JOURNAL OF MATERIALS SCIENCE **38** (2003) 683–687

Chemical beam epitaxial growth of GaInP using TBP, TIPGa and EDMIn

H. H. RYU
LP1, System IC R&D Div. Hynix Semiconductor Inc., Cheongju-Si, Choongbook,
361-725, Korea
E-mail: hyukhyun.ryu@hynix.com

In this work the effects of growth temperature on the growth of gallium indium phosphide (GaInP) by the chemical beam epitaxy technique are reported. Triisopropylgallium, ethyldimethylindium and tertiarybutyl-phosphine were used as the gallium, indium and phosphorus sources, respectively. The growth rate, surface morphology, low temperature (15 K) and room temperature (300 K) photolumine-scence (PL) were studied as functions of the growth temperature. The optimum growth temperature was found to be 520°C where the PL spectra show only a single strong and narrow band edge peak.

1. Introduction

The GaInP/GaAs heterosystem has attracted much attention as an alternative to AlGaAs/GaAs for optoelectronic applications. There are several advantages of GaInP/GaAs as compared to AlGaAs/GaAs. These include a large valence band discontinuity [1], lower reactivity with carbon and oxygen, and a lower deep level concentration [2]. However, while it is straightforward to lattice-match AlGaAs/GaAs over the entire range of Al compositions, only $Ga_{0.52}In_{0.48}P$/GaAs is lattice matched (hereafter referred to as GaInP/GaAs). Thus precise control of the source flow rates as well as other growth parameters is required in the growth of lattice matched GaInP/GaAs.

Phosphine (PH_3) has been the main phosphorus (P) source used in $Ga_xIn_{1-x}P$ growth by chemical beam epitaxy (CBE) since the epilayer quality using PH_3 is very high. However, PH_3 has a fundamental problem with toxicity that has lead to the development of safer sources, such as tertiarybutylphosphine (TBP) [3] and trisdimethylamino-phosphine (TDMAP) [4]. These alternative sources are liquids at room temperature with acceptable vapor pressures, which makes them orders of magnitude safer than PH_3 [5]. TBP has become a very important precursor in organometallic vapor phase epitaxy (OMVPE) [5]. In addition to safety considerations, the pyrolysis temperature of the TBP is lower than that of PH_3. Carbon can be removed from the surface by recombining hydrocarbon fragments with H-containing free radicals from TBP, which reduces the unintentional impurity concentration [6].

There have been only a few reports of the growth of InP [7] and GaInP [8] using TBP by CBE. Garcia *et al.* [8] reported the CBE growth of lattice matched GaInP using TBP, TMIn (trimethylindium) and TEGa (triethylgallium). They showed that the carbon impurity concentration in TBP-grown GaInP was lower than that in PH_3-grown GaInP. They also showed that the current gain of heterojunction bipolar transistors made from TBP-grown GaInP/GaAs was higher than that from PH_3-grown GaInP/GaAs.

In this paper the effects of the growth temperature on the quality of GaInP epilayers lattice matched to GaAs (001) substrates were reported. Triisopropylgallium (TIPGa) and ethyldimethylindium (EDMIn) were used together with TBP for the growth of GaInP by CBE. The room temperature and low temperature (15 K) photoluminescence (PL) spectra showed that the GaInP epilayer quality was highly dependent on the growth temperature. In this work, the optimum growth temperature was 520°C, the maximum value used in this study. At this temperature, only a single sharp, strong band edge PL peak was observed. The narrowest 15 K PL full width at half maximum (FWHM) in this study was 10.8 meV.

