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Chemical beam epitaxial growth of GaInP using uncracked trisdimethylaminophosphine

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Abstract Gallium indium phosphide ($Ga_xIn_{1-x}P$) epitaxial layers were grown on GaAs substrates by chemical beam epitaxy (CBE) without thermally precracking the group V precursor. Trisdimethylaminophosphine (TDMAP), triisopropylgallium (TIPGa), and ethyldimethylindium (EDMIn) were used as the phosphorus, gallium and indium sources, respectively. $Ga_xIn_{1-x}P$ was grown without group V precracking for substrate temperatures in the range of 400–520 °C. Above 500 °C, the epilayers had a hazy appearance presumably due to being phosphorus deficit. A strong solid composition dependence on substrate temperature was observed. The samples were In-rich at low growth temperatures and Ga-rich at high growth temperatures. It was possible to grow the $Ga_xIn_{1-x}P$ epilayers over a large composition range with good morphology and strong photoluminescence. Values of full width at half maximum were as low as 45 meV at 14 K photoluminescence measurements.

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Introduction

$Ga_{0.5}In_{0.5}P$ lattice matched to GaAs has been recognized as an attractive alternative to AlGaAs as a wide direct band gap semiconductor for heterostructures. The significant advantages of GaInP compared to AlGaAs are a large valence band discontinuity [1], lower reactivity with carbon and oxygen, and a lower deep level concentration [2]. Phosphine (PH_3) has been the most popular phosphorous source for the growth of phosphorus-containing compounds. Several published papers on GaInP grown by CBE using cracked PH_3 demonstrated the ability to produce high purity layers [3–6]. Ozasa et al. [3] reported values of 77 K photoluminescence (PL) full width at half maximum (FWHM) as low as 15.5 meV for $Ga_{0.5}In_{0.5}P$ having a carrier concentration of 1.5×10^{15} cm^{-3}. However, the toxicity of PH_3 has led researchers to explore alternate sources, such as tertiarybutylphosphine (TBP) [7], bisphosphinoethane (BPE) [8, 9] and trisdimethylaminophosphine (TDMAP) [10–12], all of which are liquids at room temperature with acceptable vapor pressures, which makes them orders of magnitude safer than PH_3 [7].

The decomposition properties of the group III precursors play a major role in the dependence of the growth rate on substrate temperature and unintentional impurity incorporation [13]. Although trimethylindium (TMIn) and triethylidium (TEIn) are commonly used indium precursors in CBE and OMVPE, they are known to have shortcomings. 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 [14]. This leads to undesirable effects such as a nonreproducible molar flow rate. TEIn is known to have a tendency to

decompose in the bubbler during storage [15]. Because of these shortcomings, an alternate In precursor, ethyldimethylindium (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 [15, 16], and in CBE for the growth of InP [11].

Triisopropylgallium (TIPGa) is known to have both a lower pyrolysis temperature and lower carbon incorporation levels than the conventional Ga precursors triethylgallium (TEGa) and trimethylgallium (TMGa) [17]. A lower pyrolysis temperature can lead to a reduction of the growth temperature, which is desirable in certain applications.

In this work, $Ga_xIn_{1-x}P$ epitaxial layers were grown on GaAs substrates by chemical beam epitaxy (CBE) without thermally precracking the group V precursor. In general, the exact conditions of the precraking for the group V precusor is known to have a large impact on the growth of III–V semiconductors including GaInP on GaAs substrates [18]. Precise control of cracker cell temperature is required for high quality growth. So, the removal of the cracker cell from the growth system can lead to easier growth control. In addition, the necessity to crack the group V source adds additional complexity and cost to the growth process. The intention of this work was to study the possibility and characteristics of growing GaInP without using a group V cracking cell. TDMAP, TIPGa and EDMIn were used as the phosphorus, gallium and indium sources, respectively. The effects of the growth temperature on the growth rate of GaInP epilayers were discussed.

Experimental details

GaAs (001) oriented semi-insulating substrates used for the growth of GaInP were cleaned by degreasing with trichloroethane, acetone and methanol to remove any organic contamination. For each growth run, the substrate was rinsed with deionized water, dipped in sulfuric acid (H_2SO_4) for 3 min, and then dipped in A-etch solution (H_2SO_4:H_2O_2:H_2O = 4:1:1) for 4 min. The substrate was then rinsed with deionized water and blown dry with N_2 gas.

