Absence of ^{13}C incorporation in $^{13}CCl_4$-doped InP grown by metalorganic chemical vapor deposition

B. T. Cunningham, J. E. Baker, S. A. Stockman, and G. E. Stillman
Center for Compound Semiconductor Microelectronics, Materials Research Laboratory and Coordinated Science Laboratory, University of Illinois at Urbana–Champaign, Urbana, Illinois 61801

(Received 7 November 1989; accepted for publication 19 February 1990)

Intentional carbon doping of low-pressure metalorganic chemical vapor deposition (MOCVD) grown InP has been attempted with a 500 ppm mixture of $^{13}CCl_4$ in high-purity H_2, which has been used to obtain carbon-acceptor concentrations as high as 1×10^{19} cm^{-3} in GaAs. Under growth conditions similar to those used for heavy carbon incorporation in GaAs, injection of $^{13}CCl_4$ into the growth reactor during growth of InP did not produce any measurable change in the carrier concentration of the InP epitaxial layers or any change in the ^{13}C concentration above the ^{13}C background in secondary-ion mass spectroscopy analysis. These results support previous low-temperature photoluminescence measurements of high-purity InP in which no residual carbon acceptor is observed under many growth techniques and growth conditions, and hence support the hypothesis that carbon is not incorporated in InP grown by MOCVD.

Carbon has recently received a great deal of attention as an intentional p-type dopant for GaAs and AlGaAs grown by metalorganic chemical vapor deposition (MOCVD),[1-4] atomic layer epitaxy,[5] chemical beam epitaxy (CBE),[6] and molecular beam epitaxy[7] due to its low diffusion coefficient compared to group II p-type impurities.[8-10] Because carbon is an intrinsic impurity in metalorganic source materials, its behavior in III/V compounds grown with these precursors is particularly important. Although carbon is a group IV element and is potentially amphoteric in GaAs, InP, and other III/V compounds, in GaAs it is only incorporated as an acceptor on the As sublattice. Low-temperature photoluminescence (PL) measurements of high-purity epitaxial InP which had been subjected to low-dose ion implantation of carbon indicates that carbon can be incorporated as a shallow acceptor in InP.[11] However, the low-temperature PL spectra of high-purity InP grown by liquid phase epitaxy (LPE), liquid-encapsulated Czochralski (LEC), and hydride vapor phase epitaxy indicate that carbon was not incorporated as a residual acceptor for any of these growth techniques,[11] and in particular, low-temperature PL measurements of high-purity InP grown by low-pressure MOCVD demonstrate that no residual carbon is incorporated into the epitaxial layers regardless of the growth conditions.[12]

Although these results indicate that residual carbon impurities are not incorporated into InP grown by many techniques, the use of carbon as an intentional dopant in InP has not been previously investigated. In this work, experiments are described in which we attempted intentional doping of low-pressure MOCVD InP with CCl_4 under conditions which result in heavy carbon doping of GaAs. Injection of CCl_4 into the reactor during growth of InP did not produce any measurable change in the carrier concentration of the InP epitaxial layers or any change in the carbon concentration measured by secondary-ion mass spectroscopy (SIMS). The results of these experiments indicate that CCl_4 is not a viable p-type dopant source for MOCVD InP, and support the hypothesis that carbon is not incorporated in MOCVD InP.

The MOCVD reactor used in this work was an Emcore GS3100. All growths were carried out on 2° off (100) oriented towards the nearest (110) LEC GaAs or InP substrates with a reactor pressure of ~100 Torr, a total H_2 flow rate of ~9 slm, and a substrate rotation speed of ~1500 rpm. For GaAs growth, TMGa and 100% AsH_3 were the respective group III and V sources. TMIn and 100% PH_3 were the precursors for the growth of InP. The CCl_4 source was a 500 ppm mixture of $^{13}CCl_4$ in high-purity H_2. The ^{13}C isotope was used to obtain increased sensitivity for carbon detection during SIMS analysis.

SIMS analysis for carbon was performed with a Cameca IMS-3f instrument using a Cs^+ primary ion beam (160 nA, 13 keV) and negative secondary-ion detection to obtain maximum carbon atom yield and detection sensitivity. Low-resolution operation of this instrument results in a detection limit for ^{12}C of only $\sim3\times10^{16}$ cm^{-3}, below which no variation in the ^{12}C concentration can be measured. However, the detection limit for ^{13}C is $\sim2\times10^{14}$ cm^{-3} under these conditions.[2,13,14]

In order to demonstrate that injection of $^{13}CCl_4$ into the reactor during GaAs growth results in ^{13}C incorporation, a $^{13}CCl_4$-doped GaAs sample was grown with a constant growth temperature ($T_G = 640$ °C) and growth rate ($R_G \sim 1000$ Å/min), while the $^{13}CCl_4$-mixture flow rate was decreased in four steps of 150, 100, 50, and 25 sccm during the growth of ~0.6-μm-thick layers. Undoped GaAs grown under these conditions was n type with an electron concentration of $n\sim1\times10^{15}$ cm^{-3} as measured by capacitance-voltage (C-V) profiling.

