

Carbon Tetrachloride Doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ 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 $1 \times 10^{19} \text{cm}^{-3}$. To understand the effect of growth parameters on carbon incorporation in CCl_4 doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$, 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 (SIMS). All layers were grown by low pressure MOCVD using TMGa and TMAI 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 $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$. A linear relationship between hole concentration and CCl_4 flow rate in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ for $0.0 \leq x \leq 0.8$ was observed. These results are interpreted to indicate that adsorption and desorption of CCl_4 ($y \leq 3$) on the $\text{Al}_x\text{Ga}_{1-x}\text{As}$ surface during crystal growth plays an important role in the carbon incorporation mechanism.

Key words: AlGaAs, MOCVD, carbon doping

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 $4 \times 10^{19} \text{cm}^{-3}$.^{1,10} HBT structures grown by MOCVD with the thin p -type ($< 1000 \text{\AA}$) base region heavily doped with CCl_4 ($p = 2 \times 10^{19} \text{cm}^{-3}$) and a current gain cutoff frequency as high as $f_t = 26 \text{ GHz}$ have been reported.¹¹ P -type doping of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ in MOCVD grown heterojunction

diode laser structures is another potentially important application of CCl_4 doping. CCl_4 doping may be used to obtain $\text{Al}_x\text{Ga}_{1-x}\text{As}$ 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 $\text{Al}_x\text{Ga}_{1-x}\text{As}$, 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).

The SIMS ^{12}C concentration in CCl_4 doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ was found to increase with decreasing growth temperature for all Al compositions considered. However, the rate of increase substantially declined as the Al composition increased. Reduced growth rate resulted in substantially decreased car-

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bon acceptor concentrations in GaAs, but had an insignificant effect in $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$. A linear relationship between p -type carrier concentration and CCl_4 flow rate was observed in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ for $0.0 \leq x \leq 0.8$.

All layers were grown by low pressure MOCVD in an Emcore GS3100 reactor using TMGa and TMAI 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 ~ 100 Torr, total H_2 flow rate of ~ 9 slm, a substrate rotation speed of ~ 1500 rpm, and a column V mole fraction of $\sim 1 \times 10^{-2}$.

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 ($R_G \sim 1000 \text{ \AA}/\text{min}$, column III mole fraction $\sim 1.5 \times 10^{-4}$), 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 $\sim 0.5 \mu\text{m}$ at a each temperature ($640^\circ \text{C} \leq T_G \leq 810^\circ \text{C}$). A 2 minute 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 ($R_G \sim 1000 \text{ \AA}/\text{min}$), and growth temperature ($T_G = 600^\circ \text{C}, 700^\circ \text{C}$) constant during a single growth run while decreasing the CCl_4 mixture flow rate after each $\sim 0.5 \mu\text{m}$ 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 was 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 $\text{Al}_x\text{Ga}_{1-x}\text{As}$ on growth rate was studied by holding the Al composition ($x = 0.0, 0.4$), growth temperature ($T_G = 660^\circ \text{C}$), and CCl_4 mixture flow rate (50 sccm) constant while the growth rate was reduced in steps after the growth of $\sim 0.5 \mu\text{m}$ at a single growth rate. 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 $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8$) grown at $\sim 1000 \text{ \AA}/\text{min}$ 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 $T_G < 700^\circ \text{C}$. The carrier concentration of CCl_4 doped $\text{Al}_{0.4}\text{Ga}_{0.6}\text{As}$ was nearly independent of growth temperature for $640^\circ \text{C} \leq T_G \leq 760^\circ \text{C}$, but increased with decreasing growth temperature when $T_G \leq 640^\circ \text{C}$ and $760^\circ \text{C} \leq T_G \leq 810^\circ \text{C}$. In contrast, reduced growth temperatures resulted in lower carrier concentrations for $x = 0.6$

