

COMMUNICATIONS

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Methyl halides as carbon sources in a hot-filament diamond CVD reactor: A new gas phase growth species

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(Received 13 April 1992; accepted 8 October 1992)

Equal amounts of carbon-12 methyl halides and carbon-13 methane, along with hydrogen, have been introduced into a hot-filament diamond CVD chamber. The isotopic ratios of the as-deposited diamond films on tantalum have been measured by Raman spectroscopy. It was found that methyl chloride yielded carbon-12 enriched diamond films, while the other methyl halides resulted in equal amounts of carbon-13 and carbon-12 in the films. Furthermore, the carbon-12 enrichment was more enhanced as the substrate temperature was lowered. Matrix-isolation FTIR analyses of the gas samples collected during the deposition indicated that there was no straightforward agreement between the $^{12}\text{C}/^{13}\text{C}$ ratios of the gas phase species, methane and acetylene, and that of the diamond films. The results imply the presence of a new chlorocarbon radical such as CH_2Cl , which is postulated as a more effective growth species than the methyl radical.

Diamond is an excellent engineering and electronic material with unparalleled physical and chemical properties. Since the evidence of feasible and effective deposition of diamond films by CVD methods in the early 80s, there have been tremendous interest and flourishing research activities in this area due to the numerous potential applications of diamond films.¹ To date, most of the effort has centered around carbon, hydrogen, and oxygen systems, in which the methyl radical is believed to be the dominant growth precursor.² The discovery of a halogen-assisted chemical vapor deposition technique in a hot-wall tube reactor revealed new chemistry that leads to diamond formation.³ However, the detailed mechanisms of halogen-assisted diamond growth in such systems or in atomic hydrogen-based systems are still lacking and remain highly speculative. Consequently, there exists a need to elucidate the roles of halogens in CVD diamond processes.

A carbon-13 labeling technique has been demonstrated to be effective in resolving mechanistic controversies.⁴ We have applied this method to these studies of systems incorporating halogens. By correlating the isotopic ratios between the gas phase species and the as-grown films, information with respect to growth species is obtained.

The experiments involved injecting equal amounts of carbon-12 halocarbons and carbon-13 methane into a

hot-filament reactor, collecting gas samples immediately adjacent to the substrate, and subsequently analyzing these samples. The $^{12}\text{C}/^{13}\text{C}$ isotopic ratios of the as-deposited diamond films on tantalum were measured by Raman spectroscopy. All the reactions were carried out under conditions where complete isotopic scrambling between the C-12 halocarbon and C-13 methane do not occur. Such scrambling would mask all halogen effects if these do exist. This was achieved by introducing halocarbon and methane with a small amount of hydrogen immediately above the substrate, instead of passing them through the filaments. The gas sampling nozzle was positioned about 7 mm away from the reactant gas inlet. The substrate ($35 \times 4 \times 0.07$ mm) was mounted between the gas inlet and the gas sampling nozzle, and was in juxtaposition with the gas sampling nozzle. The detailed experimental apparatus has been described in a previous publication,⁴ and the typical growth conditions are summarized in Table I. The isotopic ratios of the diamond films were derived from the relationship⁵:

$$\nu(\text{cm}^{-1}) = 1332.96 - 37.52x - 5.63x^2 - 8.35x^3$$

where ν is the frequency of the first-order Raman shift of diamond films and x is the carbon-13 mole fraction in the films. The gas phase compositions were quantitatively identified by matrix-isolation FTIR spectroscopy.⁶

A series of monosubstituted halocarbons, CH_3F , CH_3Cl , CH_3Br , and CH_3I , has been investigated. It was found that, for equal input of carbon-12 halocarbon

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TABLE I. Typical deposition conditions.

Hydrogen gas flow	
Inlet (over the filament)	170 sccm
Inlet (mixed with reactant gases)	10 sccm
C-13 methane gas flow	0.5 sccm
Halocarbon	0.5 sccm
Chamber pressure	24–26 Torr
Substrate temperature	900 °C
Filament temperature	2170 °C
Filament material	W wire
Substrate to filament distance	7 mm
Substrate material	Ta

and carbon-13 methane, $^{12}\text{CH}_3\text{Cl}/^{13}\text{CH}_4$ always resulted in carbon-12 enriched diamond films with a Raman frequency at 1315.6 cm^{-1} . On the other hand, $^{12}\text{CH}_3\text{F}$, $^{12}\text{CH}_3\text{Br}$, and $^{12}\text{CH}_3\text{I}/^{13}\text{CH}_4$ yielded diamond films of almost equal isotopic percentage of carbon-12 and carbon-13, with a Raman frequency around 1312 cm^{-1} . The Raman spectra of these diamond films are shown in Fig. 1. From the Raman shifts, the $^{12}\text{C}/^{13}\text{C}$ ratio in the diamond film produced from the $^{12}\text{CH}_3\text{Cl}/^{13}\text{CH}_4$ mixture was calculated to be 1.4:1, while the other halides gave a 1:1 ratio.

