Chemical Beam Epitaxial Growth of InP and GaP by Using Tertiarybutylbis (Dimethylamino) Phosphine

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We report the growth of indium phosphide (InP) by using a chemical beam epitaxy (CBE) technique with the group V source tertiarybutylbis (dimethylamino) phosphine (TBBDMAP). The photoluminescence spectra at 15 K showed that the intensity of a peak attributed to impurity recombination and the FWHM increased significantly when the cracker temperature exceed 545 °C. This paper also reports the growth of GaP without precracking of the TBBDMAP source. While it was not possible to grow InP at 450 °C, GaP was successfully grown at temperatures as low as 410 °C, possibly due to the higher Ga-P bond strength which gives a longer TBBDMAP residence time on the surface before desorption. In this study, ethyldimethylindium (EDMIn) and triisopropylgallium (TIPGa) were used as the indium (In) and the gallium (Ga) sources, respectively.

I. INTRODUCTION

In chemical beam epitaxial (CBE) technique, growth is performed under ultra high vacuum (UHV) conditions and the source is beam-like similar to the MBE (molecular beam epitaxy) technique. Thus, there are no flow pattern or gas reaction problems as there are in OMVPE (organometallic vapor phase epitaxy). Since CBE uses organometallic sources, the growth rate dependence on the growth temperature is similar to, yet more complicated than that of OMVPE [1]. Phosphine (PH_3) has been the most commonly used phosphorus (P) source for CBE growth. However, the use of PH_3 requires extreme care due to the toxic nature of PH_3 [2]. Significant effort has been devoted to developing safer P sources. There have been several candidates for P sources, including tertiarybutylphosphine (TBP) [3,4], bisphosphinoethane (BPE) [5], trisdimethylaminophosphine (TDMAP) [6], and tertiarybutylbis (dimethylamino) phosphine (TBBDMAP) [7]. All four of these precursors are liquids at

room temperature with acceptable vapor pressures. The liquid sources are orders of magnitude less hazardous due to the slow dispersion relative to PH_3 stored in high pressure cylinders [1].

Indium phosphide (InP) has been widely used for various applications [8–10]. For the growth of InP by CBE, precracking of the group V sources, such as PH_3 [11], TBP [12], BPE [13], and TDMAP [14], is required. Since the group V sources PH_3 and TBP have very strong P-hydrogen and P-R (tertiarybutyl radical) bonds, the residence time of the group V source on the heated substrate is not enough to allow complete pyrolysis. The semiconductor epilayer quality is known to be highly sensitive to the cracker cell temperature [12]. While precracking of the group V sources mentioned above is required for InP growth by CBE, it is known that an InP epilayer can be grown by using CBE without thermal precracking of the TBBDMAP source [7]. Precracking elimination can remove very expensive cracker cell and defects from a heated cracker cell. It also reduces the thermal cross-talk between a heated cracker and manipulator/other cells, and the complexity of the CBE growth apparatus.

In this study, mainly the effects of cracker cell tem-

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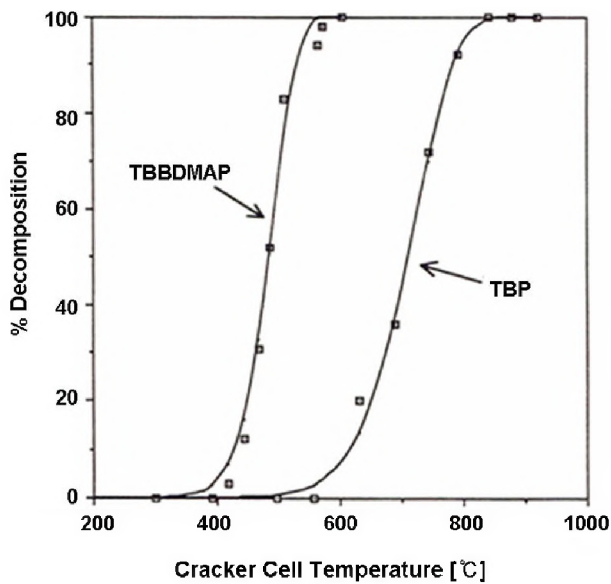Tel: +82-55-320-3874; Fax: +82-55-320-3631

