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Citation: [Applied Physics Letters](#) **71**, 1095 (1997); doi: 10.1063/1.119737

View online: <http://dx.doi.org/10.1063/1.119737>

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Selection of substrate orientation and phosphorus flux to achieve *p*-type carbon doping of Ga_{0.5}In_{0.5}P by molecular beam epitaxy

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(Received 5 May 1997; accepted for publication 24 June 1997)

We show that the *p*-type doping of Ga_{0.5}In_{0.5}P grown by solid-source molecular beam epitaxy using CBr₄ as a carbon source is very strongly dependent upon the phosphorus flux and upon the substrate misorientation from (100). High densities of *A*-type steps and low phosphorus flux favor the incorporated carbon acting as a *p*-type dopant. We demonstrate that with the substrate orientation and phosphorus flux chosen to satisfy these two criteria, doping of C:Ga_{0.5}In_{0.5}P into the mid-10¹⁸ holes/cm³ range can be achieved for the as-grown material. © 1997 American Institute of Physics. [S0003-6951(97)02634-X]

Because Ga_{0.5}In_{0.5}P (hereafter GaInP) is lattice matched to GaAs and has a band gap of ~1.9 eV, it is of importance in optoelectronic applications such as light-emitting diodes^{1,2} and solar cells.^{3,4} Although the majority of the work on GaInP has been done by metalorganic vapor-phase epitaxy (MOVPE), there has recently been increasing interest in growth of this material by molecular-beam epitaxy (MBE) with the introduction of phosphorus valved crackers for solid-source MBE,⁵ and with the progress in gas-source MBE. This interest has motivated the search for a suitable *p*-type dopant for MBE-grown GaInP.

Carbon has established itself as one of the most important *p*-type dopants for MBE GaAs due to its negligible diffusion and its ease of delivery in the form of CBr₄ or CCl₄.^{6,7} For these reasons, achieving *p*-type doping of GaInP using carbon is a highly desirable goal. However, this goal has to date proven elusive: prior studies of carbon doping of GaInP grown by gas-source MBE demonstrated *p*-type material using CCl₄ as the carbon source, but the as-grown material was only weakly *p*-type and required a postgrowth anneal to achieve a doping level of above 10¹⁸/cm³.⁸ Because of this difficulty, attention has been focused on other dopants, Be⁹ and Mg.¹⁰ However, these dopants are not as free from diffusion and/or surface segregation as is carbon,^{11–13} prompting us to revisit carbon as a dopant. In this letter, we study C:GaInP grown by solid-source MBE. The use of solid phosphorus rather than the phosphine used in gas-source MBE gives a hydrogen-free environment for which passivation of the carbon dopant by hydrogen is not an issue. In contrast, hydrogen passivation was suggested to have been responsible for the annealing behavior observed for the gas-source MBE growth.⁸ Also, we use CBr₄ to supply the carbon rather than the CCl₄ used previously,⁸ but this probably does not make a significant difference to the doping behavior. However, the main difference between the present study on C:GaInP and previous ones is our emphasis on substrate orientation and phosphorus flux as factors critically affecting the doping efficiency. We demonstrate that the doping efficiency for C:GaInP grown by solid-source MBE depends very strongly on the substrate misorientation and the phosphorus flux, and that with the proper choice of these param-

eters, *p*-type GaInP doped well above 10¹⁸/cm³ can be obtained for the as-grown material.

The GaInP was grown from solid sources, except for the CBr₄ source. Conventional effusion cells were used for the Ga and In. Valved crackers were used for the As and P sources. The P cracker zone was run at 1000 °C in order to maximize the ratio of cracked P₂ to P₄ in the phosphorus beam. The phosphorus beam-equivalent pressure (BEP) was measured during growth, and its magnitude used in a feedback loop to control the cracker valve, as described elsewhere.¹⁴ This scheme allows control of the phosphorus beam flux to better than ±1%, which proved important here due to the sensitivity of the doping to the phosphorus flux.

Epilayers were grown on GaAs substrates of various degrees of misorientation from (100) towards (111)_A or towards (111)_B. After oxide desorption, the substrate was cooled to the growth temperature of 450 °C and a ~0.1 μm GaAs buffer layer was grown on the substrate, after which a GaInP layer was grown on the buffer layer. The Ga/In ratio was chosen to give GaInP–GaAs lattice matching to Δ*a*/*a* < 1 × 10^{−3} as measured by double-crystal x-ray diffraction. Growth time for the GaInP epilayer was either one-half or one hour. The Ga BEP was 3.3 × 10^{−7} Torr, giving a nominal growth rate of 1.5 μm/h. The actual growth rate was determined by measuring the thicknesses of the epilayers. The growth rate was found to be independent of substrate misorientation and phosphorus flux, to within ±5%.

The CBr₄ was provided by the vapor from a bubbler at room temperature; no carrier gas was used. The vapor was introduced into the growth chamber through a variable leak valve and from there through an injector into the chamber. A run/vent configuration was used, with the vent line going to a dedicated ion pump. The flow rate was calibrated before each run by directing the CBr₄ through the vent line to the ion pump and using the ion pump current as a measure of the CBr₄ flow. For flows high enough that the CBr₄ BEP could be measured, the ion pump current was calibrated to the BEP. All epilayers discussed in this letter were grown at a CBr₄ BEP of ~2 × 10^{−8} Torr.

The doping levels of the grown layers were measured using capacitance–voltage (*C*–*V*) of a junction between the epilayer and a liquid electrolyte of 0.5 M HCl.

