitrogen-cooled germanium detector.

3. Results and discussion

The growth temperature is known to have a strong effect on the N composition of GaAsN [3,6]. Thus, the growth temperature was first varied from 490°C to 600°C using low N composition (<1%) structures. The N composition increases when the growth temperature is decreased, and the maximum N composition is achieved at around 530°C. These results agree with those obtained by Ougazzaden et al. [3]. Decreasing the growth temperature further does not increase the N composition. However, the growth rate is decreased below 530°C due to incomplete cracking of TMGa. Therefore, all the subsequent samples were grown at 530°C.

Next, the DMHy and TBAs fluxes were altered separately. Fig. 1 shows the effect of the DMHy/TBAs ratio on the N composition. When the TBAs flux is kept constant (TBAs/III = 2), the N composition of GaAsN increases linearly with increasing DMHy flux up to 5% and then saturates to 5.6%. A further increase of the N composition may be obtained by optimizing the growth rate and total gas flow in the reactor. Also the TBAs flux was varied while the DMHy flux was kept constant (DMHy/III = 30). The dependence of the N composition on the TBAs flux is also linear. But when the TBAs/III ratio was decreased below 2, no high-quality crystal growth was obtained. It can be also seen from Fig. 1 that the effect of the V/III ratio on the N composition is dependent on the DMHy/V ratio. Moto et al. [6] reported that when the DMHy/V ratio is 0.8 the nitrogen incorporation is fairly insensitive to the V/III ratio. This can also be seen from Fig. 1, but when the DMHy/V ratio increases, the N composition becomes more and more sensitive to the V/III ratio.

The PL peak energies of the $GaAs_{1-x}N_x$ layers at 9 K are shown in Fig. 2. The PL peak energy decreases strongly with increasing N composition

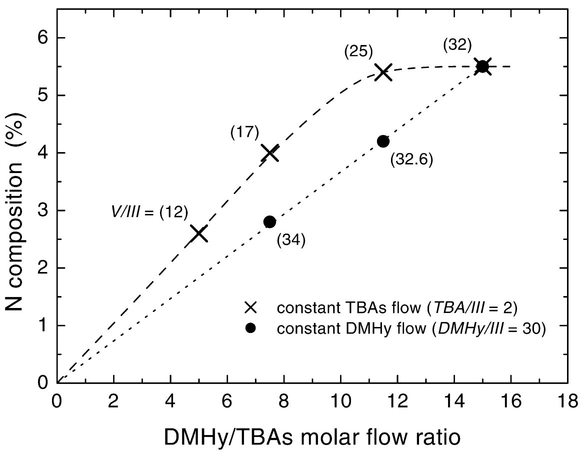

Fig. 1. Effect of DMHy/TBAs molar flow ratio on the N composition of GaAsN layers in MQW structures. The V/III ratio of each sample is shown in parentheses. The lines are guides to the eye.

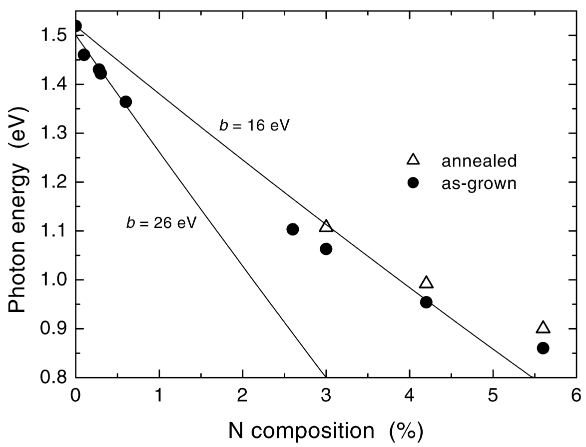

Fig. 2. PL peak energy as a function of the N composition. The solid lines are the band gap energies fitted to data with bowing parameter b of 16 and 26 eV for the average and the low N composition ($x < 1\%$), respectively.