Fig. 1. Percent decomposition of TBBDMAP and TBP versus cracker cell temperature.

perature for InP growth using a group V source, TBB-DMAP, are discussed. The growth of gallium phosphide (GaP) is also briefly reported. Ethyldimethylindium (EDMIn) and triisopropylgallium (TIPGa) were used as indium (In) and gallium (Ga) sources, respectively.

II. EXPERIMENTS

The growths of InP and GaP were performed in a custom-designed, ultra high vacuum CBE chamber equipped with a 2200 liter/s diffusion pump. In this study ethyldimethylindium (EDMIn) and triisopropyl-gallium (TIPGa) were used as indium (In) and gallium (Ga) sources, respectively. TBBDMAP is a liquid with a vapor pressure of 1.8 Torr at 25 °C [15]. The flow rates of EDMIn, TlPGa, and TBBDMAP were typically 0.035, 0.04 ~ 0.06 and 0.251 ~ 0.5 sccm, respectively.

Low temperature (15 K) photoluminescence (PL) measurements were performed using the 488-nm line of an Ar$^+$ laser operating with typical power levels between 0.1 to 10 mW. Hall effect measurements were performed to determine the electrical properties of the InP epilayers. X-ray diffraction measurement was also done for verifying GaP growth on the GaAs (001) substrate.

III. RESULTS AND DISCUSSION

Figure 1 shows the percent decomposition as a function of the cracker cell temperature for TBP and TBB-DMAP [16]. TBBDMAP pyrolyzes at much lower temperatures. The values of T_{50}, the temperature at which
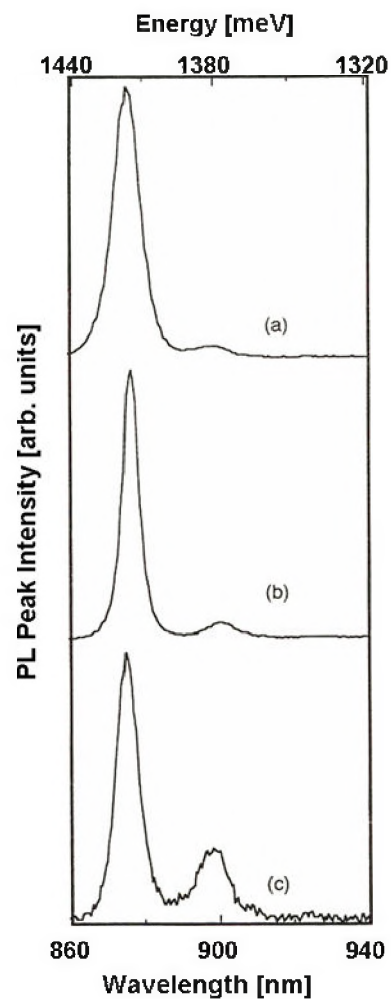

Fig. 2. Low-temperature (15 K) PL spectra for InP at three different cracker cell temperature, (a) $T_c = 87$ °C, (b) $T_c = 545$ °C and (c) $T_c = 640$ °C, at $T_g = 510$ °C for V/III = 7.2 and for an Ar$^+$ laser power of 1 mW.

the source is 50 % pyrolyzed, for TBBDMAP and TBP are 475 °C and 700 °C, respectively. For GaInP growth using a TBP source, precracking of the TBP source was necessary [12]. High-quality GaInP could be grown at a cracker temperature of 795 °C. However, high impurity peaks were found from 15-K PL measurements for lower cracker cell temperatures (below 770 °C) due to the incomplete pyrolysis of the TBP. While precracking the TBP source is required, the TBBDMAP source can be used for InP growth without precracking, possibly due to the much lower pyrolysis temperature, as can be seen from Figure 1. A lower pyrolysis temperature could also be desirable because it can lead to a reduction of the growth temperature, which is useful in certain applications. The pyrolysis behavior of TBBDMAP seen in Figure 1 indicates potential use of this material for the epitaxial growth of InP layers.