For substrates oriented to singular (100), or miscut from

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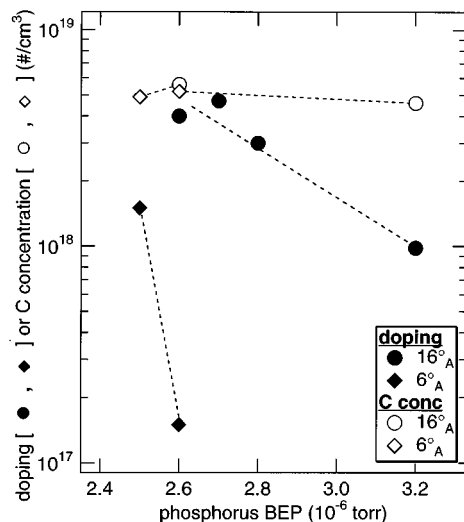


FIG. 1. Dependence of p -type carrier concentration (filled symbols) and metallurgical carbon concentration (open symbols) of C:GaInP upon phosphorus flux for substrate misorientation of 16°_A and 6°_A .

(100) towards $(111)_B$, the C:GaInP epilayers were found not to be p -type. In contrast, p -type doping becomes readily obtainable on substrates miscut 16° towards $(111)_A$ (hereafter 16°_A). Figure 1 shows the dependence of doping on phosphorus flux for substrate misorientation of 16°_A and 6° to $(111)_A$ (hereafter 6°_A). For the 16°_A miscut, the growth conditions described above yield a p -type doping level of $1 \times 10^{18}/\text{cm}^3$ for a phosphorus BEP of 3.2×10^{-6} Torr. With decreasing phosphorus flux, the doping rises rapidly, increasing to $4 \times 10^{18}/\text{cm}^3$ as the phosphorus BEP is lowered to 2.6×10^{-6} Torr. This decrease in doping with increasing phosphorus flux is presumably due to the onset of amphoteric behavior, with the carbon incorporation into the acceptor group-V sublattice sites decreasing due to the increased competition for such sites from the phosphorus.

The dependence of doping on phosphorus flux becomes extreme for substrate misorientations which are less strongly A -type than 16°_A . The doping for the 6°_A misorientation is much less efficient than for the 16°_A orientation: at a phosphorus flux of 2.6×10^{-6} Torr, the doping for the layer grown on 6°_A misorientation is about a factor of 20 less heavily doped than the layer grown on 16°_A misorientation. This dependence is consistent with the expectation that A -type steps on the growth surface provide sites at which incident atoms can incorporate into the group-V sublattice, where carbon atoms would act as acceptors. Thus as the density of A -type steps decreases, there is the onset of amphoteric behavior, with the decreasing likelihood of carbon incorporation into acceptor sites on the group-V sublattice, and increasing likelihood for incorporation of carbon atoms onto group-III sublattice or interstitial sites.

To test whether the doping dependence is due, as argued above, to a variation in the site occupation of the incorporated carbon, and not to a variation in the total amount of carbon incorporated, we measured the metallurgical concentration of carbon in several of the GaInP samples by secondary ion mass spectrometry (SIMS). The results, which are plotted in Fig. 1 as the open symbols, show that the carbon

concentration is essentially constant, thus confirming the doping dependence on substrate misorientation and phosphorus flux as being a *site occupation* dependence and not a *carbon incorporation* dependence. (It should be noted that the SIMS concentration calibration was estimated due to the lack of a C:GaInP SIMS standard—a relative sensitivity factor was calculated for C:GaInP based on published C:GaP and C:InP sensitivity factors.¹⁵ However, while the absolute carbon concentration calibration should therefore not be considered precise, the relative concentration from sample to sample should be accurate to within 15%–20%.)

It is of interest to compare the carbon doping behavior of GaInP by MBE, as discussed here, with the corresponding behavior for MOVPE growth. A previous study¹⁶ showed that p -type carbon-doped GaInP could be grown by MOVPE, but doping levels no higher than $10^{17}/\text{cm}^3$ were obtained. The substrate miscuts used in that study had only a small amount of A -type character, and the V/III ratios were relatively large at $V/\text{III} \geq 15$. If an orientation and phosphorus-flux dependence similar to that described above for MBE-grown C:GaInP holds for the MOVPE-grown material as well, it should be possible to obtain higher doping levels than $10^{17}/\text{cm}^3$ for the MOVPE-grown material. Motivated by the MBE results described above, we have started a study of the MOVPE case. The preliminary results do indeed show an increase in doping efficiency for A -type substrate miscuts and low V/III ratios, with resulting p -type doping levels as high as $10^{18}/\text{cm}^3$. The prior MOVPE study of C:GaInP also made the interesting observation that the carbon doping has a detrimental effect on the minority-carrier lifetimes even at low carrier concentrations of $\leq 10^{17}/\text{cm}^3$. A similar effect on the lifetime might be anticipated for the MBE case.

In summary, the doping behavior of CBr_4 :GaInP grown by solid-source MBE depends very strongly on the substrate orientation and on the phosphorus flux, with the doping efficiency increasing with decreasing phosphorus flux and with increasing A -type character of the substrate. We attribute this dependence to a competition between the carbon and phosphorus for sites on the group-V sublattice, and show that this dependence can be exploited to give p -type doping in the mid- $10^{18}/\text{cm}^3$ range. Finally, on a more general note, it is worth re-emphasizing the usefulness of stating the substrate orientation and group-V flux in doping studies of III–V materials.

This work was supported by DOE Contract No. DE-AC02-83CH10093. The authors thank Sarah R. Kurtz and J. M. Olson for helpful discussions.

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