# Carbon tetrachloride doped $Al_x Ga_{1-x} As$ grown by metalorganic chemical vapor deposition

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A dilute mixture of $CCl_4$ in $H_2$ has recently been shown to be a suitable carbon doping source for obtaining p-type GaAs grown by metalorganic chemical vapor deposition (MOCVD) with carbon acceptor concentrations in excess of $1 \times 10^{19}$ cm$^{-3}$. To understand the effect of growth parameters on carbon incorporation in $CCl_4$-doped $Al_x Ga_{1-x} As$, carbon acceptor concentration was studied as a function of Al composition, growth temperature, growth rate, and $CCl_4$ flow rate using electrochemical capacitance-voltage profiling. The carbon incorporation as a function of Al composition, growth temperature, and $CCl_4$ flow rate was also measured by secondary-ion mass spectroscopy. All layers were grown by low-pressure MOCVD using TMGa and TMAl as column III precursors, and 100% $AsH_3$ as the column V source. Increased Al composition reduced the dependence of carbon concentration on the growth temperature. Reduced growth rate, which resulted in substantially decreased carbon acceptor concentrations in GaAs, had an insignificant effect on the carrier concentration of $Al_{0.4} Ga_{0.6} As$. A linear relationship between hole concentration and $CCl_4$ flow rate in $Al_x Ga_{1-x} As$ for $0.0 \leqslant x \leqslant 0.8$ was observed. These results are interpreted to indicate that adsorption and desorption of $CCl_y$ ($y \leqslant 3$) on the $Al_x Ga_{1-x} As$ surface during crystal growth plays an important role in the carbon incorporation mechanism.

Carbon is an attractive alternative to conventionally used p-type impurities in MOCVD, such as Mg and Zn, due to its low diffusion coefficient.[1-7] Diffusion of p-type impurities is of particular concern in laser diode structures which are subjected to high-temperature annealing for impurity diffusion in impurity-induced layer disordering (IILD). Diffusion of p-type dopants into the active region of a quantum well heterostructure (QWH) laser or into the emitter of an Npn heterojunction bipolar transistor (HBT) has been shown to result in degraded device performance.[8,9] Carbon incorporation from the methyl radicals associated with the column III growth precursors has been used to obtain carbon doping of diode laser structures grown by MOCVD.[5] However, carbon doping from a source separate from the growth precursors may be more desirable, as it allows greater flexibility in the choice of growth parameters.

A dilute mixture of $CCl_4$ in $H_2$ has been used successfully as a p-type dopant source for low-pressure metalorganic chemical vapor deposition (MOCVD) growth of GaAs with carbon acceptor concentrations as high as $4 \times 10^{19}$ cm$^{-3}$.[1,10] HBT structures grown by MOCVD with the thin p-type ($<1000$ Å) base region heavily doped with $CCl_4$ ($p = 2 \times 10^{19}$ cm$^{-3}$) and a current gain cutoff frequency as high as $f_t = 30$ GHz have been reported.[11] p-type doping of $Al_x Ga_{1-x} As$ in MOCVD-grown heterojunction diode laser structures is another potentially important application of $CCl_4$ doping. $CCl_4$ doping may be used to obtain $Al_x Ga_{1-x} As$ with higher carbon acceptor concentration than can be obtained solely with carbon incorporation from the growth precursors in MOCVD-grown layers.

Because $CCl_4$ has not been extensively studied as a dopant source, little is understood about the gas phase and/or surface decomposition reactions which result in carbon incorporation. Thus, a knowledge of how Al composition affects carbon acceptor concentration under various growth conditions would be useful for understanding the $CCl_4$ decomposition mechanism, in addition to providing experimental data for the growth of device structures.