To determine the effect of $^{13}CCl_4$ injection into the reactor during InP growth, two $^{13}CCl_4$-doped InP samples were grown in which the growth temperature ($T_G = 580$ °C, 630 °C) and growth rate ($R_G \sim 250$ Å/min) were held constant while the $^{13}CCl_4$ mixture flow rate was decreased in four steps of 150, 100, 50, and 25 sccm during the growth of ~0.25-μm-thick layers. Undoped InP samples grown under these conditions were n type with an electron concentration of $n\sim1.5\times10^{16}$ cm^{-3} as measured by electrochemical C-V profiling.

 © 1990 American Institute of Physics

Downloaded 08 Jan 2010 to 192.17.198.94. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

The hole concentration as a function of depth for the $^{13}CCl_4$-doped GaAs samples, measured by electrochemical *C-V* profiling, is shown in Fig. 1(a). The hole concentration varied nearly linearly with the $^{13}CCl_4$ flow rate. The results of SIMS analysis of this sample for $^{13}C^-$ and $^{12}C^-$ shown in Fig. 1(b) demonstrate increased ^{13}C concentration with increased $^{13}CCl_4$ flow rate. The ^{12}C concentration was constant at the background detection limit throughout the sample, with the exception of small amounts of ^{12}C detected at the substrate and sample surface. The ^{12}C detected at the sample surface is believed to originate from ^{12}C background contamination in the SIMS instrument. The ^{12}C detected at the substrate is probably the result of surface propagation in organic solvents, and has been detected in both doped and undoped samples.

The electron concentration as a function of depth in the $^{13}CCl_4$ "doped" InP sample grown at $T_G = 630\,°C$, measured by electrochemical *C-V* profiling, is shown in Fig. 2(a). The electron concentration did not change with increased $^{13}CCl_4$ flow rate. The results of SIMS analysis for $^{12}C^-$ and $^{13}C^-$ shown in Fig. 2(b) demonstrate that the $^{13}C^-$ ion count was constant at the background detection limit throughout the sample. As in the GaAs sample, the $^{12}C^-$ ion count did not change from the background detection limit, except for ^{12}C contamination detected at the substrate and sample surface. The $^{13}CCl_4$-doped InP sample grown at $T_G = 580\,°C$ demonstrated nearly identical variation of electron concentration, $^{13}C^-$ ion count, and $^{12}C^-$ ion counts as a function of depth as the sample grown at $T_G = 630\,°C$.

In summary, we have attempted to incorporate carbon into InP grown by low-pressure MOCVD using a carbon dopant source and similar growth conditions that result in very heavy carbon acceptor doping in GaAs. SIMS and electrochemical *C-V* profiling of the InP layers indicate that the addition of $^{13}CCl_4$ to the growth ambient results in no measurable change in the ^{13}C content (with a detection-sensitivity limit of $[^{13}C] \sim 2\times10^{14}\ cm^{-3}$) and no change in the carrier concentration. These results are in agreement with PL studies of high-purity InP grown by several methods, including MOCVD, in which no residual carbon acceptor is detected. Although carbon is a very desirable *p*-type dopant in GaAs, based on these results, the use of carbon as an intentional *p*-type dopant in MOCVD InP appears to be impractical due to its lack of incorporation.

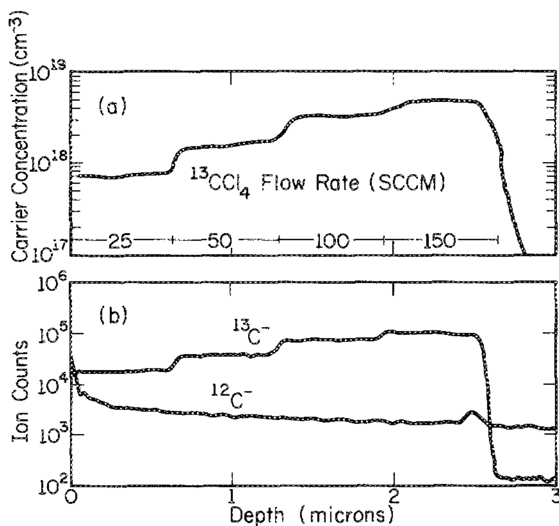

FIG. 1. (a) Hole concentration as a function of depth for a $^{13}CCl_4$-doped GaAs sample measured by electrochemical *C-V* profiling. (b) Results of SIMS analysis for $^{12}C^-$ and $^{13}C^-$ demonstrating increased ^{13}C concentration with increased $^{13}CCl_4$ flow rate.

