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Effects of cracker cell temperature and V/III ratio on GaInP grown by chemical beam epitaxy using TIPGa, EDMIn and TBP

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This paper reports a systematic study of the effects of the cracker cell temperature and the input V/III ratio on the growth of GaInP. GaInP epilayers were grown on GaAs (001) substrates using triisopropylgallium, ethyldimethylindium and tertiarybutylphosphine by chemical beam epitaxy. The surface morphology, growth rate, low temperature (15 K) and room temperature (300 K) photoluminescence (PL) were studied as a function of the cracker cell temperature and input V/III ratio. At an optimum cracker cell temperature and input V/III ratio, the PL spectrum showed only a strong band edge peak with a full width at half maximum of 10.8 meV.

1. Introduction

The chemical beam epitaxy (CBE) technique has been widely used for the growth of phosphorus containing III–V semiconductor compounds [1]. The CBE technique combines the advantages of organometallic vapor phase epitaxy (OMVPE) and molecular beam epitaxy (MBE). In CBE, the growth is performed under ultra high vacuum (UHV) conditions and the source is beam-like as in MBE. However, CBE uses organometallic gas sources, as in OMVPE. Since CBE does not use effusion cells for beam generation, there are no accompanying problems in beam flux control or oval defects, which can be critical problems in MBE growth [2].

In CBE growth, the choice of sources is very important since it can affect the growth process and thus the semiconductor epilayer quality and properties [3]. Trimethylindium (TMIn), triethylgallium (TEGa) and phosphine (PH_3) have been the most widely used sources for CBE growth of GaInP, In the work, triisopropylgallium (TIPGa) ethyldimethylindium (EDMIn) and tertiarybutylphosphine (TBP) were used for the growth of GaInP epilayers. The standard precursors are known to have several disadvantages. TMIn is a solid at room temperature and tends to recrystallize, resulting in a decrease in surface area over a period of a few months [4]. This leads to undesirable effects such as a non-reproducible molar flow rate. Because of these shortcomings, the alternate In precursor, EDMIn, was used in this work. EDMIn has already been shown to be an effective In source in OMVPE for the growth of InP and GaInAs [5]. TIPGa is known to have a lower pyrolysis temperature [6] and to produce epilayers with lower carbon incorporation levels than for the conventional Ga precursor, TEGa [7]. A lower pyrolysis temperature can lead to a reduction of the growth temperature, which is desirable in certain applications.

PH_3 has been the most popular phosphorus source for the growth of phosphorus—containing compounds. However, the major disadvantage of PH_3 is its high toxicity. This safety problem has led to significant efforts to develop alternative precursors, such as TBP [8], bisphosphinoethane (BPE) [9] and trisdimethylaminophosphine (TDMAP) [10]. All three alternative precursors are liquids at room temperature with acceptable vapor pressures. Liquid sources are orders of magnitude less hazardous [11].

Garcia *et al.* [12] reported the growth of $Ga_{0.5}In_{0.5}P$ using TBP by CBE with a cracker cell temperature of 850°C. They obtained high quality material with values of photoluminescence (PL) full width at half maximum (FWHM) at room temperature as low as 40 meV and were able to fabricate functional devices. In this work, the effects of input V/III ratio (hereafter referred to as V/III ratio) and cracker cell temperature on the GaInP epilayer growth were studied.

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2. Experimental details

The CBE growth of GaInP was performed in a custom-made, ultra high vacuum CBE chamber equipped with a 2200 l/s, LN_2 trapped diffusion pump. The source materials, TIPGa, EDMIn and TBP were contained in bubblers kept at room temperature. The group III gas injection system was custom designed to operate without a carrier gas, using closed-loop pressure-controlled flow rates. The TBP flow rate was controlled by an electronic mass flow controller. Halogen lamps were used to heat the substrate. TBP was thermally cracked by a custom designed, quartz cracker cell heated by a tungsten filament. The hot zone was surrounded by a tantalum heat shield with a reference thermocouple attached. The 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 water (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 the CBE system. After growth, a Nikon-AFX Nomarski interference contrast microscope was used for the examination of surface morphology. The growth rate was determined by measuring the step height between the epilayer and the masked part of the substrate using a Sloan Dektak IIA. The composition was determined by X-ray measurements. Room temperature (RT) and low temperature (15 K) PL measurements were performed using the 488 nm line of an Ar^+ laser operating with typical power levels between 0.1 to 10 mW.