2. Experimental details

GaInP epilayers were grown on semi-insulating (001) oriented GaAs substrates. The substrates were cleaned by degreasing with organic solvents including trichloroethane, acetone and methanol to remove any organic contamination. After a deionized (DI) water rinse, the substrates were dipped in $NH_4OH:H_2O:H_2O_2 = 12:2:1$ for 80 seconds. The substrates were then rinsed in DI water and blown dry with nitrogen and loaded into the load-lock chamber of a custom-designed ultra high vacuum (UHV) stainless steel CBE growth chamber which was equipped with a 2200 1/s LN_2 trapped diffusion pump. TIPGa, EDMIn and TBP, kept at room temperature, were used for the growth of the GaInP epilayers. The TIPGa and EDMIn sources were introduced onto the heated substrate without a carrier gas, using closed-loop pressure-control. The TBP flow rate was mass flow controlled. A custom-designed quartz tube cracker cell was used for precracking TBP

[9]. Halogen lamps were used to heat the substrate. In this work the growth temperature was varied from 440 to 520°C, the maximum temperature possible in this apparatus. The cracker cell temperature was held constant at 795°C. The flow rates of TIPGa, EDMIn and TBP were 0.07, 0.06 and 9 sccm, respectively. A constant input V/III ratio of 66 was used. Typical chamber pressures during growth were in the 10^{-5} to low 10^{-4} torr range. The concentrations of Ga and In in the GaInP epilayers were determined from X-ray diffraction results.

After growth, a Nikon-AFX Nomarski interference contrast microscope was used to examine the surface morphology. The growth rate was determined by measuring the step height between the epilayer and a masked region of the substrate using a Sloan Dektak IIA. Room temperature and low temperature (15 K) PL measurements were performed using the 488 nm line of an Ar^+ laser operating with a typical power level of between 0.1 to 10 mW. GaInP epilayers were highly resistive, so no electrical properties are reported.

3. Results and discussion

Fig. 1 shows the morphologies of the GaInP samples at four growth temperatures: 460, 480, 500 and 520°C. At 460°C, the surface was rough. As the growth temperature increased, the surface morphology significantly improved.

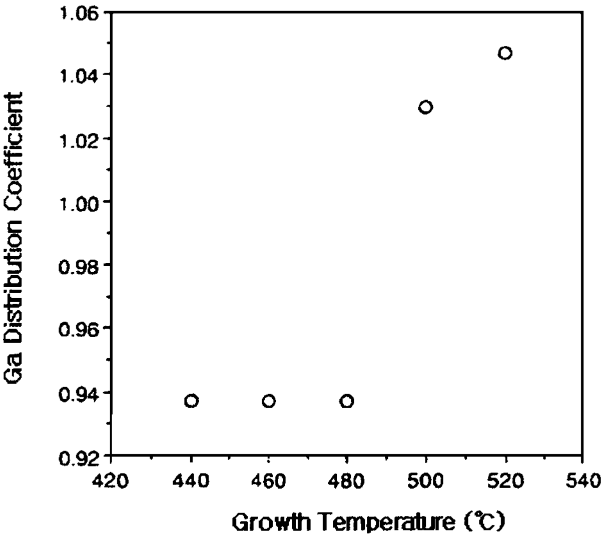
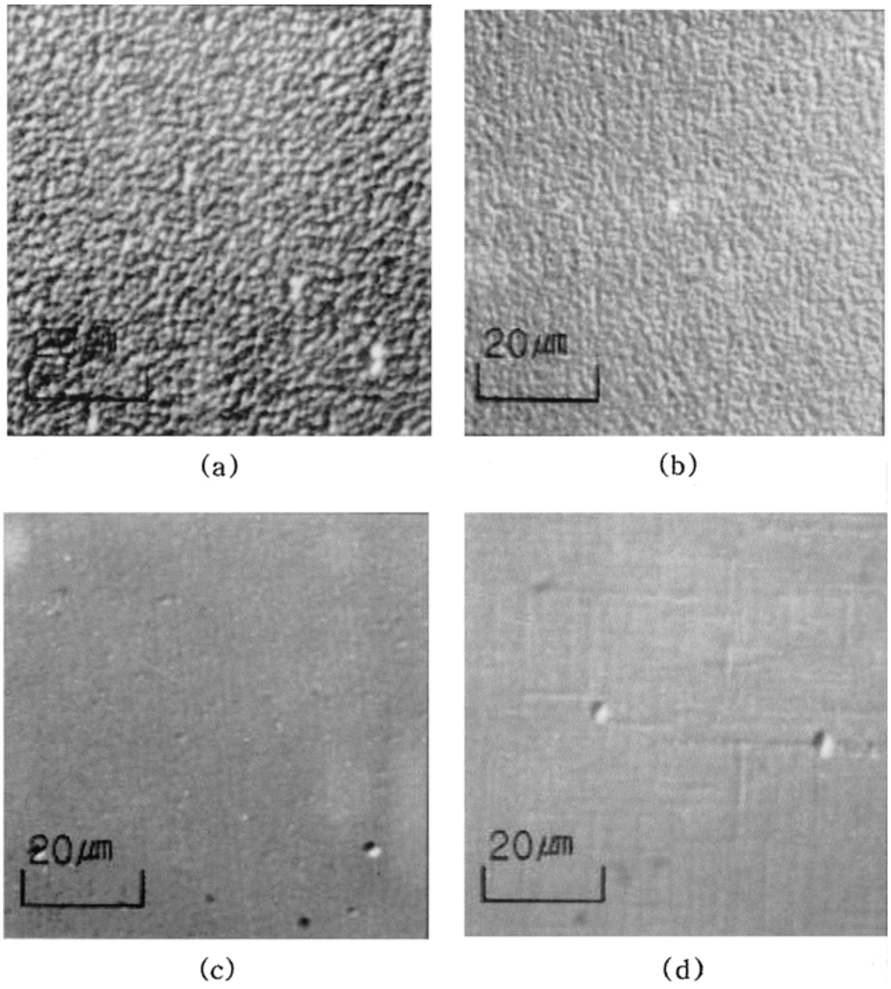