InP was grown on (001) semi-insulating InP substrates at values of the growth temperature, T_g, between 450 °C
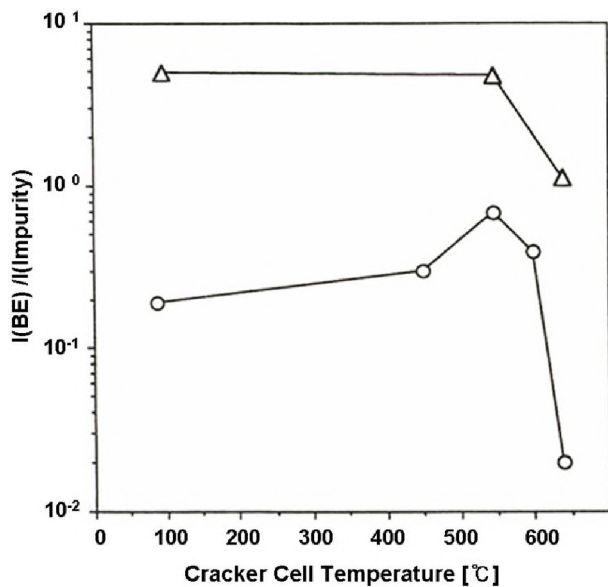
Fig. 3. Low-temperature (15 K) PL intensity ratio of the band-edge to the impurity-related peaks as a function of the cracker cell temperature for InP grown at (○) 480 °C and (△) 510 °C for V/III = 7.2 and an Ar$^+$ laser power of 0.1 mW.
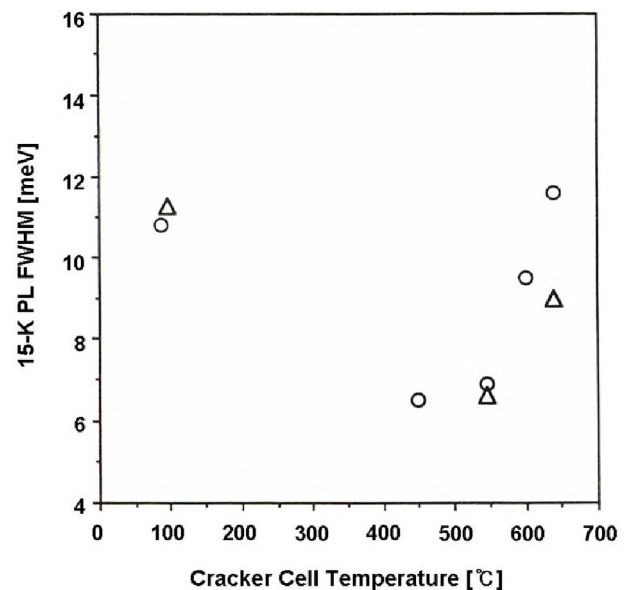

Fig. 4. Low-temperature (15 K) PL full width at half maximum (FWHM) for InP at two growth temperatures, (○) T_g = 480 °C (△) T_g = 510 °C, as a function of the cracker cell temperature for V/III = 7.2 for an Ar$^+$ laser power of 0.1 mW.

and 530 °C. For T_g = 480 °C and 510 °C, InP epilayers with smooth morphologies were grown without precracking the TBBDMAP while In-rich surfaces were observed from the samples with T_g = 450 °C and 530 °C due to the incomplete pyrolysis of the TBBDMAP source and the rapid desorption of P from the surface, respectively. The details of the InP epilayer growth by using the CBE technique with / without precracking the TBBDMAP have been published elsewhere [7].