The flow rates of the TIPGa and EDMIn were between 0.07–0.074 and 0.06–0.068 sccm, respectively. The TBP flow rate was between 4–11 sccm.

3. Results and discussion

Fig. 1 shows the percent decomposition of TBP as a function of the cracker cell temperature reported by Hill *et al.* [13] using the same cracker cell design as that used in this work. TBP starts to pyrolyze at approximately 600°C and decomposes completely by about 800°C. PH_2 and P_2 are the main phosphorus species detected.

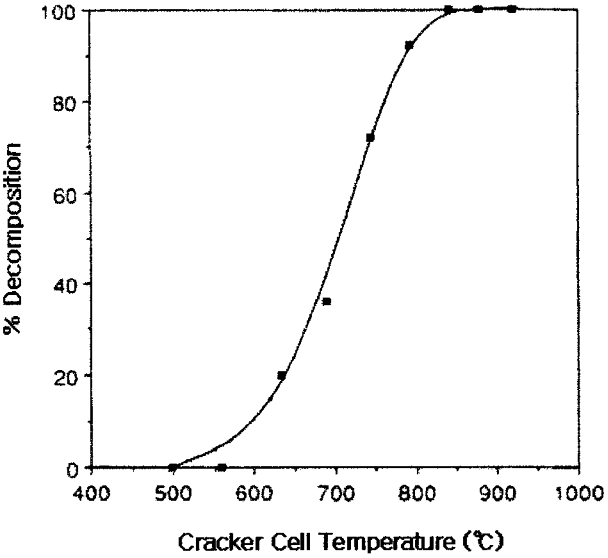

Figure 1 Percent decomposition of TBP vs. cracker cell temperature. Data from Hill *et al.* [13].

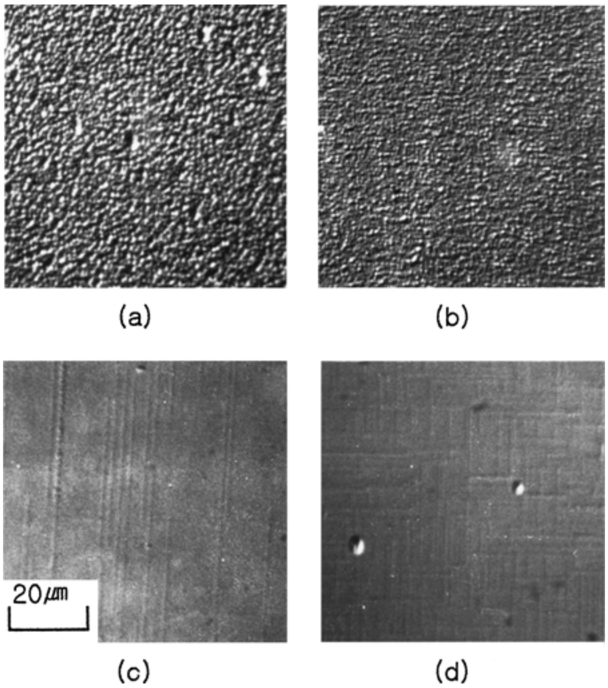

Figure 2 Surface morphologies of GaInP layers grown on (001) GaAs substrates at four different cracker cell temperatures: (a) 730°C, (b) 750°C, (c) 795°C, and (d) 830°C. $T_g = 520°C$ and V/III = 50.