Figure 2 Ga distribution coefficient as a function of the growth temperature. $T_c = 795$°C and V/III = 66.

Fig. 2 shows the gallium distribution coefficient as a function of the growth temperature. The Ga distribution coefficient was calculated from the following equation: K (Ga) = [$x/(1-x)$ in $Ga_xIn_{1-x}P$]/[TIPGa molar flow rate/EDMIn molar flow rate]. As seen in Fig. 2, the Ga distribution coefficient is constant from



(a) (b)

(c) (d)

Figure 1 Surface morphologies of GaInP layers grown on GaAs (001) substrates at four different growth temperatures with $T_c = 795$°C and V/III = 66: (a) 460°C, (b) 480°C, (c) 500°C and (d) 520°C.

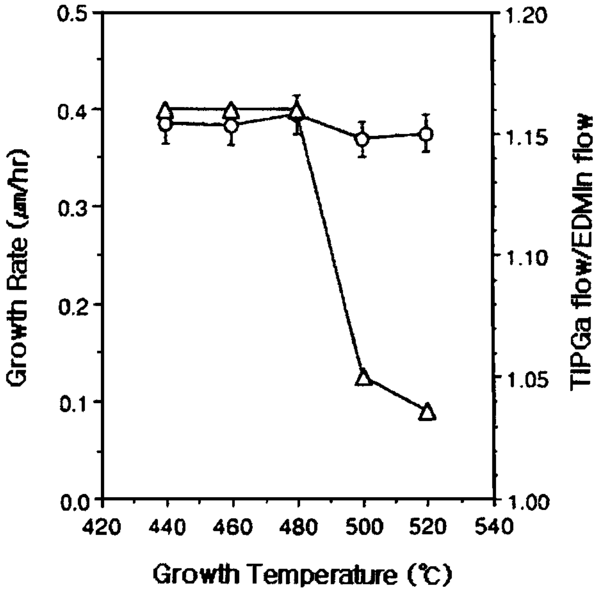


Figure 3 The GaInP growth rate dependence and the TIPGa/EDMIn flow rate ratio for lattice matching as a function of the growth temperature at $T_c = 795°C$ and V/III = 66. (o) GaInP growth rate and (Δ) TIPGa/EDMIn flow rate ratio.