The cleaned substrate was loaded into the load-lock chamber of a custom-designed ultra high vacuum (UHV) stainless steel CBE growth chamber equipped with both ion and 2,200 l/s LN_2 trapped diffusion pumps. The group III and V gas injection systems were custom designed to operate without a carrier gas, using closed-loop pressure-controlled flow rates. Halogen lamps were used to heat the substrate. The temperature was measured with thermocouples calibrated against a thermocouple attached to the substrate holder. Before epitaxial growth, the substrate was heated under TDMAP to thermally desorb the oxide and then heated to the desired growth temperature. The group III flow was initiated to start growth. Typical chamber pressures during growth were in the 10^{-5} to low 10^{-4} torr range.

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. Low temperature (14 K) photoluminescence (PL) measurements were performed using the 488 nm line of an Ar^+ laser operating with a typical power level of between 1 mW and 100 mW.

Results and discussion

$Ga_xIn_{1-x}P$ was successfully grown directly on (001) GaAs substrate at growth temperatures between 400 °C and 520 °C without precracking the group V precursor. The growth parameters were chosen to obtain near lattice-matching compositions at a substrate temperature of 500 °C. The flow rates of undiluted TIPGa, EDMIn and TDMAP were 0.06, 0.04 and 1.0 sccm, respectively. This gave an input V/III ratio of 10. The typical epilayer thickness in this work ranged from 0.4 to 0.6 microns. Group III-rich epilayers with poor morphology were observed with lower V/III ratios. The epilayers were highly resistive, so no electrical properties are reported. Figure 1 shows typical $Ga_xIn_{1-x}P$ morphologies for several substrate temperatures. As seen, the morphology was good at substrate temperatures near 400 °C. They became rough, probably due to group III-rich conditions, at temperatures above 500 °C.

Figure 2 shows the $Ga_xIn_{1-x}P$ composition as a function of substrate growth temperature. All flow rates were unchanged for these runs. The composition was determined from both X-ray diffraction (X-ray) and electron microprobe (E.M.) measurements. Also plotted in Fig. 2 are data reported by Ozasa et al. [3] using TEGa, TEIn and PH_3, and Garcia et al. [19], using TEGa, TEIn and PH_3. Similar trends in the Ga composition are observed as a function of temperature.

The composition versus temperature data in Fig. 2 can be divided into three regions. Region I, at low temperatures, is Ga-deficient for lattice matching. At higher temperatures, in Region II, the solid composition is nearly independent of temperature. In Region