The 15-K PL was found to be a function of cracker cell temperature. Figure 2 shows the 15-K PL spectra of the InP epilayers grown at T_g = 510 °C with three different cracker cell temperatures, 87 °C, 545 °C and 640 °C. The cracker cell temperature of 87 °C is due to the heat from the substrate heater with no power applied to the cracker cell heater. The PL spectra were found to consist of two peaks, a high energy peak due to neutral donor bound exciton (D^{0}X) recombination and a peak at ~37 meV below the D^{0}X peak due to the neutral donor to neutral acceptor transition (D^{0}A^0) [17, 18]. As the cracker cell temperature was increased from 545 °C to 640 °C, the D^{0}A^0 peak intensity increased. A similar result was found as the V/III ratio was increased [7]. This suggests that the D^{0}A^0 peak is most likely associated with the TBBDMAP source. Secondary ion mass spectroscopy (SIMS) measurements indicate that sulfur (S) and carbon are the major donor impurities in the InP epilayers grown in this study, even though carbon was reported as an acceptor in an earlier paper [7]. Carbon is known to be a group-III substitutional donor in InP epilayers [18,19]. The InP epilayers were all N-type. The lowest carrier concentration, 5.2 × 10^{16} cm^{-3}, at room temperature was measured for a sample grown at T_g =

510 °C and T_c = 545 °C with a V/III ratio of 7.2.

Figure 3 shows the 15-K PL intensity ratio of the D^{0}X peak to the D^{0}A^0 peak as a function of the cracker cell temperature for two growth temperatures, 480 °C and 510 °C. For T_g = 480 °C, the intensity ratio increased as the cracker cell temperature increased from 87 °C and 545 °C. It then decreased significantly for cracker cell temperatures above 545 °C. For T_g = 510 °C, the intensity ratio of a sample grown at T_c = 87 °C was similar to that of the sample grown with a cracker cell temperature of 545 °C. However, as the cracker cell temperature was increased further to 640 °C, the intensity ratio decreased significantly, similar to the data for T_g = 480 °C. As seen from Figure 3, the intensity ratios of all samples grown at T_g = 510 °C are higher than that of those grown at T_g = 480 °C. The effect of the cracker cell temperature on the full width at half maximum (FWHM) of the 15-K PL band edge peak is shown in Figure 4 for T_g = 480 °C and 510 °C. The FWHM is near a minimum for cracker cell temperatures near 545 °C with significant increases at both higher and lower cracker cell temperatures. There is no significant difference in FWHM between the samples grown at temperatures of 480 °C and 510 °C. In this experiment, the FWHM and the carrier concentration values are minimum for T_c = 545 °C, T_g = 510 °C and V/III = 7.2.