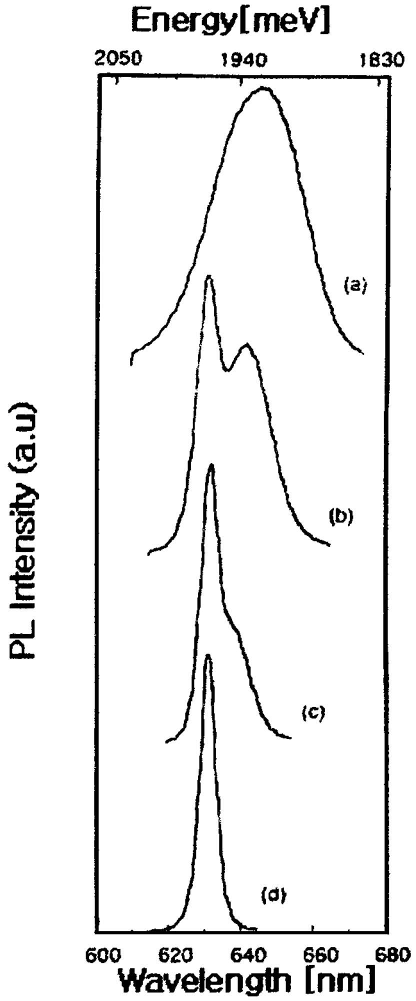


Figure 4 Low temperature (15 K) photoluminescence (PL) spectra for several growth temperature: (a) 460°C, (b) 480°C, (c) 500°C and (d) 520°C. The laser power was 1 mW. $T_c = 795°C$ and V/III = 66.

440 to 480°C, and increases at higher temperature. The reduced indium (In) incorporation at 500°C and beyond is partially attributed to elemental In desorption. There have been similar reports from other CBE [10], molecular beam epitaxy (MBE) [11] and gas source molecular beam epitaxy (GSMBE) [12] groups indicating that In desorption occurs at growth temperature (T_g) of approximately 500°C and above. In desorption apparently occurs at nearly the same temperature for all sources, indicating that it is related to the desorption of elemental In from the GaInP surface. To obtain lattice matched GaInP/GaAs at 500 and 520°C, the flow rates of TIPGa and EDMIn were adjusted to maintain the same total group III (TIPGa + EDMIn) flow rate, i.e., the TIPGa flow rate was decreased and the EDMIn flow rate was increased.

Fig. 3 shows the GaInP growth rate and the TIPGa/EDMIn flow rate ratio required for lattice matching as a function of growth temperature. The growth rate is approximately constant from 440 to 520°C. The ratio is constant from 440 to 480°C and decreases at 500°C and higher. This can be understood in terms of increased In desorption which results in an increased Ga concentration. The increased Ga incorporation approximately compensates the decreased In incorporation. Therefore, the GaInP growth rate is almost constant from 440 to 520°C. Kapre *et al.* [10] reported a similar result. They found that In desorption occurred at 490°C and above for the growth of GaInP by CBE using TMIn, TEGa and PH_3. To obtain lattice matched GaInP epilayers on GaAs, they needed to progressively increase the TMIn flow rate at $T_g = 490°C$ and above for constant flow rates of TEGa and PH_3. There was a sharp increase in the TMIn flow required for lattice matching above 520°C.