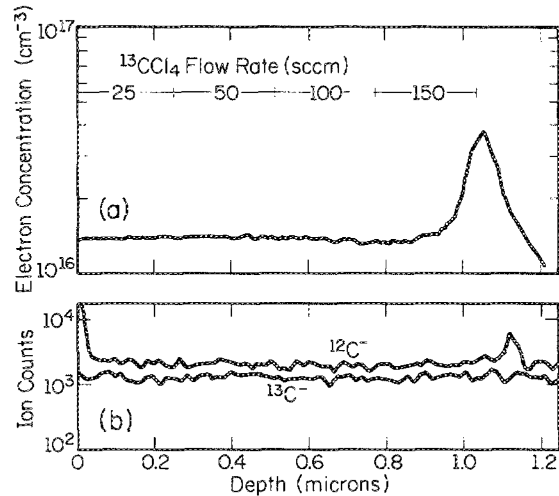

FIG. 2. (a) Electron concentration as a function of depth for a $^{13}CCl_4$-doped InP sample measured by electrochemical *C-V* profiling. No change in carrier concentration with increased $^{13}CCl_4$ flow rate was detected. (b) Results of SIMS analysis for $^{12}C^-$ and $^{13}C^-$ demonstrating no change in ^{13}C or ^{12}C concentration with increased $^{13}CCl_4$ flow rate.

The amphoteric behavior of group IV impurities in III/V compounds has been the subject of considerable study. Recent results have shown that the amphoteric behavior of group IV impurities cannot be explained by equilibrium thermodynamics alone, but that this behavior is also dependent on kinetic effects which influence impurity incorporation.[15] Group IV atoms such as Si and Ge are well known to be amphoteric dopants in III/V compounds with which the degree of autocompensation depends on the covalent radius of the impurity relative to the host atoms and upon the relative availability of the two lattice sites. Usually, the impurity will occupy a lattice site which most closely matches its covalent radius, since this will minimize the lattice strain and therefore the free energy of the crystal.[16] If a host atom of equal covalent radius is not available, the impurity will occupy the lattice site which is most energetically favorable. However, the free energy does not increase to a large extent for incorporation of an impurity on a larger lattice site, but increases rapidly with size difference for incorporation of a large impurity on a smaller lattice site. Although these arguments have been successful in explaining Si and Ge incorporation, they cannot explain why carbon will occupy only As sites in GaAs. It is interesting to note, however, that for the case of carbon incorporation in LPE GaAs, the equilibrium thermodynamic model of Teramoto[17] has been used by Low *et al.* to predict an amphoteric ratio $[C_{Ga}]/[C_{As}] = 6.4\times10^{-7}$ at a growth temperature of 700 °C, due to the large lattice-strain energy contribution to the free-energy difference $\Delta G_{A/B}$ between IV_{Ga} and IV_{As} site occupation which forces the small carbon impurity onto the small As

Downloaded 08 Jan 2010 to 192.17.198.94. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp

site rather than the larger Ga site.[18] Additional contributions to the free-energy difference $\Delta G_{A/B}$ in InP due to electronegativity corrections to the binding energy might preclude incorporation of carbon in InP entirely at the pressures and temperatures typically used in MOCVD epitaxy.

A recent study of CCl_4 doping in $Al_xGa_{1-x}As$ has demonstrated the importance of surface adsorption and desorption of CCl_y ($y \leqslant 3$) on carbon incorporation. The authors found that carbon incorporation in $Al_xGa_{1-x}As$ ($x \geqslant 0.4$) did not decrease significantly with increased growth temperature, as is the case for GaAs, presumably because the Al — C (64 kcal/mole) bond is stronger than the Ga — C (59 kcal/mole) bond.[19] The In — C bond, with an activation energy of 47 kcal/mole, is much weaker than the Ga — C or Al — C bond.[20] If the weak In — C bond prevents adsorption of CCl_y, carbon incorporation from CCl_4 would not be possible unless extremely low growth temperatures were used. Likewise, the adsorption of other carbon-bearing species, such as methyl radicals from TMIn, would be inhibited. This theory is supported by studies of carbon incorporation in CBE-grown InP which measure significant carbon incorporation only at growth temperatures below 450 °C.[21] At growth temperatures above 500 °C, the carbon concentration may already be well below 1×10^{14} cm^{-3}, due to decreased adsorption of ethyl radicals. More work remains to be done on experimental studies of possible orientation dependence of carbon incorporation in InP and on theoretical studies of impurity incorporation in GaAs and InP to fully understand this problem.