Fig. 2 shows the morphologies of GaInP samples for a growth temperature of 520°C at four different cracker cell temperatures: 730, 750, 795 and 830°C. The typical epilayer thickness in this work ranged from 0.4 to 0.6 microns. It is possible that the films were either partially or fully strain relaxed. Due to the slight lattice mismatch observed in the samples, no attempt was made to investigate whether the epilayers were strained or partially or completely relaxed. The percent decomposition of TBP was calculated from Fig. 1 at the four temperatures giving values of 55, 74, 92, and 98%, respectively. The two lower cracker cell temperatures, 730 and 750°C, give rough surfaces. The poor morphologies obtained at the lower cracker cell temperatures are thought to be due to the incomplete pyrolysis of the TBP source, resulting in group III rich epilayers. Decreasing the cracker cell temperature beyond a certain point has a similar effect on the surface morphology as decreasing the V/III ratio. There is not a significant difference between the two samples grown at cracker cell temperatures of 795 and 830°C. However, at 830°C, the sample has a slightly cross hatched surface due to a slight unintentional lattice mismatch possibly resulting from slight run-to-run changes in other growth parameters and conditions.

The dependence of the growth rate on the cracker cell temperature, T_c, is shown in Fig. 3 for two different growth temperatures, 480 and 520°C. GaP epilayers were also grown at 480°C. As seen in Fig. 3, the growth rates for both GaP and GaInP decrease as the cracker cell temperature increases. The dependence of the growth rate on the V/III ratio is shown in Fig. 4. The growth rate also decreases with increasing V/III

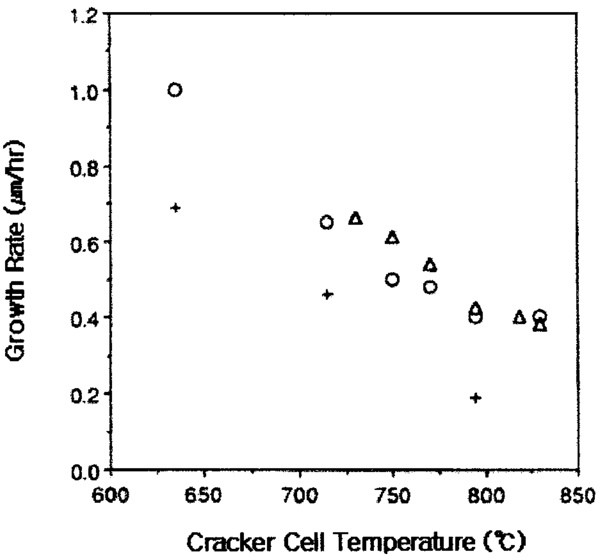

Figure 3 Growth rate dependence on cracker cell temperature. (+)GaP, $T_g = 480°C$. (○) GaInP, $T_g = 480°C$. (△) GaInP, $T_g = 520°C$.

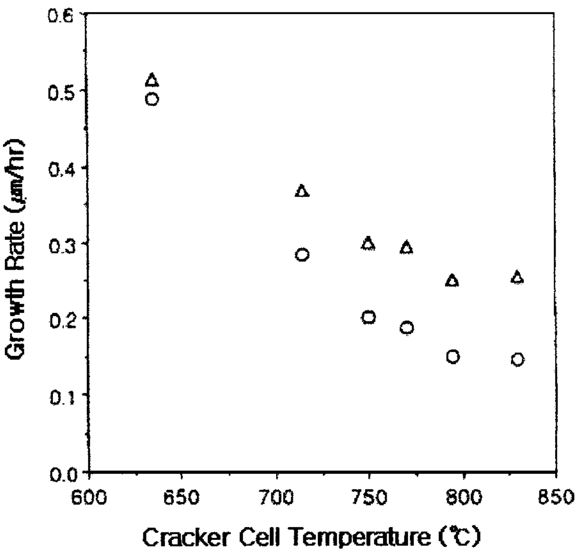

Figure 5 The quasi-binary growth rates of (△) GaP and (○) InP as a function of the cracker cell temperature at $T_g = 480°C$.