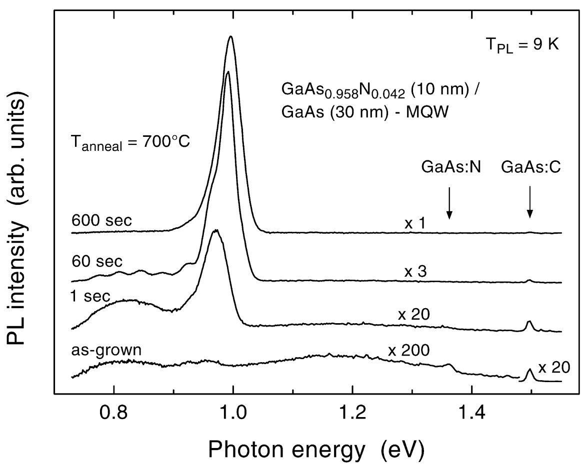

Fig. 3. PL spectra of a MQW structure after post-growth annealing at 700°C for different times. The luminescence of the structure annealed for 10 min is several hundred times more intense than luminescence of the as-grown structure. The FWHM of the topmost spectrum is 45 meV.

when $x < 1\%$. With higher N composition the decrease of the PL peak energy is not that rapid. The fitted value for the band gap bowing parameter is 16 eV. It is in good agreement with the values reported by other groups [7,8]. However, Fig. 2 shows that the band gap energy calculated using a constant bowing parameter does not agree with the data very well. At low N composition ($<1\%$) the bowing parameter value of 26 eV describes the data more accurately. The luminescence from GaAsN has been reported to originate from localized excitons [9]. Thus, the photon energy of the PL peak is lower than the band gap energy. This difference between the PL peak and the band gap energy is one reason for the discrepancy between the PL data and the fitted band gap bowing parameter. Another reason is that the huge band gap bowing of GaAsN is composition dependent as measured by Bi and Tu [10] and calculated by Wei and Zunger [11].

The PL intensity of the as-grown samples having high N composition was weak and dominated by luminescence from defect states [12]. To enhance the PL intensity the structures were annealed by in-situ and post-growth rapid thermal annealing under excess As ambient. Fig. 3 shows the PL spectra of a MQW structure after a post-growth annealing at 700°C for different times. Spectrally integrated PL of the sample annealed for 10 min is several hundred times more intense than that of the as-grown sample. Due to annealing the near band gap excitonic luminescence of the GaAsN alloy is enhanced, and the broad defect band is transformed into a series of PL peaks with a spacing of about 35 meV. The origin of these peaks is unknown, but based on the energy spacing, they could be related to LO-phonon-assisted transitions. The PL peak is shifted to blue by about 40 meV and the full-width at half-maximum (FWHM) of the peak is decreased to 45 meV as a consequence of the annealing. A weak PL peak at 1.36 eV was observed in almost every PL spectrum of the GaAsN MQW structures and is most likely related to nitrogen diffused into the GaAs barriers [13]. The luminescence peak at about 1.5 eV is related to carbon acceptor state in GaAs.

The luminescence intensity of as-grown $GaAs_{1-x}N_x$ decreases with increasing N composition. However, when x was more than 5%, the luminescence was enhanced by a factor of 10 as compared to the luminescence of GaAsN containing about 4% nitrogen. The PL intensity of the similarly annealed samples was of the same order of magnitude regardless of the N composition, as also reported by Moto et al. [6]. Fig. 4 shows the PL peak energy and intensity of a MQW structure

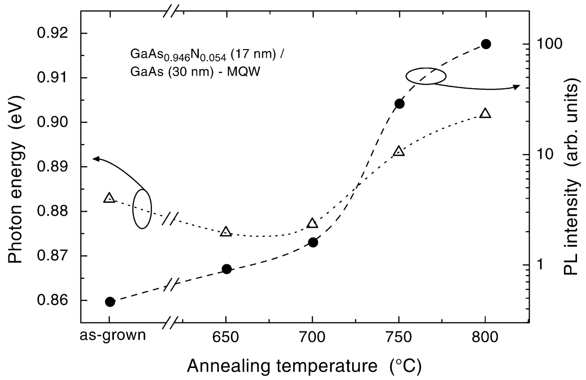

Fig. 4. PL peak energy and intensity of a $GaAs_{0.946}N_{0.054}$ (17 nm)/GaAs (30 nm) MQW structure as a function of the temperature for a 1 s post-growth annealing. The lines are guides to the eye.