Fig. 4 shows the low temperature (15 K) photoluminescence (PL) spectra for lattice matched GaInP on (001) GaAs substrates at four different growth temperatures of 460, 480, 500 and 520°C. As can be seen from Fig. 4, the PL spectrum is highly dependent on the growth temperature. At a growth temperature of 460°C, a single, broad peak is observed at a position 76 meV below that expected for band edge recombination. This is indicative of a high impurity concentration. For $T_g = 480°C$, there are two peaks, the band edge peak and the impurity related peak. For $T_g = 500°C$, the band edge peak dominates and at $T_g = 520°C$, the impurity peak has essentially disappeared and there is only one sharp band edge peak in the PL spectrum. The lower energy impurity component was identified as a donor-acceptor pair (DAP) related peak due to the dependence of peak energy on laser power [13]. The lower energy peak shifts to higher energy as the laser power is increased. The impurity concentration apparently decreases as T_g is increased as seen from the PL spectra in Fig. 4. Fig. 5 shows the 15 K PL full width at half maximum (FWHM) versus growth temperature. As the growth temperature increases, the value of the FWHM decreases, presumably due to the reduction in impurity concentration. At $T_g = 520°C$, the FWHM value is 13.9 meV. The FWHM value was further reduced to 10.8 meV when the V/III ratio was decreased to 50. Ozasa *et al.* [14] reported that the FWHM value for GaInP grown by CBE using TEGa, TEIn and PH_3 was

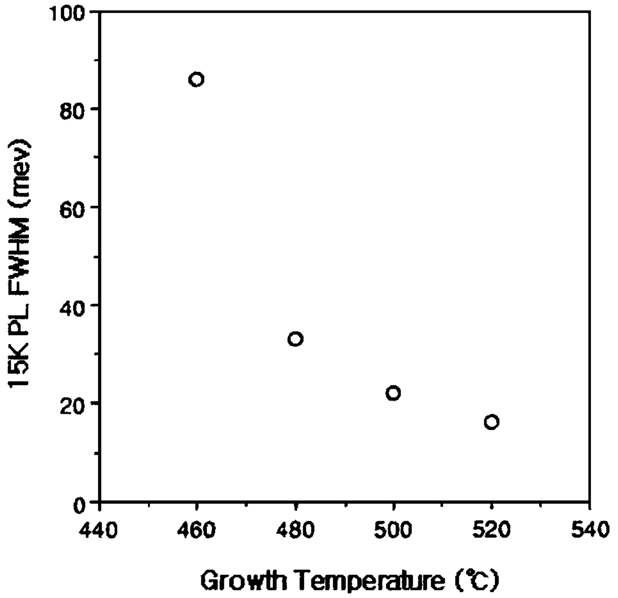


Figure 5 15 K photoluminescence (PL) full width at half maximum (FWHM) as a function of the growth temperature at $T_c = 795°C$ and $V/III = 66$.

15.5 meV at 77 K. The 10.8 meV 15 K PL FWHM value from this work compares favorably with OMVPE results of 7.2 meV at 10 K [15], GSMBE of 11 meV at 10 K [16], LPE of 10.6 meV at 14 K [17] and MBE of 6.7 meV at 4.2 K [18].

Fig. 6 shows the dependence of 15 K PL peak intensity on the growth temperature. The strongest PL signal was obtained from the sample grown at 520°C which is about 4 orders of magnitude stronger than that from the sample grown at 460°C. This suggests that the crystalline quality is poor at low growth temperature, which results in layers with a high density of non-radiative recombination centers. As the growth temperature is increased, the density of non-radiative recombination centers decreases, which increases the radiative efficiency.

Room temperature (RT) PL measurements were also performed. Fig. 7 shows the RT and 15 PL peak energies of lattice matched GaInP for different growth temperature. No RT PL was detected for the sample grown at 460°C. This is probably due to the poor quality of the layer and is consistent with a poor morphology and a single broad impurity 15 K PL peak (see Fig. 4). The RT PL peak energies for the lattice matched GaInP samples grown at 480, 500 and 520°C are 1896, 1890 and 1893 meV, respectively. The 15 K PL peak energies of the lattice matched GaInP samples grown at 480, 500 and 520°C are 1964.9, 1961.8 and 1964.9 meV, respectively. The energy difference between the RT energy peak and the low temperature band edge peak is about 70 meV, similar to the result reported by Takamori *et al.* [19] but smaller than the result to reported by Zachau *et al.* [20] who reported PL peak energy shift of 87 meV between 300 K and 2 K PL. The low temperature PL peak energy for lattice matched disordered GaInP is known to be 2.0 eV [21, 22]. There is a 35 meV difference between the reported disordered lattice matched peak energy value and the results from this study. This indicates that these samples may be slightly ordered.