To determine the effect of growth parameters on carbon incorporation in $CCl_4$-doped $Al_x Ga_{1-x} As$, carbon acceptor concentration was studied as a function of Al composition, growth temperature, growth rate, and $CCl_4$ flow rate through electrochemical capacitance-voltage profiling of the hole concentration. The carbon incorporation as a function of Al composition, growth temperature, and $CCl_4$ flow rate was also measured by secondary-ion mass spectroscopy (SIMS).

All layers were grown by low-pressure MOCVD in an Emcore GS3100 reactor using TMGa and TMAl as column III precursors and 100% $AsH_3$ as the column V source. The carbon doping source was a 1500 ppm mixture of $CCl_4$ in $H_2$. All growths were done on 2° off (100) liquid-encapsulated Czochralski GaAs substrates at a pressure of $\sim 100$ Torr, total $H_2$ flow rate of $\sim 9$ slm, and a substrate rotation speed of $\sim 1500$ rpm.

The carbon acceptor concentration was studied as a function of growth temperature by keeping the Al composition ($x = 0.0, 0.2, 0.4, 0.6, 0.8$), growth rate ($R_G \sim 1000$ Å/min), and $CCl_4$ mixture flow rate (50 sccm) fixed during a single growth run while the growth temperature was increased in steps after the growth of $\sim 0.5$ $\mu$m at each temperature ($640$ °C $\leqslant T_G \leqslant 810$ °C). A 2 min growth pause under $AsH_3$ and $H_2$ was used between layers while the growth temperature was increased to a new value. The carbon acceptor concentration as a function of $CCl_4$ flow rate was studied by keeping the Al composition ($x = 0.0, 0.4, 0.8$), growth rate ($R_G \sim 1000$ Å/min), and growth temperature ($T_G = 600$ °C, 700 °C) constant during a single growth run while decreasing the $CCl_4$ mixture flow rate after each $\sim 0.5$ $\mu$m of growth. The flow rate was limited to a maximum of

150 sccm by the range of the mass flow controller. The carrier concentration as a function of depth in these layers was measured by electrochemical $C$-$V$ profiling. The $^{12}$C ion count as a function of depth as measured by SIMS using a $Cs^+$ primary beam (211 nA, 12.6 kV) and negative secondary-ion detection with a Cameca IMS-3f instrument. The Al composition for each growth was verified by double-crystal x-ray diffraction.

The dependence of hole concentration of CCl$_4$-doped Al$_x$Ga$_{1-x}$As on growth rate was studied by holding the Al composition ($x = 0.0$, 0.4), growth temperature ($T_G = 660$ °C), and CCl$_4$ mixture flow rate (50 sccm) constant while the growth rate was reduced in steps after the growth of $\sim 0.5\,\mu$m at a single growth rate, under a constant AsH$_3$ flow rate (100 sccm). The carrier concentration of these layers was measured as a function of depth by electrochemical $C$-$V$ profiling.

