Use of triethylindium and bisphosphinoethane for the growth on InP by chemical beam epitaxy

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We have demonstrated the first CBE growth of InP using bisphosphinoethane as a group V source. Mirrorlike surface morphology and excellent reflection high-energy electron diffraction patterns were observed. Room temperature and 77 K Hall mobilities for a 2.0 μm thick InP epitaxial layer were 4200 and 22 000 cm^2/V s, with carrier densities of 5.7×10^{15} and 4.0×10^{15} cm^{-3}, respectively. Although a high n-type impurity concentration is observed at the epitaxial layer-substrate interface, the epitaxial layer background impurity concentration is low enough for device fabrication. The full width at half maximum linewidth of the dominant donor bound exciton is 0.84 meV.

High quality InGaAsP and all its ternary and binary parent compounds are routinely grown by using gas-source molecular beam epitaxy (GSMBE),[1] chemical beam epitaxy (CBE),[2] and metalorganic chemical vapor deposition (MOCVD).[3] Unfortunately, a major obstacle to the eventual production of these materials is the use of the highly toxic compounds AsH_3 and PH_3. Other disadvantages of PH_3, in particular, are its pyrophoric nature and high temperatures required for pyrolysis. The development of new nontoxic organo-metallic sources for PH_3 is urgently needed. Tertiarybutyl phosphine (TBP) is an attractive alternative due to its low toxicity ($LC_{50} > 1100$ ppm) and excellent InP growth by MOCVD.[4] Its application in CBE, however, has not yielded films with comparable purity.[5] Another difficulty is the high vapor pressure of TBP in a liquid nitrogen cooled CBE chamber. We have observed that the chamber pressure builds to the 10^{-3} Torr level during growth, limiting the practical epilayer thickness.

A possible solution to these problems is bisphosphinoethane (BPE, PH_2-CH_2-CH_2-PH_2), a low vapor pressure (17.5 Torr at 20 °C) phosphine substitute. BPE also has only one carbon per phosphorus atom and decomposes by releasing the PH_2 units, leaving a stable C_2H_2 unit. High quality InP and laser diodes have already been demonstrated by BPE using MOCVD.[5,6] In this work we report, what is to our knowledge, the first CBE growth study of InP using BPE.

Our samples were grown in a Vacuum Generators V80H molecular beam epitaxy system (MBE) with diffusion-pumped chamber and a custom gas manifold. Both the group III and the group V metalorganics were introduced into the MBE system by means of H_2 carrier gas flow and down stream pressure control. The samples were grown on semi-insulating Fe-doped InP at substrate temperatures of 450–480 °C, as measured by infrared pyrometry. Typical growth rates for InP were 1.0 μm/h, as measured by reflection high-energy electron diffraction (RHEED) oscillations.

In situ mass spectroscopy was used to monitor BPE decomposition. With the cracker at temperatures up to 300 °C the mass spectrum was invariant and showed only the fragmentation of the BPE molecule inside the mass spectrometer. This spectrum served as a reference, allowing us to separate decomposition effects inside the cracker and fragmentation effects inside the mass spectrometer. We find that all the phosphorus species show a sharp increase as we increase the cracker temperature above ∼400 °C. At ∼400 °C, cracking of the parent molecule begins. The total amount of free phosphorus increased with cracker temperature up to 800 °C. The decomposition chemistry and the cracker temperature dependence of fragment ratios of C_2H_2/C_2H_4 or C_2H_3/C_2H_4 shows that the phosphorus species are mainly from the loss of the first PH group rather than from both PH groups. This is understandable from the high thermodynamic energy required for the loss of the second PH group. However, that these ratios increase with cracking temperature is an indication the 2nd PH group is being released. More detailed analysis will be presented elsewhere.