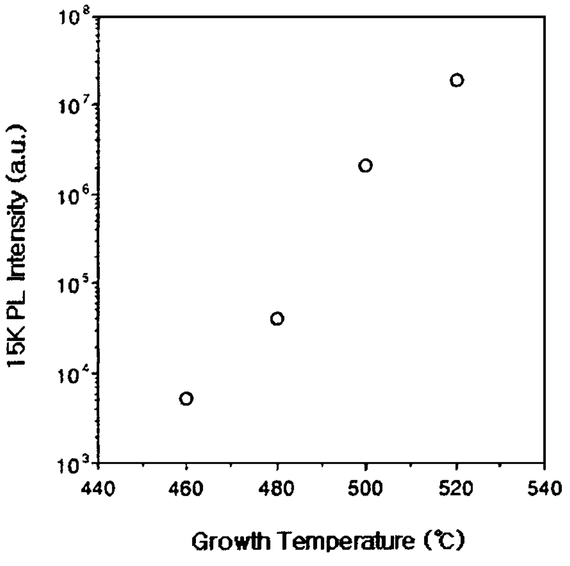


Figure 6 15 K photoluminescence (PL) peak intensity as a function of the growth temperature. $T_c = 795°C$ and $V/III = 66$.

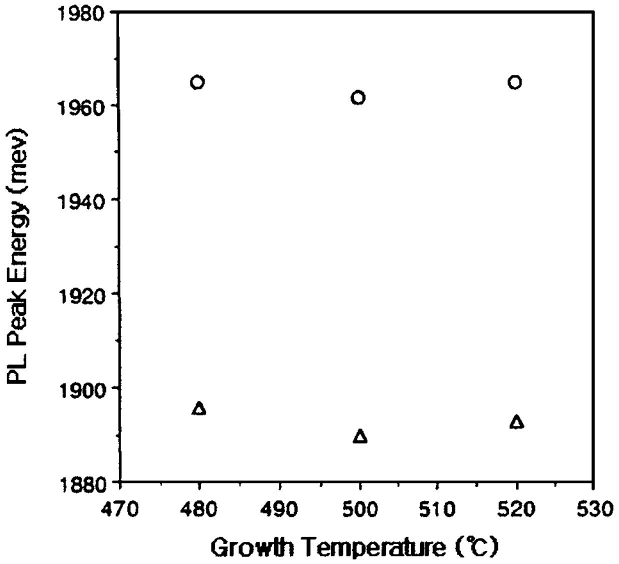


Figure 7 Room temperature and 15 K photoluminescence (PL) peak energy (meV) as a function of the growth temperature. (o) 15 K PL and (Δ) room temperature PL. $T_c = 795°C$ and $V/III = 66$.

4. Conclusions

In this work, a detailed study of the effects of growth temperature on CBE-grown GaInP lattice matched to (001) GaAs was reported. TIPGa and EDMIn were used, for the first time, together with TBP for the CBE growth of GaInP. The morphology, growth rate, Ga incorporation efficiency and photoluminescence were investigated as functions of the growth temperature. As the growth temperature decreased, the morphology became rough. The growth rate was approximately constant from 440 to 520°C. The Ga incorporation efficiency was constant from 440 to 480°C. At growth temperature of 500°C and above, the Ga incorporation efficiency increased due to In desorption. The low temperature PL spectra indicate that an impurity peak dominates at lower growth temperatures and that the band edge peak is dominant at higher growth temperature.

At a growth temperature of 520°C, only a sharp band edge peak was observed. The GaInP samples grown at $T_g = 520°C$, under optimized conditions, had the smallest FWHM value of 10.8 meV and the strongest PL peak intensity.