The variation of hole concentration with growth temperature for CCl$_4$-doped Al$_x$Ga$_{1-x}$As ($x = 0.0$, 0.2, 0.4, 0.6, 0.8) grown at $\sim 1000$ Å/min is shown in Fig. 1. The carrier concentration increased with decreasing growth temperature for both $x = 0.0$ and $x = 0.2$, although the rate of increase for $x = 0.2$ was substantially reduced when $T_G < 700$ °C. The carrier concentration of CCl$_4$-doped Al$_{0.4}$Ga$_{0.6}$As was nearly independent of growth temperature for 640 °C $\leqslant T_G \leqslant 760$ °C, but increased with decreasing growth temperature when $T_G \leqslant 640$ °C and 760 °C $\leqslant T_G \leqslant 810$ °C. In contrast, reduced growth temperature resulted in lower carrier concentrations for $x = 0.6$ with $T_G \leqslant 760$ °C and for $x = 0.8$ with $T_G \leqslant 700$ °C. This effect, observed in doped and undoped Al$_x$Ga$_{1-x}$As samples when $x \geqslant 0.6$, is attributed to oxygen incorporation. Oxygen is a deep hole trap which reduces the free-carrier concentration in Al$_x$Ga$_{1-x}$As. A decrease in the gettering of O$_2$ with Al at low growth temperatures results in increased oxygen incorporation in Al$_x$Ga$_{1-x}$As.[12] The deleterious effect of oxygen incorporation on the free-carrier concentration of Al$_x$Ga$_{1-x}$As grown at low temperatures results in such significant reduction in the free-hole concentration that $C$-$V$ measurement becomes an inaccurate means of measuring
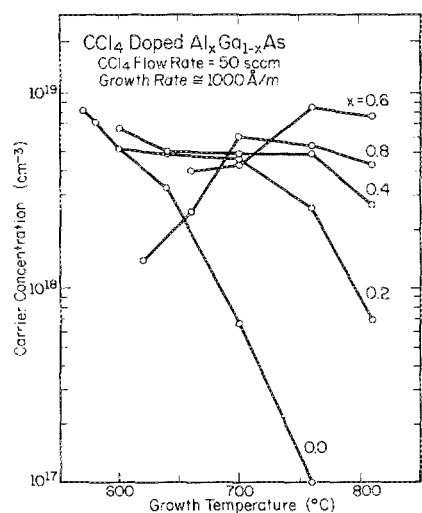
the carbon concentration. Therefore, SIMS was used to study the effect of growth temperature on the $^{12}$C incorporation.

The SIMS results for $^{12}$C ion count as a function of growth temperature for CCl$_4$-doped Al$_x$Ga$_{1-x}$As ($x = 0.0$, 0.2, 0.4, 0.6, 0.8) grown at $\sim 1000$ Å/min are shown in Fig. 2. The $^{12}$C concentration increased with decreasing growth temperature for $x = 0.0$ and $x = 0.2$, and the rate of increase for $x = 0.2$ is smaller in the temperature range 640 °C $\leqslant T_G \leqslant 760$ °C. The temperature variation of the $^{12}$C concentration for these compositions is similar to the hole concentrations measured by electrochemical $C$-$V$ profiling. For $0.4 \leqslant x \leqslant 0.8$, the $^{12}$C concentration varied only slightly with growth temperature for 640 °C $\leqslant T_G \leqslant 760$ °C, but increased with decreasing growth temperature with $T_G \leqslant 640$ °C and $T_G \geqslant 760$ °C. Figure 2 clearly demonstrates that the effect of growth temperature on carbon incorporation from CCl$_4$ doping changes with Al$_x$Ga$_{1-x}$As alloy composition.

The variation of hole concentration with CCl$_4$ flow rate in Al$_x$Ga$_{1-x}$As ($x = 0.0$, 0.4, 0.8) grown at $T_G = 600$ °C and $T_G = 700$ °C is shown in Fig. 3. The carrier concentration is directly proportional to the CCl$_4$ flow rate for each growth temperature and Al composition considered.

The variation of the hole concentration with growth rate in CCl$_4$-doped Al$_x$Ga$_{1-x}$As for two compositions ($x = 0.0$, 0.4) grown at $T_G = 660$ °C is shown in Fig. 4. For $x = 0.0$, the hole concentration was nearly independent of the growth rate for $R_G \geqslant 1000$ Å/min, but the hole concentration decreased significantly with growth rate for $R_G \leqslant 1000$ Å/min. However, for $x = 0.4$, the carrier concentration was insensitive to variations in growth rate over the entire range of growth rates considered.