The authors would like to thank M. K. Suits, R. MacFarlane, and J. Gladin for help in manuscript preparation. This work was supported by the National Science Foundation (NSF) under contracts NSF CDR 85-22666 and NSF DMR 86-12860, and by the Strategic Defense Initiative Organization/Innovative Science and Technology under contract DAAL 03-89-K-0080, managed by the Army Research Office (ARO). B. Cunningham was supported by an ARO fellowship under contract DAAL 03-86-G-0047. S. Stockman was supported by a NSF graduate fellowship under contract RCD 88-54814.

[1]T. F. Kuech and E. Veuhoff, J. Cryst. Growth **68**, 148 (1984).
[2]R. M. Lu, J. K. Klingert, D. W. Kisker, D. M. Tennant, M. D. Morris, D. L. Malm, J. Kobalchick, and L. A. Heimbrook, J. Electron. Mater. **17**, 101 (1988).
[3]L. J. Guido, G. S. Jackson, D. C. Hall, W. E. Plano, and N. Holonyak, Jr., Appl. Phys. Lett. **52**, 522 (1988).
[4]B. T. Cunningham, M. A. Haase, M. J. McCollum, and G. E. Stillman, Appl. Phys. Lett. **54**, 1905 (1989).
[5]R. Bhat, J. R. Hayes, E. Colas, and R. Esagui, Electron. Device Lett. **9**, 442 (1988).
[6]N. Putz, H. Heinecke, M. Heyen, P. Balk, M. Weyers, and H. Luth, J. Cryst. Growth **74**, 292 (1986).
[7]R. J. Malik, R. N. Nottenburg, E. F. Schubert, J. F. Walker, and R. W. Ryan, Appl. Phys. Lett. **53**, 2661 (1988).
[8]T. F. Kuech, M. A. Tischler, P. -J. Wang, G. Scilla, R. Potemski, and F. Cardone, Appl. Phys. Lett. **53**, 1317 (1988).
[9]K. Tamamura, J. Ogawa, K. Akimoto, Y. Mori, and C. Kojima, Appl. Phys. Lett. **50**, 1149 (1987).
[10]B. T. Cunningham, L. J. Guido, J. E. Baker, J. S. Major, Jr., N. Holonyak, Jr., and G. E. Stillman, Appl. Phys. Lett. **55**, 687 (1989).
[11]B. J. Skromme, G. E. Stillman, J. D. Oberstar, and S. S. Chan, J. Electron. Mater. **13**, 463 (1984).
[12]K. Uwai, S. Yamada, and K. Takehei, J. Appl. Phys. **61**, 1059 (1987).
[13]R. L. Lum, J. K. Klingert, D. W. Kisker, S. M. Abys, and F. A. Stevie, J. Cryst. Growth **93**, 120 (1988).
[14]Y. Homma and Y. Ishii, J. Vac. Sci. Technol. A **3**, 356 (1985).
[15]B. Lee, I. Szafranek, G. E. Stillman, K. Arai, Y. Nashimoto, N. Iwata, and I. Sakuma, Surf. Interface Anal. **14**, 619 (1989).
[16]W. I. Wang, R. F. Marks, and L. Vina, J. Appl. Phys. **59**, 937 (1986).
[17]I. Teramoto, J. Phys. Chem. Solids **33**, 2089 (1972).
[18]T. S. Low, B. J. Skromme, and G. E. Stillman, in *Proceedings of the 10th International Symposium on GaAs and Related Compounds*, edited by G. E. Stillman, Conf. Ser. no. 65 (Institute of Physics, London, Bristol, 1983).
[19]B. T. Cunningham, J. E. Baker, and G. E. Stillman, Appl. Phys. Lett. **56**, 836 (1990).
[20]S. J. W. Price, in *Comprehensive Chemical Kinetics*, edited by C. H. Bamford and C. F. H. Tipper (Elsevier, New York, 1972), Vol. 4, pp. 197–259.
[21]J. L. Benchimol, F. Alaoui, Y. Gao, G. Le Roux, F. V. K. Rao, and F. Alexandre (unpublished).

Downloaded 08 Jan 2010 to 192.17.198.94. Redistribution subject to AIP license or copyright; see http://apl.aip.org/apl/copyright.jsp