Acknowledgments

The author appreciates Dr. L.P. Sadwick and Dr. G.B. Stringfellow for their technical supports during the work.

References

1. D. BISWAS, N. DEBBAR, P. BHATTACHARYA, M. RAZEGHI, M. DEFOUR and F. OMNES, *Appl. Phys. Lett.* **56** (1990) 833.
2. H. TANAKA, Y. KAWAMURA, S. NOJIMA, K. WAKITA and H. ASAHI, *J. Appl. Phys.* **61** (1987) 1713.
3. G. B. STRINGFELLOW, *J. Electron. Mater.* **17** (1988) 327.
4. D. A. BOHLING, C. A. ABERNATHY and K. F. JENSEN, *J. Cryst. Growth* **136** (1994) 118.
5. G. B. STRINGFELLOW, "Organometallic Vapor Phase Epitaxy: Theory and Practice" (Academic Press, Boston, 1989).
6. *Idem., J. Cryst. Growth* **105** (1990) 260.
7. G. HINCELIN, M. ZAHZOUH, R. MELLET and A. M. POUGNET, *ibid.* **120** (1992) 119.
8. J. Ch. GARCIA, Ph. REGRENY, S. L. DELAGE, H. BLANCK and J. P. HIRTZ, *ibid.* **127** (1993) 255.
9. C. W. HILL, G. B. STRINGFELLOW and L. P. SADWICK, *J. Electron. Mater.* **24** (1995) 731.
10. R. M. KAPRE, W. T. TSANG, Y. K. CHEN, M. C. WU, M. A. CHIN and F. S. CHOA, *J. Cryst. Growth* **124** (1992) 176.
11. M. ALLOVON, J. PRIMOT, Y. GAO and M. QUILLEC, *J. Electron. Mater.* **18** (1989) 505.
12. D. BISWAS, H. LEE, A. SALVADOR and M. V. KLEIN, *J. Vac. Sci. Technol.* B **10** (1992) 962.
13. J. S. ROBERTS, G. B. SCOTT and J. P. GOWERS, *J. Appl. Phys.* **52** (1981) 4018.
14. K. OZASA, M. YURI, S. TANAKA and H. MATSUNAMI, *ibid.* **65** (1989) 2711.
15. D. S. CAO, A. W. KIMBALL, G. S. CHEN, K. L. FRY and G. B. STRINGFELLOW, *ibid.* **66** (1989) 5384.
16. J. H. QUIGLEY, M. J. HAFICH, H. Y. LEE, R. E. STAVE and G. Y. ROBINSON, *J. Vac. Sci. Technol.* B **7** (1989) 358.
17. Y. K. SU, M. C. WU, C. Y. CHUNG and K. Y. CHENG, *J. Crystal Growth* **76** (1986) 299.
18. D. J. MOWBRAY, O. P. KOWALSKI, M. S. SKOLNICK, M. C. DELONG, M. HOPKINSON and J. P. R. DAVID, *J. Appl. Phys.* **75** (1994) 2029.
19. A. TAKAMORI, T. YOKOTSUKA, K. UCHIYAMA and M. NAKAJIMA, *J. Crystal Growth* **108** (1991) 99.
20. M. ZACHAU and W. T. MASSELINK, *Appl. Phys. Lett.* **60** (1992) 2099.
21. L. C. SU, I. H. HO and G. B. STRINGFELLOW, Int. Symp. Compound., San Diego, 18–22 September 1994, p. 195.
22. M. C. DELONG, D. J. MOWBRAY, R. A. HOGG, M. S. SKOLNICK, J. E. WILLIAMS, K. MEEHAN, S. R. KURTZ, J. M. OLSON, R. P. SCHNEIDER, M. C. WU and M. HOPKINSON, *Appl. Phys. Lett.* **66** (1995) 3185.

Received 5 June
and accepted 31 October 2002