RHEED reconstruction pattern and RHEED oscillation measurements were performed before each growth to study InP growth dependence on temperature, triethylindium (TEI) flow, and BPE flow. The cracker temperature was set to 650 °C. RHEED oscillations were observed for substrate temperatures above 450 °C. The variation in RHEED oscillations with BPE for a constant TEI flow can be summarized in the following discussion. At 8.0 sccm H_2 carrier gas flow rate through the BPE bubbler, the RHEED oscillations show a very smooth layer-by-layer two-dimensional growth. At 6.0 sccm flow rate, the RHEED oscillation intensity decreases with layer thickness, which is an indication of less perfect layer-by-layer two-dimensional growth. At 4.0 sccm flow rate, the RHEED oscillations only last a few periods. The growth front cannot maintain a smooth growth, and so changes from a layer-by-layer two-dimensional growth to three-
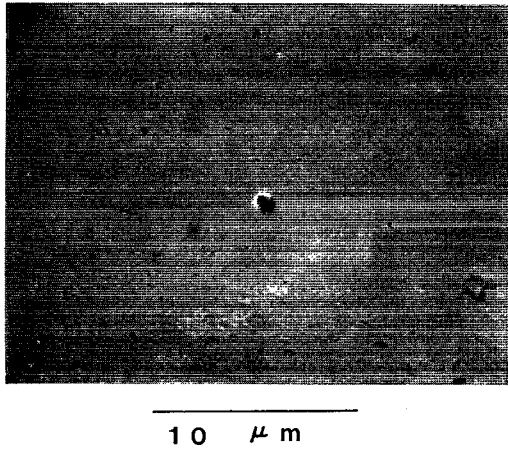
FIG. 1. Surface morphology of 0.5 μm thick layer of InP grown by CBE at 475 °C, using 8.0 sccm H_2 flow for BPE, 7.0 sccm H_2 flow for TEI and a cracker temperature of 650 °C. A reference defect is at the center to enhance the contrast.

TABLE I. Cracking temperature dependent impurity incorporation.

	T_C (°C)	μRT (cm^2/V s)	nRT (cm^{-3})	μ77 K (cm^2/V s)	n77 K (cm^{-3})
No. 1	750	3400	5.4×10^{16}	6100	3.2×10^{16}
No. 2	650	4200	5.7×10^{15}	22 000	4.0×10^{15}

The cracking temperature dependent impurity incorporation, as obtained from Hall measurements, is summarized in Table I. All layers were n-type, with residual carrier concentrations in the 5×10^{15}–5×10^{16} cm^{-3} range. The free-electron concentration increased by an order of magnitude (from 5.7×10^{15} to 5.4×10^{16} cm^{-3}) as cracking temperature increased (from 650 to 750 °C). Because of this strong dependence of free-electron concentration on cracking temperature, we suspect that the PBE is the most likely source of impurities. Detailed analysis from SIMS profiling showed that S is the primary impurity, with a concentration that increases with cracking temperature. C, Si and other n-type impurities were below the SIMS detection limit. We excluded the possibility that S is from the cracker. We have carefully outgassed the cracker at 1200 °C; growth of GaAs with the same cracker at 1000 °C yields no observed S related n-type impurity.

At 8.0 sccm H_2 flow rates and 1.0 μm/h growth, room temperature and 77 K Hall mobilities for a 2.0 μm thick InP epitaxial layer were 4200 and 22 000 cm^2/V s, with carrier densities of 5.7×10^{15} and 4.0×10^{15} cm^{-3}, respectively. The C-V profile, shown in Fig. 2, measures a surface depletion of $\sim$0.4 μm. An electron concentration $\sim$2 $\times 10^{16}$ cm^{-3} was measured at the substrate interface, which can be attributed to interface impurities. This impurity buildup at the substrate interface correlates with the S profile by SIMS and is thus believed to be from BPE decomposition, and is responsible for the low mobility in epitaxial layers. Since the carrier concentration derived from Hall measurement is an average over the layer thickness, we can conclude that by growing thicker InP epitaxial layers the electron mobility can be further increased. A typical 2.2 K PL spectra is shown in Fig. 3, deconvoluted
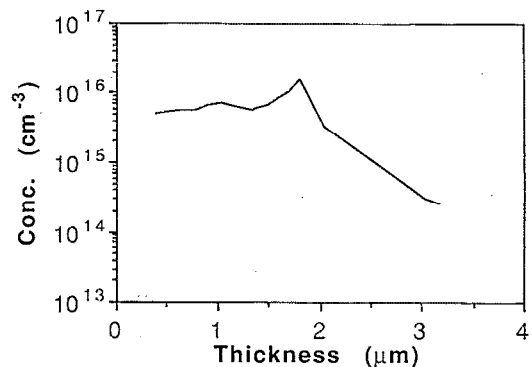
dimensional growth. We attribute this to a roughening of the surface, which is anticipated in phosphorus deficient growth. There is a marked contrast in the RHEED pattern at flow rates of $\sim$20.0 sccm. The growth rate is dramatically reduced from 1.0 μm/h to only $\sim$0.2 μm/h, associated with a reduction in the RHEED intensity as growth proceeds. At this low flow rate, the growth is controlled by group V arrival rate, instead of normal group III limited growth. The surface defects build up and the RHEED pattern gradually changes from (2×4) to (4×2). Further growth would generate an irreversible surface roughness.