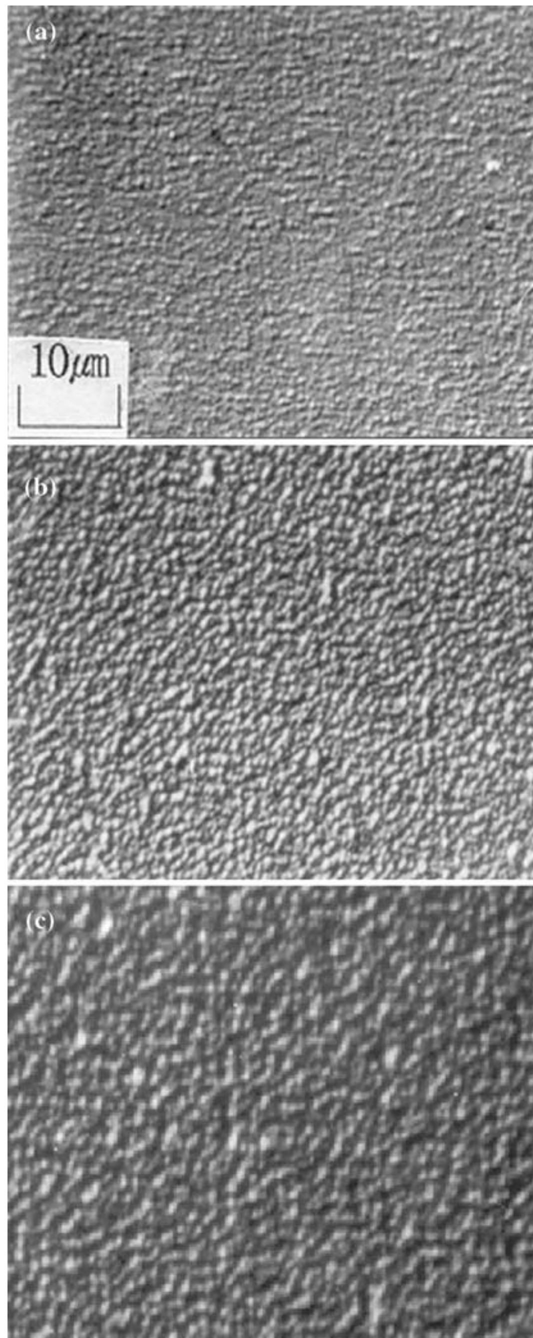

Fig. 1 Surface morphologies GaInP layers lattice matched to (001) GaAs substrates at three different growth temperatures. (**a**) 400 °C, (**b**) 460 °C, and (**c**) 520 °C. The marker represents 10 μm

III, at even higher temperatures, the Ga content increases with increasing temperature. The temperature at which the onset of Region III begins is apparently nearly independent of the source materials used. Similar results were obtained from other CBE [20], molecular beam epitaxy (MBE) [21] and gas source MBE studies [22]. The reduced In incorporation

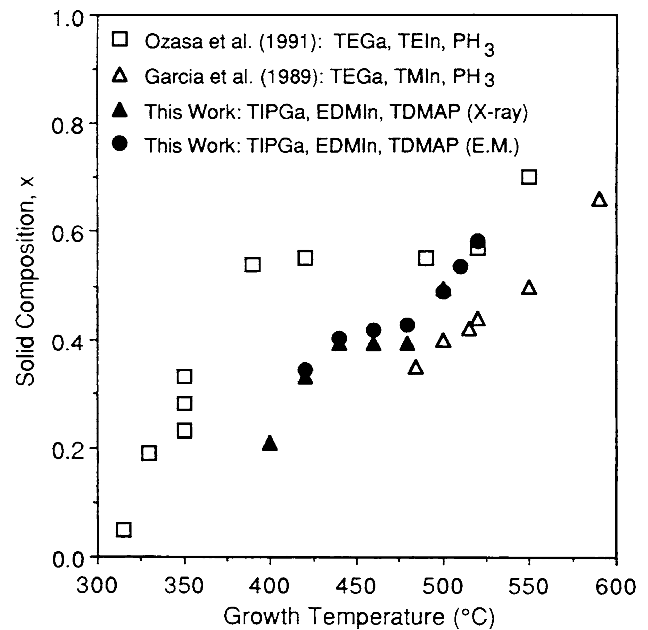

Fig. 2 Solid composition, x, versus substrate temperature. Data of Ozasa et al. [3] and Garcia et al. [19] are included for comparison

in the $Ga_xIn_{1-x}P$ films grown in region III is partially attributed to elemental In desorption. This would be expected to occur at the same temperature for all sources, because it relates to the attraction of absorbed In to the GaInP surface. This, in turn, will cause increased Ga incorporation as discussed in detail below. In Region II both the Ga and In sources are completely pyrolyzed, and the In desorption is small, resulting in epilayers having a nearly constant composition. Region II extends from 440 °C to 480 °C for the group III precursors TIPGa and EDMIn. It extends from 390 °C to 520 °C for TEGa and TEIn. Modulated beam mass spectroscopy (MBMS) studies of several Ga precursors during GaAs growth have shown that the temperature at which the peak growth rate occurs is 390 °C for TIPGa and 440 °C for TEGa [23, 24]. However, additional MBMS studies of TIPGa and TEGa in the presence of TMIn [25, 26] have shown that the decomposition of TIPGa is inhibited. This was attributed to methyl site-blocking effect. The pyrolysis temperature of TIPGa increases by 40–50 °C. The opposite effect is observed for the pyrolysis of TEGa in the presence of In precursors [25]. The results in this study are consistent with these MBMS studies in that the onset of growth for the GaP quasi-binary using TIPGa is approximately 50 °C higher than that reported by Ozasa et al. [3] using TEGa. This indicates that the transition from Region I to Region II is probably determined by pyrolysis of the Ga Precursor.

Apparently EDMIn behaves in a similar fashion to TMIn in terms of surface site-blocking of TIPGa.