The observed relationships between carbon incorporation and Al composition, growth rate, and CCl$_4$ flow rate help elucidate the carbon incorporation mechanism from CCl$_4$ doping. The most likely decomposition pathway for halogenated methanes is by homolytic scission of C—X bonds, rather than by the simultaneous alpha-alpha elimination of two ligands.[13] A gas phase dissociation energy of approximately 72 kcal/mole is required to break the first
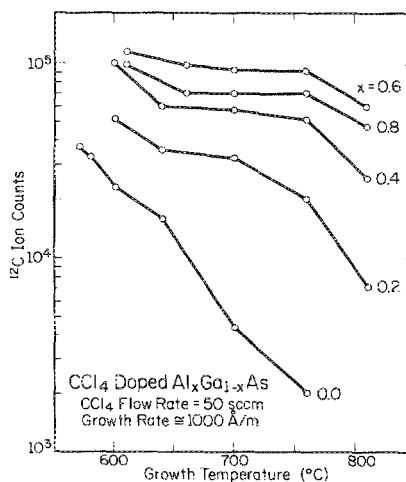


FIG. 1. Variation of hole concentration with growth temperature for CCl$_4$-doped Al$_x$Ga$_{1-x}$As grown at 1000 Å/min.



FIG. 2. Variations of SIMS $^{12}$C ion count with growth temperature for CCl$_4$-doped Al$_x$Ga$_{1-x}$As grown at 1000 Å/min.
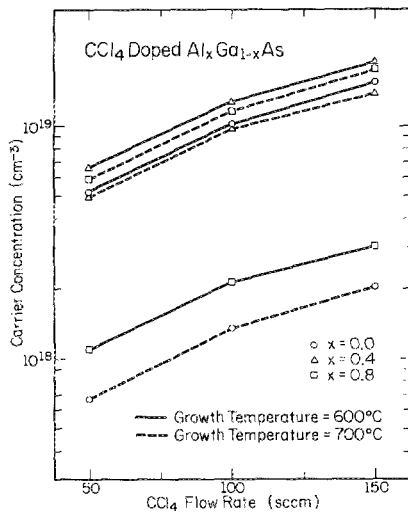
FIG. 3. Variation of hole concentration with $CCl_4$ flow rate (1500 ppm mixture in $H_2$) for $CCl_4$-doped $Al_xGa_{1-x}As$ grown at $T_G = 600\,°C$ and $T_G = 700\,°C$.

$CCl_3$—Cl bond.[14] Upon rupture of this first bond, the $CCl_2$—Cl bond (67 kcal/mole) is almost certain to break immediately afterwards. However, the C—Cl bonds in $CCl_2$ are unlikely to rupture (~91 kcal/mole for each), thus it is unlikely that carbon incorporation results from the complete homolytic fission of $CCl_4$ in the gas phase.

A possible mechanism for carbon incorporation from $CCl_4$ which is consistent with the observed trends is the adsorption of $CCl_y$ ($y \leqslant 3$) on the $Al_xGa_{1-x}As$ surface. During growth of GaAs, elevated growth temperatures result in increased desorption of $CCl_y$ from the GaAs surface, and thus reduced carbon acceptor concentration. As shown in Fig. 1, the carbon acceptor concentration in $Al_xGa_{1-x}As$ ($x \geqslant 0.2$) is much higher than in GaAs($x = 0.0$) at growth temperatures greater than 675 °C. The observed increased carbon doping efficiency with the addition of Al can be explained by the difference in bond strength between Al—C (63–66 kcal/mole) and Ga—C(59 kcal/mole).[15–18] The increased strength of the Al—C bond results in a decrease in the rate of $CCl_y$ desorption, especially at elevated growth temperatures. The data in Fig. 2 indicate that the Al—C bond must be of sufficient strength to prevent desorption of $CCl_y$ until growth temperatures greater than 760 °C are obtained, because the $^{12}C$ ion count for $CCl_4$-doped $Al_xGa_{1-x}As$



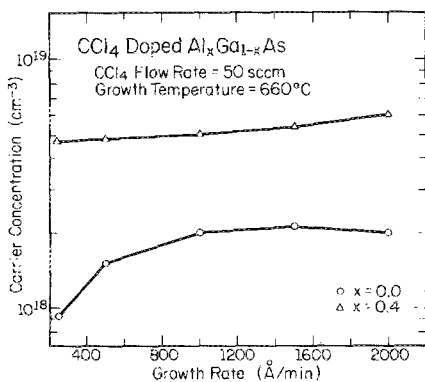FIG. 4. Hole concentration as a function of growth rate for $CCl_4$-doped GaAs and $Al_{0.4}Ga_{0.6}As$ grown at $T_G = 660\,°C$.