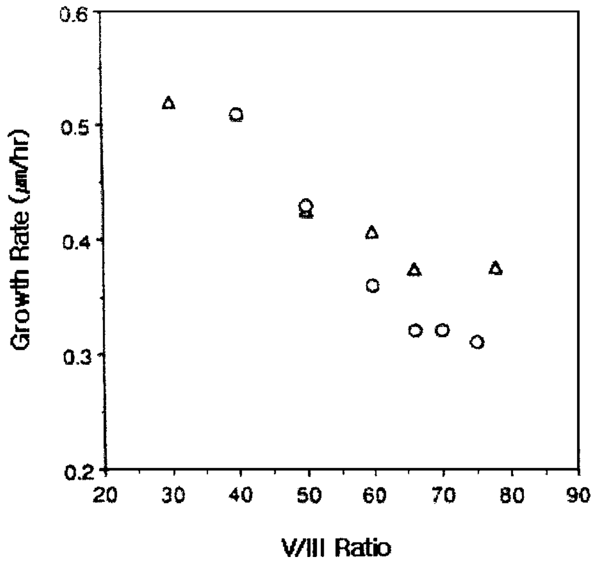

Figure 4 The growth rate of GaInP at two different growth temperatures as a function of the V/III ratio. (○) $T_g = 480°C$ and (△) $T_g = 520°C$. $T_c = 795°C$.

ratio. The decrease of the growth rate as the cracker cell temperature or V/III ratio increases is possibly due to a site blocking effect [14]. As the cracker cell temperature or V/III ratio increases, more TBP intermediate species arrive on the growing surface. The increased number of intermediate species on the growth surface possibly hinders absorption of gallium and indium. The site blocking effects on growth rate for CBE growth of GaAs and GaInAs were reported in several papers [14–16]. The data reported here follows the trend observed in these references. It is also possible that hydrogen from the decomposition of the TBP could react with Ga and/or In resulting in the creation of volatile hydrides. This would also be consistent with the data in Fig. 5 as indium hydride should be the more volatile of the two binary compounds. Both explanations are plausible and consistent with the observed experimental results.

As the cracker cell temperature increases, the relative Ga concentration increases in the GaInP epilayer. Fig. 5 shows the dependence of the quasi-binary growth rates of GaP and InP on the cracker cell temperature. The GaP and InP quasi-binary growth rates were calculated as the total growth rate multiplied by the appropriate mole fraction in the solid. Both the GaP and InP quasi-binary growth rates decrease with increasing cracker cell temperature; however, the InP growth rate decreases more rapidly, which effectively increases the Ga concentration in the $Ga_xIn_{1-x}P$ epilayer.

Fig. 6 shows the 15 K PL spectra for the samples grown at a temperature of 520°C for several different cracker cell temperatures. The growth temperature, T_g, is a very important parameter in obtaining high quality GaInP. The PL properties improves at $T_g = 520°C$ compared to $T_g = 480°C$. As can be seen from Fig. 6, the PL spectra are strongly dependent on the cracker cell temperature. At a cracker cell temperature of 730°C, only an impurity related peak is observed. At $T_c = 750°C$, a weak band edge peak appears. At $T_c = 795°C$, the impurity peak disappears but reappears at $T_c = 830°C$. The energy separation between the band edge peak and the impurity peak for a laser power of 1 mW is about 30 meV for the sample grown at $T_c = 830°C$. However, when the laser power is reduced to 0.1 mW, the energy separation increases to about 37 meV. The impurity peak shifts to lower energy as the laser power decreases, while the band edge peak position does not change. This behavior is known to be a characteristic of donor acceptor pair (DAP) recombination [17].