GaP epilayers were grown on (001)-oriented GaAs semi-insulating substrates without precracking the TBBDMAP, as verified by X-ray diffraction measurements (Figure 5). While it was not possible to grow InP at a growth temperature of 450 °C [7], GaP was grown at growth temperatures as low as 410 °C. This marked dif-
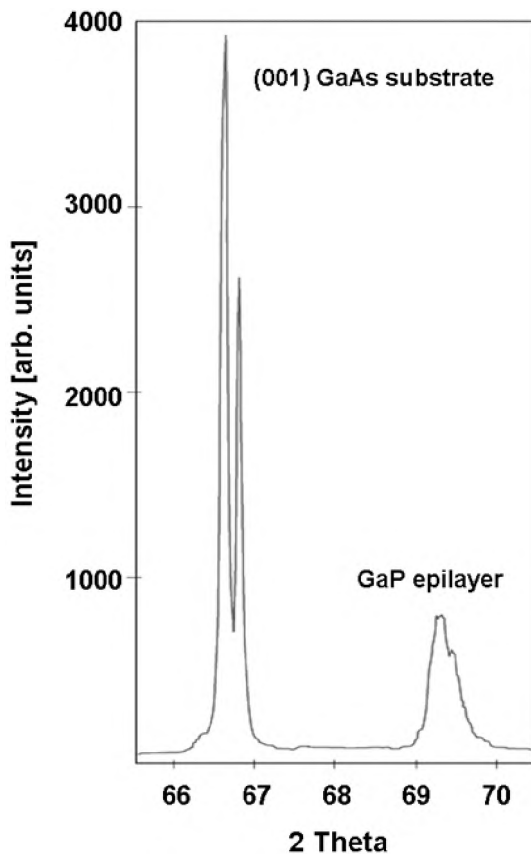
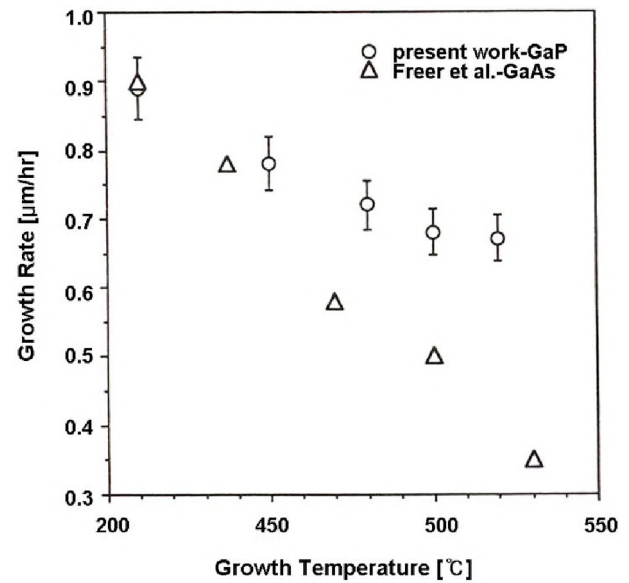Fig. 5. X-ray scan for GaP epilayer grown on (001) GaAs substrate.

Fig. 6. GaP growth rate versus temperature. Previously reported GaAs growth rate data [16] are included for comparison. The flow rates of TIPGa and TBBDMAP were 0.06 and 0.5 sccm, respectively, giving an input V/III ratio of 8.3.

ference between the behavior of GaP and InP is probably due to the longer residence time of TBBDMAP on the GaP surface before desorption than on the InP surface because of the larger Ga-P bond strength. Figure 5 shows the GaP growth rate as a function of growth temperature. As seen in Figure 6, the growth rate decreased as the temperature increased from 410 °C to 520 °C. This result is similar to the result reported by Freer *et al.* [20] for GaAs grown by CBE with TIPGa and arsine (AsH$_3$), which is also plotted in Figure 6. Using the modulated beam mass spectrometry technique, Freer et al. determined that the desorption of di-isopropylgallium was primarily responsible for the reduction of the growth rate.

IV. CONCLUSION

In this study, InP epilayers were grown using CBE with a TBBDMAP source. This was accomplished at growth temperatures of 480 °C and 510 °C for a V/III ratio of 7.2. The effects of the cracker cell temperature on InP growth and on the optical properties of InP were studied for a constant V/III ratio of 7.2. The 15-K PL spectra showed that the intensity of a peak attributed to impurity recombination and the FWHM increased signif-

icantly when the cracker temperature exceeded 545 °C. SIMS measurements suggest that the donors are sulfur and carbon.

GaP epilayers were also grown on (001) GaAs substrates. While it was not possible to grow InP at 450 °C, GaP was successfully grown at temperatures as low as 410 °C. The difference between the GaP and the InP growth can be explained by the higher Ga-P bond strength, which gives a longer TBBDMAP residence time on the surface before desorption. The GaP growth rate decreased as the growth rate decreased, probably due to the desorption of di-isopropyl gallium before pyrolysis.

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