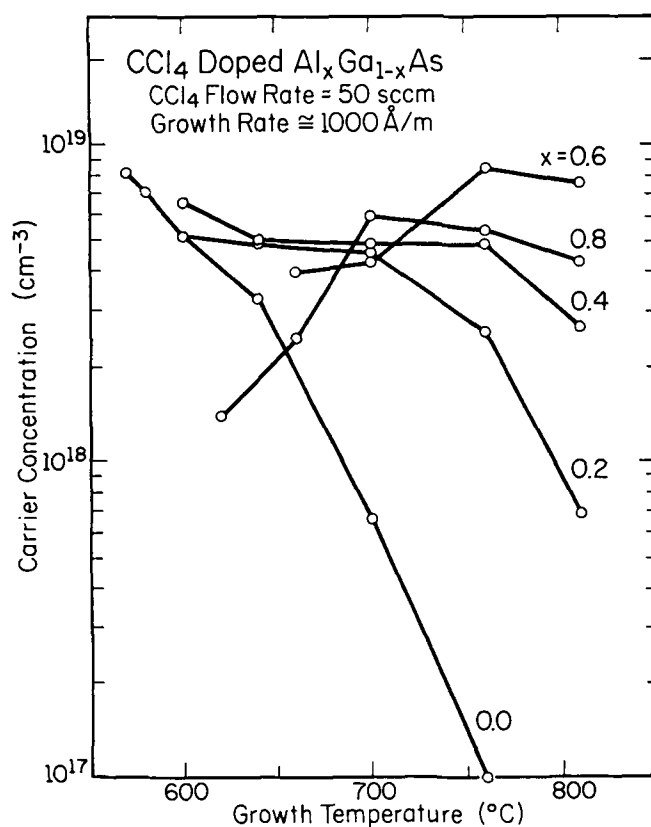


Fig. 1 — Variation of hole concentration with growth temperature for CCl_4 doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ grown at $1000 \text{ \AA}/\text{min}$.

with $T_G \leq 760^\circ \text{C}$ and for $x = 0.8$ with $T_G \leq 700^\circ \text{C}$. This effect, observed in doped and undoped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ samples when $x \geq 0.6$, is attributed to oxygen incorporation. Oxygen is a deep hole trap which reduces the free carrier concentration in $\text{Al}_x\text{Ga}_{1-x}\text{As}$. A decrease in the gettering of O_2 with Al at low growth temperatures results in increased oxygen incorporation in $\text{Al}_x\text{Ga}_{1-x}\text{As}$.¹² The deleterious effect of oxygen incorporation on the free carrier concentration of $\text{Al}_x\text{Ga}_{1-x}\text{As}$ 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 $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloy compositions ($x = 0.0, 0.2, 0.4, 0.6, 0.8$) grown at $\sim 1000 \text{ \AA}/\text{min}$ is 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 $640^\circ \text{C} \leq T_G \leq 760^\circ \text{C}$. The temperature variation of the ^{12}C concentration of these compositions are similar to the hole concentrations measured by electrochemical C-V profiling. For $0.4 \leq x \leq 0.8$, the ^{12}C concentration varied only slightly with growth temperature for $640^\circ \text{C} \leq T_G \leq 760^\circ \text{C}$, but increased with decreasing growth temperature when $T_G \leq 640^\circ \text{C}$ and $T_G \geq 760^\circ \text{C}$. Figure 2 clearly demon-

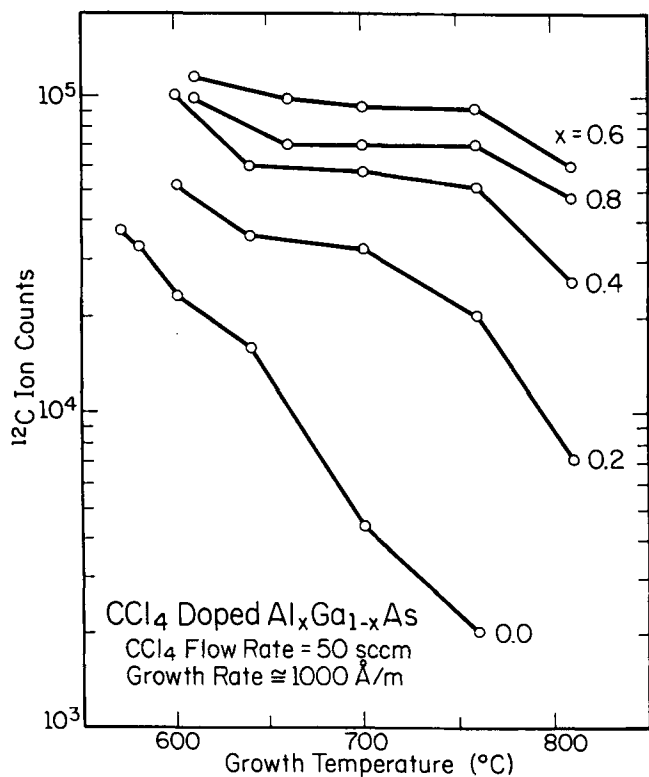


Fig. 2 — Variation of SIMS ^{12}C ion count with growth temperature for CCl_4 doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ grown at 1000 Å/min.

states that the effect of growth temperature on carbon incorporation from CCl_4 doping changes with $\text{Al}_x\text{Ga}_{1-x}\text{As}$ alloy composition.