($x \geqslant 0.4$) does not decline significantly until $T_G \geqslant 760\,°C$. More evidence for $CCl_4$ decomposition by surface adsorption rather than by gas phase homolytic fission is provided by the lack of carrier concentration variation with growth rate in $CCl_4$-doped $Al_{0.4}Ga_{0.6}As$ where the Al—C bond on the substrate surface prevents significant $CCl_y$ desorption at low growth rates. In contrast, for $CCl_4$-doped GaAs where the Ga—C bond is weaker, a low growth rate increases the probability that a $CCl_y$ molecule on the surface will desorb, resulting in lower carbon doping.

For heavily carbon doped GaAs($p \sim 1 \times 10^{19}$ cm$^{-3}$), the ratio of $CCl_4$ to TMGa in the reactor is $\sim 1/10$. Thus, only approximately 1/100 carbon atoms are incorporated into the lattice, even at low growth temperatures. Therefore, either the adsorption process is very slow, or adsorption on the surface is followed by rapid desorption of $CCl_y$ or other reaction products such as $CCl_yH_{4-y}$. Based on the results presented in this work, it is not possible to identify the precise adsorption mechanism, or the desorption products.

[1] B. T. Cunningham, M. A. Haase, M. J. McCollum, J. E. Baker,and G. E. Stillman, Appl. Phys. Lett. 54, 1905 (1989).
[2] T. F. Kuech, M. A. Tischler, P.-J. Wang, G. Scilla, R. Potemski, and F. Cardone, Appl. Phys. Lett. 53, 1317 (1988).
[3] T. F. Kuech and E. Veuhoff, J. Cryst. Growth 68, 148 (1984).
[4] R. M. Lum, 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).
[5] L. J. Guido, G. S. Jackson, D. C. Hall, W. E. Plano, and N. Holonyak, Jr., Appl. Phys. Lett. 52, 522 (1988).
[6] K. Tamamura, J. Ogawa, K. Akimoto, Y. Mori, and C. Kojima, Appl. Phys. Lett. 50, 1149 (1987).
[7] 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).
[8] L. J. Guido, B. T. Cunningham, D. W. Nam, K. C. Hsieh, W. E. Plano, J. S. Major, Jr., E. J. Vesely, A. R. Sugg, N. Holonyak, Jr., and G. E. Stillman (unpublished).
[9] P. M. Enquist, J. Cryst. Growth 93, 637 (1988).
[10] B. T. Cunningham and G. E. Stillman (unpublished).
[11] B. T. Cunningham, G. S. Jackson, and G. E. Stillman (unpublished).
[12] T. F. Kuech, D. J. Wolford, E. Veuhoff, V. Deline, P. M. Mooney, R. Potenski, and J. Bradley, J. Appl. Phys. 62, 632 (1987).
[13] K. P. Schug, Ber. Bunsenges Phys. Chem. 83, 167 (1979).
[14] Handbook of Chemistry and Physics, 1987–1988 edition (CRC, Boca Raton, Florida, 1988), p. f181; D. R. Stull and H. Prohet, Nat. Std. Ref. Data Series NBS No. 37 (1971).
[15] 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.
[16] H. A. Skinner, in Advances in Organometallic Chemistry, edited by F. G. A. Stone and R. West (Academic, New York, 1964), Vol. 2, pp. 49–114. (Ref. 3).
[17] T. L. Cottrell, The Strength of Chemical Bonds (Butterworth, London, 1954).
[18] L. H. Long, Pure Appl. Chem. 2, 61 (1961).