The dominance of the impurity peak for low cracker cell temperatures is probably due to the incomplete pyrolysis of the TBP. Since hydrogen atoms from the PH_2 radical may help remove carbon containing species from the surface of the epilayer, the incomplete pyrolysis may increase impurity incorporation. In addition, the incorporation of impurities residing on the group V lattice is known to be enhanced at low group V partial pressures [11]. The impurity peak at $T_c = 830°C$ is probably due to an impurity from the TBP source or, perhaps, carbon.

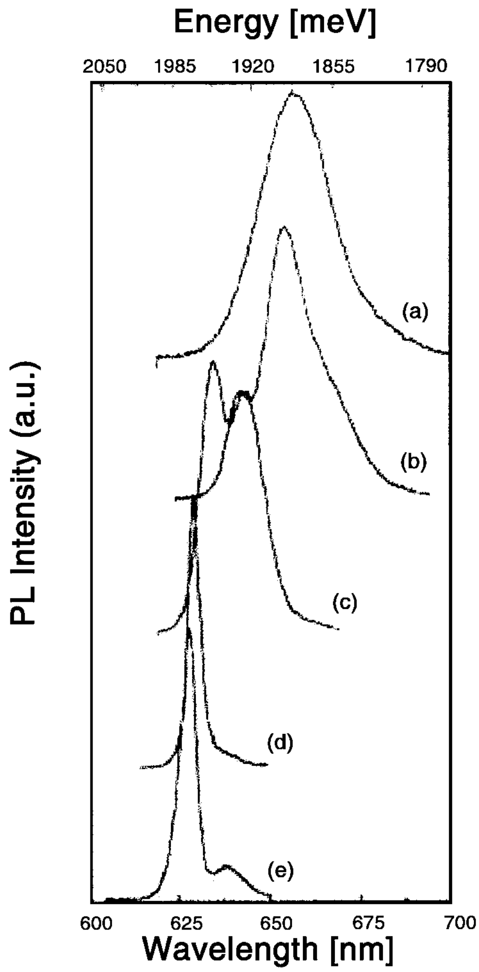

Figure 6 15 K photoluminescence spectra using a laser power of 0.1 mW at several cracker cell temperatures: (a) 730°C, (b) 750°C, (c) 770°C, (d) 795°C, and (e) 830°C. $T_g = 520°C$ and V/III = 50.

Fig. 7 shows the 15 K PL full width at half maximum (FWHM) as a function of the cracker cell temperature for $T_g = 480$ and 520°C. For $T_c = 795°C$, the values of FWHM are the smallest for both growth temperatures.

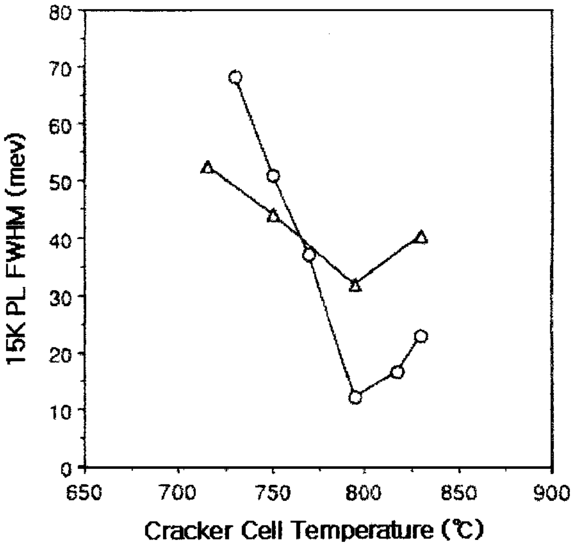

Figure 7 15 K photoluminescence full width at half maximum (FWHM) at two different growth temperatures as a function of the cracker cell temperature: (△) $T_g = 480°C$ and (○) $T_g = 520°C$. The Ar$^+$ laser power was 0.1 mW.