Matrix-isolation FTIR analyses of the gas samples from this study, along with the control experiment where $^{12}\text{CH}_4/^{13}\text{CH}_4 = 1$, have been carried out. The results are summarized in Table II. As expected, the $^{12}\text{CH}_4/^{13}\text{CH}_4$ gas sample gave 1:1 $^{12}\text{C}/^{13}\text{C}$ ratios in both methane and acetylene within experimental error, which agrees well with the 1:1 $^{12}\text{C}/^{13}\text{C}$ ratio in the diamond film. For $^{12}\text{CH}_3\text{F}$, $^{12}\text{CH}_3\text{Br}$, and $^{12}\text{CH}_3\text{I}/^{13}\text{CH}_4$ reactions, all of the 1:1 $^{12}\text{C}/^{13}\text{C}$ ratios in methane are approximately 1:1 and close to that of the diamond films, but substantially different from that of acetylene. These observations

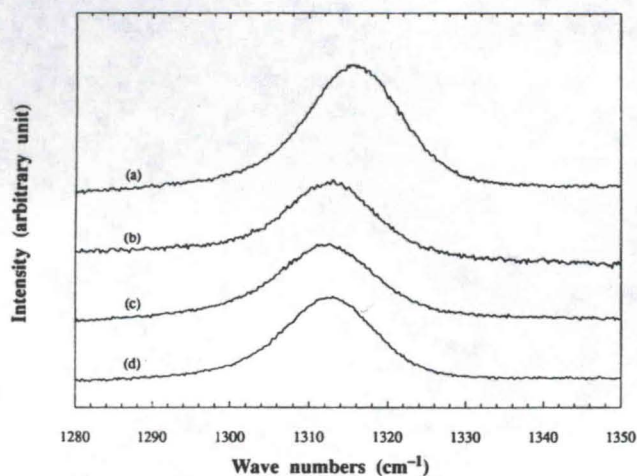


FIG. 1. Raman spectra of the diamond films from equal ratios of carbon-12 methyl halides/ $^{13}\text{CH}_4$ mixture, 0.2 cm^{-1} resolution, and 488 nm laser line. (a) CH_3Cl , (b) CH_3Br , (c) CH_3I , and (d) CH_3F .

reinforce the current belief that the methyl radical is the dominant growth species under our deposition conditions. However, it is significant that in the case of the $^{12}\text{CH}_3\text{Cl}/^{13}\text{CH}_4$ reaction, the gas phase compositions are similar to the other halocarbons, whereas neither the isotopic ratio of methane nor that of acetylene correlates with the $^{12}\text{C}/^{13}\text{C}$ ratio of the as-grown diamond film.

In addition to the tantalum substrate temperature being held at 900 °C, we also carried out depositions at 700 °C, 600 °C, and 500 °C for the $^{12}\text{CH}_3\text{Cl}/^{13}\text{CH}_4$ system. Raman spectroscopy revealed a trend toward more carbon-12 incorporation into diamond films as the substrate temperature was decreased. The Raman spectra of the four diamond films, illustrating this temperature effect, are shown in Fig. 2. The $^{12}\text{C}/^{13}\text{C}$ ratios are 1.4, 1.5, 1.9, and 2.3, respectively, for substrate temperatures at 900 °C, 700 °C, 600 °C, and 500 °C. The significant enrichment in carbon-12 suggests a possible role for chlorocarbons in the low temperature deposition of diamond films, which has been a goal sought by many researchers in this field.

Gas samples were also collected during the lower temperature depositions and analyzed thereafter. The $^{12}\text{C}/^{13}\text{C}$ ratios in methane at all substrate temperatures remained essentially 1:1, while those in acetylene approached 1:1 at lower temperatures. It is interesting to note that acetylene $^{12}\text{C}/^{13}\text{C}$ ratios are dependent on the substrate temperature, which suggests that the gas phase chemistry and surface chemistry are coupled. The implication of this phenomenon needs to be further examined. However, the measured isotopic compositions in the diamond films, once again, do not match those of methane and acetylene or combinations of both. These apparent discrepancies unequivocally indicate the existence of another growth precursor to diamond formation, in addition to methyl radicals.