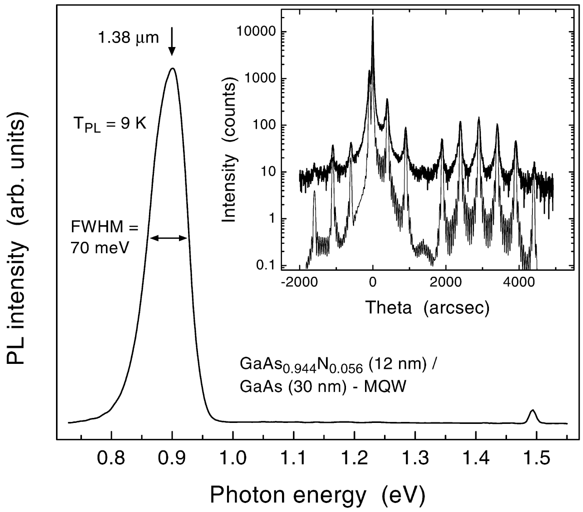

Fig. 5. PL spectra and an X-ray rocking curve of a $GaAs_{0.944}N_{0.056}$ (12 nm)/GaAs (30 nm) – MQW structure annealed in-situ at 700°C for 10 min. The lower curve in the inset is the simulated X-ray rocking curve.

after post-growth annealing at different temperatures for 1 s. The PL intensity increases with increasing annealing temperature. The PL peaks of the samples annealed at 650°C and at 700°C are shifted to red from the PL peak of the as-grown sample, but the intensities are not enhanced by more than two and four times, respectively. The most significant change is observed when the annealing temperature is increased from 700°C to 750°C. The PL intensity increases more than one order of magnitude, but the peak is also shifted to blue. Annealing at 800°C produces the highest PL intensity, but the blue shift of the peak is further enhanced. Anyway, the same increase in the PL intensity can be reached by annealing at 700°C for longer times (> 60 s) as also observed by Moto et al. [6]. Therefore, it may be preferable to use lower temperatures and longer annealing times to minimize intermixing at QW interfaces.

Fig. 5 shows a PL spectrum of a highly luminescent GaAsN/GaAs MQW structure. The N composition of the 12 nm thick QWs is 5.6% and the GaAs barrier thickness is 30 nm. The MQW structure was annealed in-situ for 10 min at 700°C. No difference between in-situ and post-growth annealing was observed. The maximum of the PL peak is at 0.9 eV (1.38 μm) and the FWHM is 70 meV. The low temperature PL intensity of the sample is high, but at room temperature the PL intensity is more than two orders of magnitude lower. The rapid thermal quenching of PL at around 80 K was observed for all the structures. This suggests that the dominant mechanism for the thermal quenching of PL is the activation of an efficient nonradiative recombination channel [9], which is common for all the structures studied.

4. Conclusion

Bulk GaAsN and GaAsN/GaAs MQW structures were successfully grown by atmospheric pressure MOVPE using TMGa, TBAs and DMHy as precursors. The band gap bowing parameter of 16 eV was obtained by fitting the PL peak energies of the GaAsN/GaAs MQW structures. High-quality layers with N composition of as high as 5.6% were obtained. In-situ and post-growth rapid thermal annealing was performed to obtain high luminescence intensity. The low-temperature PL peak wavelength of 1.38 μm was observed from an in-situ annealed $GaAs_{1-x}N_x$/GaAs MQW structure having $x = 0.056$.

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