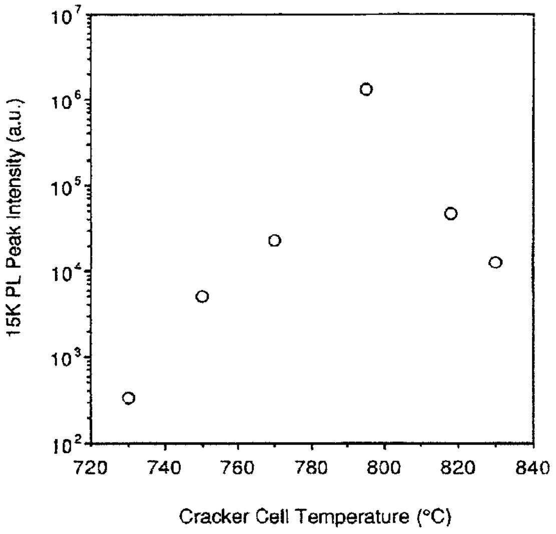

Figure 8 15 K photoluminescence peak intensity as a function of the cracker cell temperature. $T_g = 520°C$ and V/III = 50. The Ar$^+$ laser power was 0.1 mW.

Fig. 8 shows the PL peak intensity dependence on the cracker cell temperature for a growth temperature of 520°C. The strongest PL intensity was obtained for the sample that also had the narrowest FWHM value. This suggests that at non-optimum cracker cell temperatures, the layer quality is poor because of high unintentional impurity concentrations.

Fig. 9 shows the low temperature (15 K) PL spectra for the closely lattice matched GaInP samples grown at several V/III ratios between 30 and 78, at a growth temperature of 520°C and a cracker cell temperature of 795°C. For V/III ratios of 30 and 40, only a broad impurity peak is observed. As discussed above, this is probably due to insufficient phosphorus species on the growth surface and is consistent with the poor morphology and the lack of a room temperature (RT) PL signal as discussed below. For V/III ratios of 50 and above, only a sharp and narrow band edge peak is observed. The peak energy for a V/III ratio of 50 is shifted to a slightly higher energy due to a slight increase in the Ga composition of the solid, although all layers are nearly lattice matched as determined by X-ray measurements.

Fig. 10 shows the 15 K PL FWHM of the GaInP epilayers as s function of the V/III ratio. The narrowest peak is obtained for a V/III ratio of 50. The broader peaks for samples grown at V/III ratios of 30 and 40 (Fig. 9) are due to impurity related recombination as discussed above. The FWHM value is relatively constant above a V/III ratio of 50. The smallest value of FWHM is 10.8 meV, obtained for the growth conditions: $T_g = 520°C$, $T_c = 795°C$, and V/III = 50. Ozasa *et al.* [18] reported a value of 15.5 meV at 77 K for GaInP by CBE using TEGa and PH_3. The FWHM value of 10.8 meV reported here compares favorably with OMVPE results of 7.2 meV at 10 K [19]. GSMBE of 11 meV at 10 K [20], LPE of 10.6 meV at 14 K [21] and MBE of 6.7 meV at 4.2 K [22].

Fig. 11 shows the dependence of the 15 K PL peak intensity on the V/III ratio. The trend is similar to that observed in Fig. 10. The intensity is very weak for the lower V/III ratios. For V/III ratios of 50 and above, the