In Table II the isotopic compositions of the gas phase and the diamond films for all the depositions have been tabulated. It can be easily noticed that there are several trends in the gas phase compositions. Firstly, the $^{12}\text{C}/^{13}\text{C}$ ratios in the methane stay almost unchanged at 1:1 for all deposition systems, which indicates that the steady state concentrations of $^{12}\text{CH}_3$ and $^{13}\text{CH}_3$ radicals are achieved under all conditions in the gas phase. This should result in equal amounts of carbon-12 and carbon-13 in the as-deposited diamond films, if there is no other route for diamond formation. Secondly, the total $^{12}\text{C}/^{13}\text{C}$ ratios in the gas phase show an increase in C-12 enrichment with increasing mass of the halocarbons, resulting in an imbalance in carbon-13 concentrations. This is believed to be due to the difference in mass diffusion rates among methyl halides, acetylene, and methane, causing local carbon-13 deficiency as a result of faster diffusion of methane away from the hot zone. Nevertheless, the carbon-12 enrichment in the diamond

TABLE II. Calculated isotopic compositions for the gas phase and the as-deposited diamond films.

Deposition systems	$^{12}\text{C}/^{13}\text{C}$ in methane	$^{12}\text{C}/^{13}\text{C}$ in acetylene	Total $\text{C}_2\text{H}_2/\text{CH}_4$	Total $^{12}\text{C}/^{13}\text{C}$ in gas phase	$^{12}\text{C}/^{13}\text{C}$ in diamond films
$^{12}\text{CH}_4/^{13}\text{CH}_4$	0.9	0.9	2.5	0.9	1.0
$^{12}\text{CH}_3\text{F}/^{13}\text{CH}_4$	0.9	1.5	1.2	1.3	1.0
$^{12}\text{CH}_3\text{Cl}/^{13}\text{CH}_4$	1.0	1.7	1.4	1.4	1.4
$^{12}\text{CH}_3\text{Br}/^{13}\text{CH}_4$	0.9	2.0	2.0	1.7	1.1
$^{12}\text{CH}_3\text{I}/^{13}\text{CH}_4$	1.1	2.0	2.2	1.8	1.0
$^{12}\text{CH}_3\text{Cl}/^{13}\text{CH}_4$ ($T_s = 700^\circ\text{C}$)	0.9	1.0	1.2	1.0	1.5
$^{12}\text{CH}_3\text{Cl}/^{13}\text{CH}_4$ ($T_s = 600^\circ\text{C}$)	1.1	1.2	1.8	1.2	1.9
$^{12}\text{CH}_3\text{Cl}/^{13}\text{CH}_4$ ($T_s = 500^\circ\text{C}$)	2.3

films is not a result of the preferential loss of methane, as exemplified by the results from the methyl bromide and iodide reactions.

Based on thermodynamics, it can be argued that all methyl halides should be fully hydrogenated in the presence of atomic hydrogen to methyl radicals and hydrogen halides. However, under normal CVD conditions where perfect thermodynamic equilibrium is usually not reached, chemical kinetics actually determines the concentration of each intermediate species and the fractional conversion of the parent compound. From our *ex situ* matrix-isolation FTIR analyses of the gas samples, it is observed that all the methyl bromides and iodides disappear completely, while about 1% of methyl chloride and 15% of methyl fluoride can be detected in the gas phase after passing over the deposition surface. These observations reflect the trend in the rate constants for hydrogen abstraction of halogen reactions, which are listed in Table III. Although transient species cannot be detected in our gas analyses, the existence of some halogen-containing intermediates during the depositions seems likely.

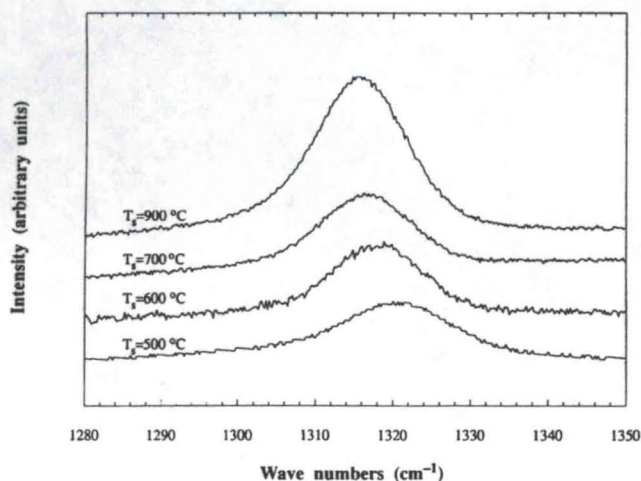
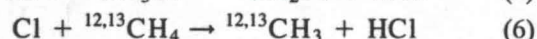
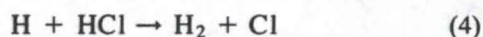


FIG. 2. Raman spectra of the diamond films from $^{12}\text{CH}_3\text{Cl}/^{13}\text{CH}_4$ at different substrate temperatures, 0.2 cm^{-1} resolution, and 488 nm laser line.