The variation of hole concentration with CCl_4 flow rate in $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($x = 0.0, 0.4, 0.8$) grown at $T_G = 600^\circ\text{C}$ and $T_G = 700^\circ\text{C}$ 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. This trend was verified by SIMS analysis, as shown in Fig. 4. These results confirm that CCl_4 is responsible for the increased carbon acceptor concentrations observed in CCl_4 doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ samples.

The variation of the hole concentration with growth rate for two compositions of CCl_4 doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ($x = 0.0, 0.4$) grown at $T_G = 660^\circ\text{C}$ is shown in Fig. 5. For $x = 0.0$, the hole concentration was nearly independent of the growth rate for $R_G \geq 1000 \text{ Å/min}$, but the hole concentration decreased significantly with growth rate for $R_G \leq 1000 \text{ Å/min}$. 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 $\text{CCl}_3\text{-Cl}$ bond.¹⁴ Upon rupture of this first bond, the

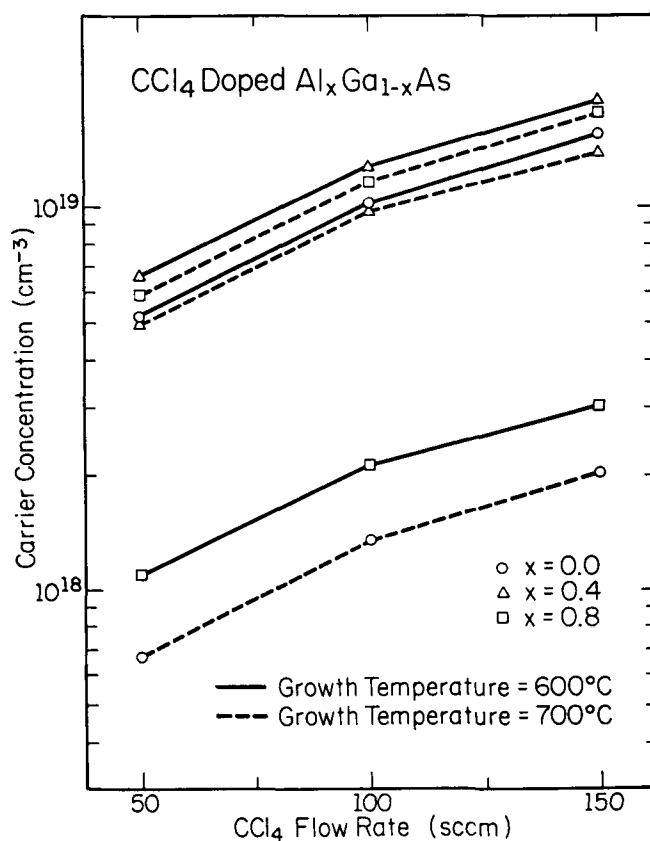


Fig. 3 — Variation of hole concentration with CCl_4 flow rate (1500 ppm mixture in H_2) for CCl_4 doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ grown at $T_G = 600^\circ\text{C}$ and $T_G = 700^\circ\text{C}$.

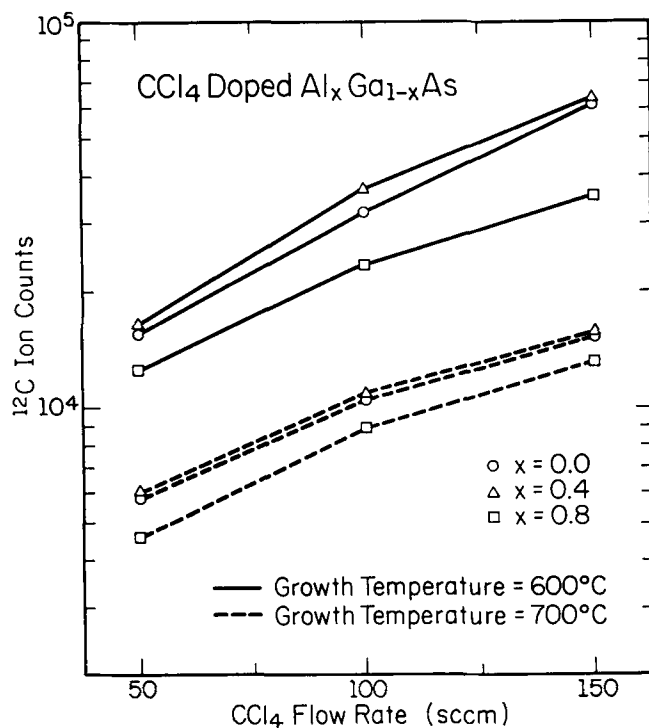


Fig. 4 — Variation of SIMS ^{12}C ion count with CCl_4 flow rate for CCl_4 doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$ grown at $T_G = 600^\circ\text{C}$ and $T_G = 700^\circ\text{C}$.