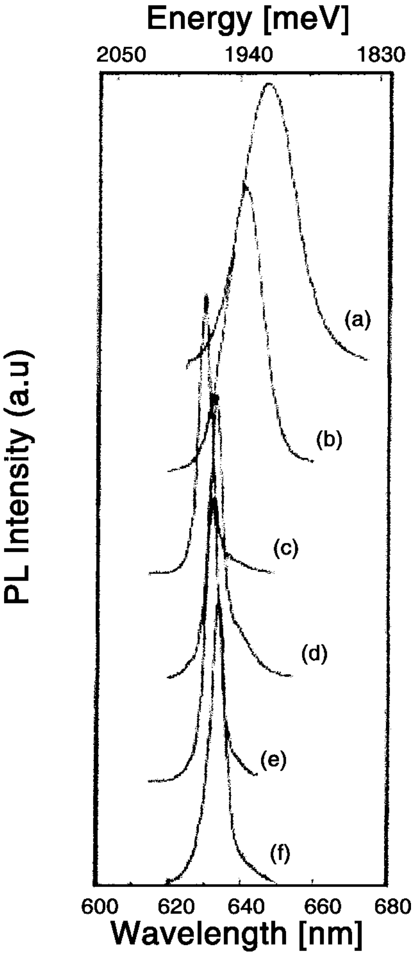

Figure 9 15 K photoluminescence spectra using a laser power of 0.1 mW at several V/III ratios: (a) 30, (b) 40, (c) 50, (d) 60, (e) 66 and (f) 78. $T_g = 520°\text{C}$ and $T_c = 795°\text{C}$.

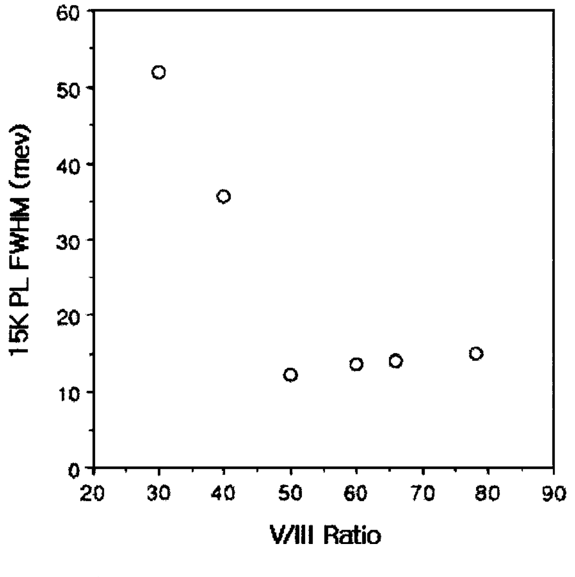

Figure 10 15 K photoluminescence full width at half maximum (FWHM) as a function of the V/III ratio. $T_g = 520°\text{C}$ and $T_c = 795°\text{C}$. The Ar^+ laser power was 0.1 mW.

intensities are similar. Quigley *et al.* [20] also reported very weak or no PL for low V/III ratios.

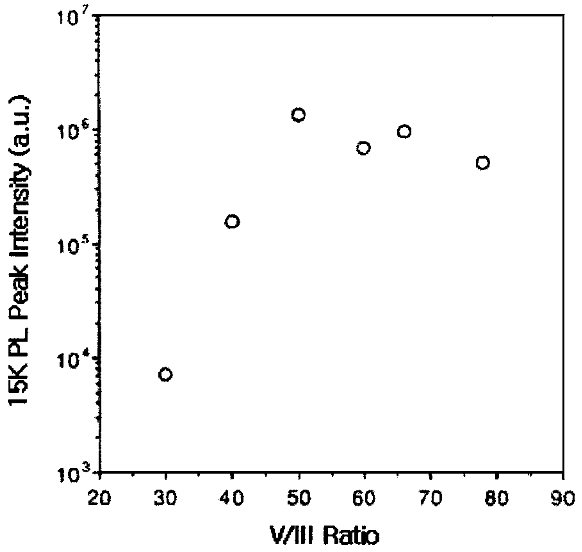

Figure 11 15 K photoluminescence peak intensity as a function of the V/III ratio. $T_g = 520°\text{C}$ and $T_c = 795°\text{C}$. The Ar^+ laser power was 0.1 mW.