In the $^{12}\text{CH}_3\text{Cl}/^{13}\text{CH}_4$ system, the monochloromethyl radical, CH_2Cl , seems to be a reasonable additional growth precursor. In an atomic hydrogen environment, the following parallel reactions will simultaneously occur:



The elementary reaction between atomic hydrogen and C-13 methane produces only C-13 methyl radicals. On the other hand, the reaction between atomic hydrogen and methyl chloride leads to the formation of two types of radicals. Additionally, there are other pathways that can also enhance the production of CH_2Cl and CH_3 :



Obviously, the sum of reactions (4) and (6) yields reaction (1). This provides an atomic chlorine catalyzed route to methyl radical formation. Reaction (4) is essentially thermoneutral, with $\Delta G_f \approx 0$ at 1000°C . Moreover, its rate constant is large enough for the reaction to occur readily, which means that in an atomic hydrogen environment, chlorine atoms will always exist, in the presence of HCl in equilibrium with atomic hydrogen. Accordingly, CH_2Cl and CH_3 will form in the gas phase via reactions (5) and (6).

Interestingly, it is found that the reverse process for the second reaction is thermodynamically unfavorable. This implies that $^{13}\text{CH}_3\text{Cl}$ molecules, which would otherwise yield $^{13}\text{CH}_2\text{Cl}$ radicals, cannot be formed even in the presence of HCl. As a result, monochloromethyl radical will be present only as carbon-12 species; thus its contribution to diamond growth will be evident as carbon-12 enrichment.

The concentration of this radical is not expected to be as large as that of the methyl radical, since the residual amount of methane in the gas phase is many

TABLE III. Rate constants^{7,8} and equilibrium constants^{9,10} for selected gas phase reactions.

	log k_f [T (K)]				log K_{eq} [T (K)]			
	300	500	800	1200	300	500	800	1200
H + CH ₄ → CH ₃ + H ₂	5.5	8.9	11.0	12.1	0.8	1.0	1.2	1.4
H + CH ₃ Cl → CH ₃ + HCl	8.4	9.6	11.0	12.2	15.3	9.9	6.8	5.0
H + CH ₃ Cl → CH ₂ Cl + H ₂	4.3	3.2	2.6	2.2
H + CH ₃ F → CH ₃ + HF	6.2	9.0	10.7	11.6	20.8	13.2	8.9	6.5
H + CH ₃ Br → CH ₃ + HBr	9.5	11.1	12.1	12.6	14.2	9.2	6.0	4.1
H + CH ₃ I → CH ₃ + HI	12.8	12.2	8.0	5.6	4.2
H + HCl → CH ₃ + Cl	10.4	11.7	12.2	12.5	0.5	0.2	0.03	-0.1
Cl + CH ₄ → CH ₃ + HCl	10.8	11.7	12.1	12.8	0.3	0.8	1.2	1.4
Cl + CH ₃ Cl → CH ₂ Cl + HCl	11.5	12.2	12.6	12.8	3.9	3.0	2.6	0.0

times higher than that of methyl chloride, as indicated by gas sampling. This implies that addition of the CH₂Cl radical to the diamond surface occurs much more readily than the methyl radical. Perhaps this is caused by a more favorable abstraction of the chlorine on the diamond surface relative to hydrogen abstraction. The uniqueness of CH₃Cl versus the other methyl halides may result from the difficulty in forming atomic fluorine in the case of CH₃F and the inability of bromine and iodine to abstract hydrogen from C-H bonds in the CH₃Br and CH₃I systems.

Studies are currently underway to determine whether CH₂Cl and other possible chloro-radicals permit faster growth rates. Accelerated growth at lower substrate temperatures is also a possibility since atomic chlorine-hydrogen abstraction generally occurs with a lower activation barrier than atomic hydrogen-hydrogen abstraction.

ACKNOWLEDGMENTS

The authors acknowledge the National Science Foundation (CHE-8807546), the Office of Naval Research (SDIO/ONR-N00014-91-C-0113), and the Defense Advanced Research Project Agency (DARPA/ONR-N00014-91-C-0176) for financial support of this work.

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