Figure 3 shows the temperature dependence of the measured $Ga_xIn_{1-x}P$ growth rate and the growth rates of the constituent quasi-binaries calculated from the overall growth rate and the solid composition. The $Ga_xIn_{1-x}P$ growth rate shows a small decrease at substrate temperatures below 440 °C and is virtually constant for substrate temperatures between 440 °C and 520 °C. This result is similar to that reported by Ozasa et al. [3] where the growth rate of $Ga_xIn_{1-x}P$ using TEGa, TMIn, and PH_3 was nearly substrate temperature independent from 400 °C to 520 °C. The behavior of the GaP and InP growth rates indicates that InP growth rate is relatively constant in Region I and II and experiences a rapid decrease in region III due to In desorption, as described above. The GaP growth rate experiences a rapid increase with increasing temperatures in both Region I and III. In Region I, this is due to the pyrolysis rate of TIPGa. The increase of the GaP growth rate in Region III may be due to an increase in the Ga incorporation efficiency resulting from a decrease in the In concentration of the solid leading to a decrease in the branching ratio for Ga-alkyl desorption in comparison to Ga incorporation in the solid [25]. Thus, the overall constant growth rate of $Ga_xIn_{1-x}P$ in Region II and III observed in this work can be explained in terms of the summation of the individual GaP and InP quasi-binary growth rates with the decrease in the InP growth rate in Region III being offset by the increase in the GaP growth rate.

14 K PL data were obtained for all samples grown using substrate temperatures greater than 440 °C as shown in Fig. 4. With the exception of samples grown in the range of 460 °C and 500 °C, a strong PL peak significantly below the bandgap of both disordered and ordered GaInP was observed, presumably due to deep donor-to-acceptor (DAP) transitions. The 14 K PL peak energy for the $Ga_{0.39}In_{0.61}P$ layer grown at 480 °C was approximately 1.8 eV, which is about 50 meV lower than expected for strain-free, totally-disordered material [27]. This might be caused by either an impurity related recombination center or a reduction in the bandgap energy due to ordering [24]. It was reported that $Ga_xIn_{1-x}P$ samples grown by solid source MBE at a substrate temperature of approximately 500 °C had a bandgap considerably less than that expected for disordered material [28]. Transmission electron diffraction (TED) measurements contained weak superlattice spots indicative of CuPt ordering [28].

For the $Ga_{0.39}In_{0.61}P$ sample grown at 480 °C, discussed here, an increase in the PL peak energy of 16 meV (from 1,780 meV to 1,796 meV) for a two order of magnitude increase in PL excitation energy (1 mW to 100 mW) is consistent with results obtained on ordered GaInP grown by OMVPE [27]. $Ga_xIn_{1-x}P$ samples grown at substrate temperatures of 460 and 500 °C exhibited PL peak energies approximately

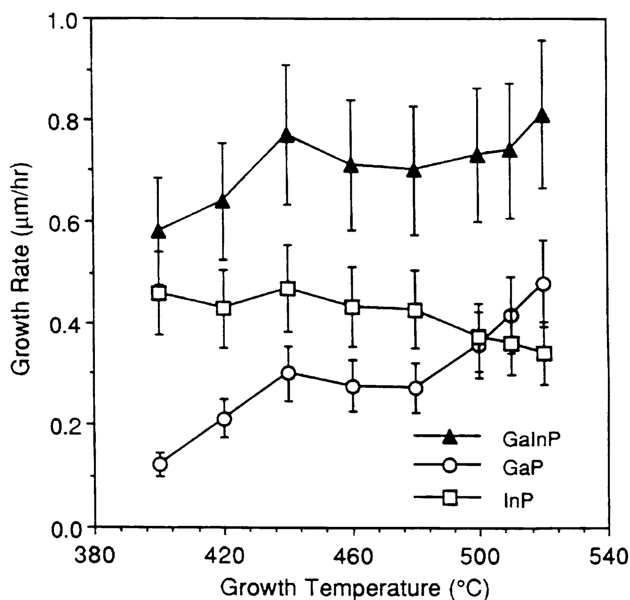

Fig. 3 Growth rate of GaInP and the quasi-binaries GaP and InP versus substrate temperature