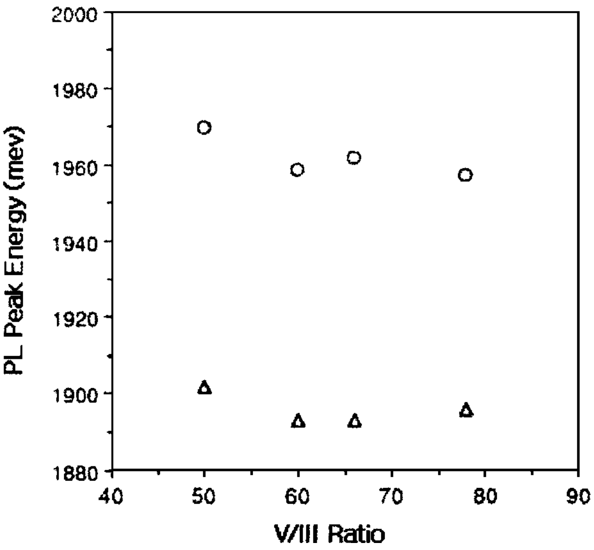

Figure 12 Room temperature and 15 K photoluminescence peak energy (meV) as a function of the V/III ratio: (△) room temperature and (○) 15 K. $T_g = 520°\text{C}$ and $T_c = 795°\text{C}$.

300 K (RT) PL was also measured. Fig. 12 shows the RT PL peak energy and 15 K PL band edge peak position for the lattice matched GaInP samples grown at 520°C for several V/III ratios. No RT PL is detected for V/III ratios below 50. The RT PL peak energies for the lattice matched GaInP samples grown at a V/III ratio of 50, 60, 66 and 78 are 1902, 1893, 1893 and 1896 meV, respectively. The 15 K PL peak energies are 1970, 1959, 1962 and 1957 meV, respectively. The low temperature PL peak energy of the lattice matched disordered GaInP is known to be 2.0 eV [23, 24]. Thus, the 15 K PL peak energy of the lattice matched GaInP epilayers from this study is about 30–40 meV lower than the reported value for disordered GaInP. This indicates some degree of ordering in the samples obtained in this study.

4. Conclusions

GaInP epilayers were grown on GaAs (001) substrates using triisopropylgallium, ethyldimethylindium and tertiarybutylphosphine by chemical beam epitaxy.

A study was performed to find the optimum cracker cell temperature for CBE growth of high quality GaInP. At lower cracker cell temperatures, the morphology was poor because of the incomplete pyrolysis of the TBP. As the cracker cell temperature increased, both the GaInP and GaP growth rates decreased, possibly due to site blocking effects or creation of volatile hydrides. For GaInP, the quasi-binary growth rates of both GaP and InP decreased as the cracker cell temperature increased. The InP quasi-binary growth rate decreased faster than that of GaP which resulted in an increase of the Ga concentration in $Ga_xIn_{1-x}P$ as the cracker cell temperature increased. Low temperature PL measurements clearly show the effects of the cracker cell temperature on the GaInP sample quality. At cracker cell temperatures of 730 and 750°C, impurity peaks were dominant and the epilayer quality was poor, presumably due to the incomplete pyrolysis of TBP. As the cracker cell temperature increased above 750°C, the band edge peak started to dominate. At a cracker cell temperature of 795°C, the optimum value in this work, only a sharp band edge peak was observed. At this temperature, the intensity of the band edge PL peak was a maximum and the FWHM was a minimum.

The effects of the V/III ratio on the quality of TBP-grown GaInP were, in many ways, similar to the effects of cracker cell temperature. A low V/III ratio led to poor morphologies and weak, impurity dominated, broad PL spectra. As the V/III ratio increased, the GaInP growth rate decreased, again, possibly due to site blocking effects or creation of volatile hydrides. For V/III ratios of 50 and above, band edge emission dominated the PL spectra. The optimum V/III ratio in this study was 50. The narrowest FWHM value from this work was 10.8 meV from the sample grown at $T_g = 520°C$, $T_c = 795°C$ and a V/III ratio of 50.

Acknowledgments

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