Based on the observed RHEED data we confined our initial InP growths to the temperature range 460–480 °C, with the H_2 carrier gas flow rate through the BPE bubbler set at the minimum necessary (8 sccm) to maintain a layer-by-layer growth mode. The choice of minimum BPE flow is extremely important for InP grown by BPE. At too high a flow rate, the impurity incorporation increases. Whereas for flow rates too low, there is insufficient phosphorus for InP growth. The partial pressure of phosphorus species and the observed incorporation of impurities both increase with cracking temperature. Therefore the BPE cracker temperature needs to be optimized. Two cracking temperatures (650 and 750 °C) were chosen in this study, in order to examine BPE cracking and impurity incorporation. For a 8.0 sccm H_2 carrier gas flow rate for BPE and a 7.0 sccm H_2 flow rate for TEI, the growth rate (1.0 μm/h for InP growth) is independent of BPE cracking temperature for the above mentioned temperatures. Typical epitaxial layer thicknesses were 0.5–2.0 μm in this study.

The quality of the CBE grown InP was characterized by low temperature (2.2 K) photoluminescence (PL), van der Pauw Hall measurements, secondary ion mass spectroscopy (SIMS) profile, and polaron C-V profiles. Figure 1 shows the surface morphology of a 0.5 μm InP layer grown at 475 °C. Layer morphology was generally mirror smooth with typically $\sim$10 surface defects per cm^2. The absence of x-hatch features or rice defects show the excellent quality of the film.

FIG. 2. C-V profile of 2.0 μm thick InP epitaxial layer grown by CBE. The impurity buildup at the substrate interface correlates with the S profile by SIMS and is believed to be from BPE decomposition. The same growth condition as specified for layer pictured in Fig. 1.
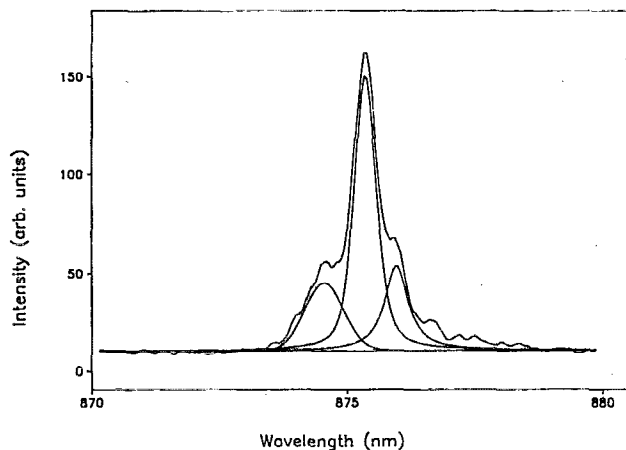
FIG. 3. 2.2 K PL spectrum of 2.0 μm thick InP epitaxial layer grown by CBE. The FWHM linewidth of the dominant donor bound exciton is 0.84 meV. The same growth condition as specified for layer pictured in Fig. 1.

into three transitions. The excitation was a 514.5 nm line from an Ar^+ ion laser. The spectra is characterized by bound exciton transitions related to neutral donor (D^0,X) neutral acceptor (A^0,X), and hole transition to donor (D^0,h). The full width at half maximum (FWHM) linewidth of the dominant donor bound exciton is 0.84 meV.

In conclusion, we have demonstrated CBE growth of InP using BPE as a group V source. Mirrorlike surface morphology and the excellent RHEED patterns observed suggest that the epitaxial layer surface is smooth, well ordered, and free from molecular debris. Although a high n-type impurity concentration is observed at the epitaxial

layer-substrate interface, the epitaxial layer background impurity concentration is low enough for device fabrication. This impurity buildup at the substrate interface is similar to that observed in InP grown with TBP in a CBE system. A 2.2 K PL linewidth of 0.84 meV needs to be improved relative to that of CBE InP grown using PH_3(0.07 meV).[7,8] However, this is the first CBE demonstration of BPE as a group V source. We are hopeful that with improved BPE purity the background impurity concentration can be substantially reduced, leading to better electrical and optical properties.

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