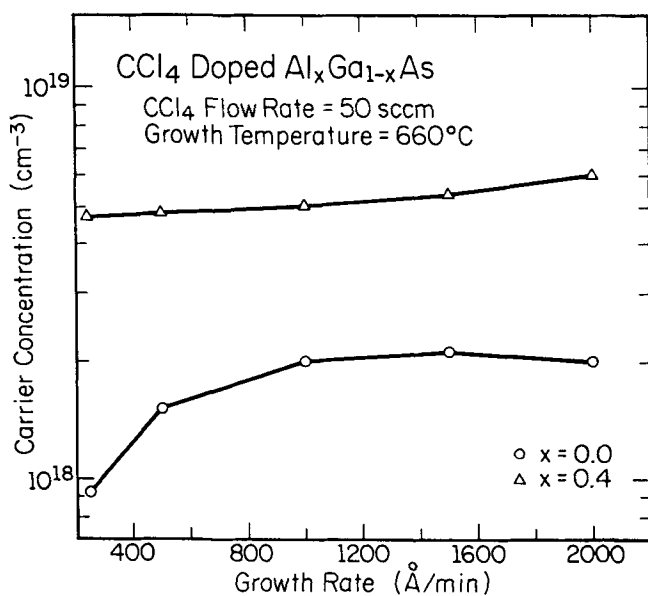


Fig. 5 — Hole concentration as a function of growth rate for CCl₄ doped GaAs and Al_{0.4}Ga_{0.6}As grown at T_G = 660° C.

CCl₂-Cl bond (67 kcal/mole) is almost certain to break immediately afterwards. However, the C-Cl bonds in CCl₂ are unlikely to rupture (~91 kcal/mole for each), thus it is unlikely that carbon incorporation results from the complete homolytic fission of CCl₄ in the gas phase.

A possible mechanism for carbon incorporation from CCl₄ which is consistent with the observed trends is the adsorption of CCl_y (y ≤ 3) on the Al_xGa_{1-x}As surface. During growth of GaAs, elevated growth temperatures result in increased desorption of CCl_y (y ≤ 3) 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 ≥ 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).^{15,19} The increased bond strength of the Al-C bond results in a decrease in the rate of CCl_y (y ≤ 3) 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 (y ≤ 3) until growth temperatures greater than 760° C are obtained, because the ¹²C ion count for CCl₄ doped Al_xGa_{1-x}As (x ≥ 0.4) does not decline significantly until T_G ≥ 760° C. More evidence for CCl₄ decomposition by surface adsorption rather than by gas phase homolytic fission is provided by the lack of carrier concentration variation with growth rate in CCl₄ doped Al_{0.4}Ga_{0.6}As where the Al-C bond on the substrate surface prevents significant CCl₄ desorption at low growth rates. In contrast, for CCl₄ doped GaAs where the Ga-C bond is weaker, a low growth rate increases the probability that a CCl_y (y ≤ 3)

molecule on the surface will desorb, resulting in lower carbon doping.

For heavily carbon doped GaAs (p ~ 1 × 10¹⁹ cm⁻³), the ratio of CCl₄ to TMGa in the reactor is ~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 (y ≤ 3) 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.

In conclusion, CCl₄ has been used as a p-type dopant source for Al_xGa_{1-x}As grown by low pressure MOCVD. The effect of growth parameters on carbon incorporation in CCl₄ doped Al_xGa_{1-x}As was studied as a function of Al composition, growth temperature, growth rate, and CCl₄ flow rate using electrochemical C-V profiling and SIMS. Increased Al composition reduced the effect of growth temperature on the carbon acceptor concentration. Reduced growth rates resulted in significant reduction in the carbon acceptor concentration of GaAs but had very little effect on the hole concentration of Al_{0.4}Ga_{0.6}As. A linear relationship between p-type carrier concentration and CCl₄ flow rate was observed for all combinations of Al composition and growth temperature considered. These results are most simply explained if surface adsorption and desorption of CCl_y (y ≤ 3) on the substrate surface are the dominant mechanisms involved in carbon incorporation from CCl₄ doping, rather than complete homolytic fission of the CCl₄ molecule in the gas phase.

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