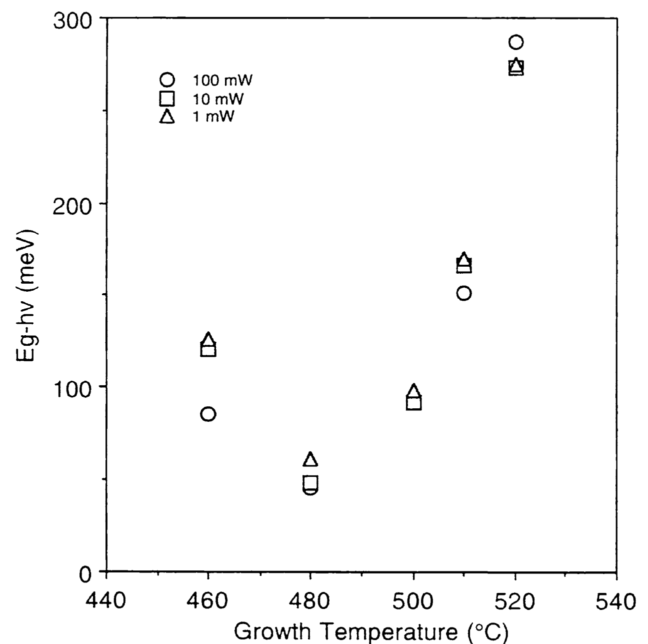

Fig. 4 Values of (Eg – hv) measured at 14 K versus growth temperature

85 meV lower than the expected bandgap value. At 520 °C, the difference between the expected bandgap and the peak PL energy increased to over 200 meV and was highly excitation dependent.

Figure 5 shows the 14 K PL FWHM plotted versus substrate temperature. In this study, the $Ga_xIn_{1-x}P$ (x = 0.39) sample grown at 480 °C had the smallest FWHM (approximately 45 meV) of the sample set and was invariant with PL excitation intensity. Note that these samples were not lattice-matched to the GaAs substrates and therefore a larger PL FWHM is to be expected. There are many published reports in the literature of GaInP PL FWHM results. These results include OMVPE growth of GaInP on GaAs with a 7.2 meV FWHM at 10 K [29], a GSMBE GaInP on GaAs PL FWHM of 11 meV at 10 K [30], a LPE GaInP on GaAs of 10.6 meV at 14 K [31] and a MBE GaInP on GaAs of 6.7 meV at 4.2 K [32].

Conclusions

In conclusion, $Ga_xIn_{1-x}P$ epitaxial layers were grown on GaAs substrates by CBE without thermally precracking the group V precursor. TDMAP, TIPGa and EDMIn were used as the phosphorus, gallium and indium sources, respectively. Growth of high quality layers occurred without precracking for substrate temperatures between 400 °C and 520 °C. Good morphology and strong PL were observed. Growth parameters were chosen so that near lattice-matching $Ga_xIn_{1-x}P$ composition was realized at 500 °C. The best optical properties were obtained at a substrate temperature of 480 °C. For substrate temperatures lower than 440 °C, the GaInP epilayers were In-rich due to incomplete pyrolysis of TIPGa. At substrate temperatures above 500 °C, the epilayers were Ga-rich due to In desorption.

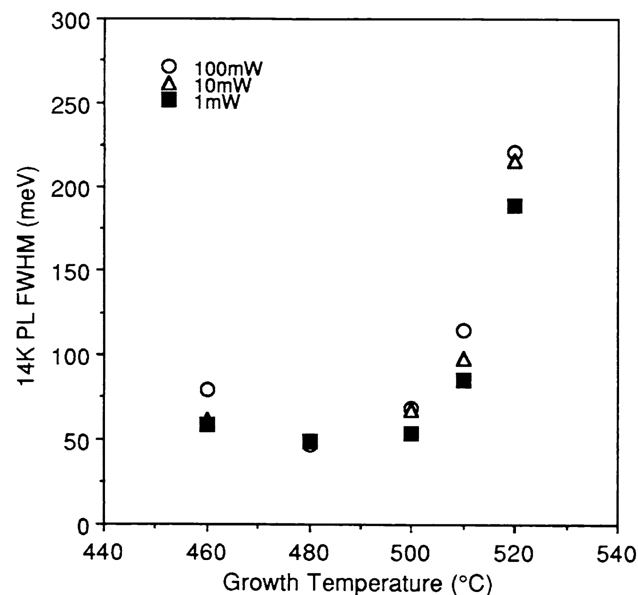

Fig. 5 Values of PL FWHM measured at 14 K versus growth temperature

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