

Mechanism of diamond growth by chemical vapor deposition: Carbon-13 studies

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(Received 23 September 1991; accepted for publication 23 October 1991)

Previous ¹³CH₄/¹²C₂H₂ isotopic competition experiments on the mechanism of diamond growth by chemical vapor deposition are reanalyzed in light of recent evidence for a nonlinear dependence of the first-order Raman shift frequency on ¹³C mole fraction. The new Raman data imply a ¹³C mole fraction for mixed-isotope diamond films several percent higher than that reported previously. The corrected carbon-13 mole fractions of polycrystalline diamond films and homoepitaxial films grown on (100), (111), and (110) natural diamond substrates were each equal, within experimental error, to that of the methane above the substrate but significantly different from that of gas-phase acetylene. As the ¹³C mole fractions of methyl radical and methane should be nearly identical, the methyl radical is concluded to be the predominant growth precursor regardless of the crystallographic orientation of the diamond substrate.

The growth of diamond films at low pressure by chemical vapor deposition (CVD) has generated tremendous interest within the past five years,¹ and much recent effort has been focused on determining fundamental aspects of the growth mechanism. The identity of the gas phase precursor primarily responsible for diamond growth has been highly controversial, and both methyl radical^{2,3(e)} and acetylene³ mechanisms have been proposed. We recently obtained the first direct evidence that the methyl radical is the primary growth precursor in hot-filament CVD of polycrystalline diamond films⁴ and homoepitaxial films grown on (100), (111), and (110) natural diamond substrates⁵ through isotopic competition experiments involving growth from a mixture of ¹³CH₄ and ¹²C₂H₂. Martin and co-workers⁶ have shown that diamond grows more readily when CH₄ is injected into a plasma-generated stream of hydrogen atoms than when acetylene is injected, indicating that the methyl radical is a more effective growth precursor than acetylene. Johnson *et al.*⁷ have very recently grown polycrystalline diamond films from a mixture of ¹³CH₄ and ¹²C₂H₂ by microwave plasma CVD, avoiding complete isotopic scrambling by operating at high flow rates. They found that the ¹³C mole fraction of diamond was only slightly below that of methane, indicating that ≈90% of the carbon atoms in the diamond resulted from species derived from methane (presumably methyl radicals). Indirect evidence suggesting growth predominantly by the methyl radical has been obtained by several groups,⁸ while indirect evidence suggesting growth predominantly by acetylene or from a combination of both precursors has also been seen.⁹

Our experiments, carried out under conditions where complete isotopic scrambling between ¹³CH₄ and ¹²C₂H₂ did not occur, involved comparing the isotopic composition of gases collected immediately adjacent to the substrate to that of the diamond films. The experimental ap-

paratus and growth conditions have been described in detail.^{4,5} The isotopic composition of the diamond films was derived from the first-order Raman shift frequency, which we determined⁴ to be approximately linear in ¹³C mole fraction. However, recent experiments by Hass *et al.*,¹⁰ Banholzer *et al.*¹¹ and by Nisida and Kanda¹² have shown that the dependence of Raman frequency on ¹³C mole fraction has a significant downward curvature. The new results are shown in Fig. 1, together with a cubic polynomial fit to the data of Banholzer *et al.* Earlier Raman data of Chrenko¹³ showed a similar effect but the ¹³C compositions were subsequently found to be slightly inaccurate.¹⁴ The cubic fit is seen to fit all the data rather well. Hass *et al.*¹⁰ have shown that the curvature results from isotopic disorder in diamond as a consequence of the nonsymmetric way that ¹²C and ¹³C couple to lattice phonons.

It is not entirely clear why the curvature in the dependence of Raman shift on mole fraction was not evident in our CVD-grown polycrystalline films.⁴ The apparent linear dependence was discussed⁴ in a framework equivalent to the virtual crystal approximation described by Hass *et al.*¹⁰ The relative flow rates of ¹³CH₄ and ¹²CH₄ were determined in our initial work using factory-calibrated mass flowmeters but the isotopic composition of the gas phase was not independently verified. As the ¹³CH₄/¹²CH₄ studies were the first growth experiments we performed, the error bars on either the Raman frequency or mole fraction may have been larger than was thought, or perhaps impurities or stress were present in the films.

As discussed previously,⁵ our analysis presumes that the incorporation rates of ¹²CH₃ and ¹³CH₃ (or the carbon isotopes of C₂H₂) into the growing diamond film are identical. Derjaguin and Fedoseev¹⁵ have claimed that carbon-13 is preferentially incorporated into diamond, but recent preliminary results of Banholzer¹⁶ indicate no significant ¹³C/¹²C kinetic isotope effect.

We have reanalyzed the Raman data for our mixed-isotope diamond films^{4,5} using the cubic polynomial fit shown in Fig. 1. The results are summarized in Table I.

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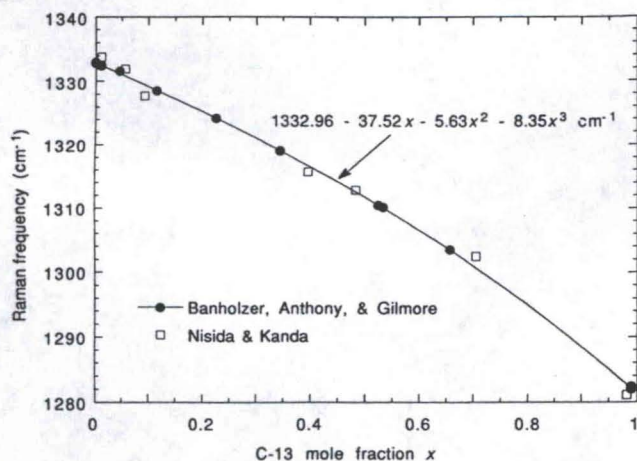


FIG. 1. Dependence of first-order Raman shift of diamond on carbon-13 mole fraction. Data are shown from Banholzer *et al.* (see Ref. 11) and Nisida and Kanda (see Ref. 12).

Also included in Table I are the ^{13}C mole fraction of methane and acetylene determined previously^{4,5} by matrix isolation infrared spectroscopy after collection via a probe located immediately adjacent to the substrate. The ^{13}C mole fraction of the diamond films, polycrystalline and homoepitaxial films grown on (100), (111), and (110) substrates, were each equal, within experiment error, to that of methane and significantly different from that of acetylene.

As discussed previously,⁴ the ^{13}C mole fraction of CH_3 is approximately equal to

$$\frac{[^{13}\text{CH}_4]}{[^{12}\text{CH}_4] + [^{13}\text{CH}_4]} \approx \left\{ 1 + \frac{1}{2} \frac{[^{12,13}\text{C}_2\text{H}_2]}{[^{13,13}\text{C}_2\text{H}_2]} \right\}^{-1} \quad (1)$$

in the limit of quasiequilibrium between $^{13}\text{CH}_3$, $^{12}\text{CH}_3$ and $^{13,13}\text{C}_2\text{H}_2$, $^{12,13}\text{C}_2\text{H}_2$. However, as pointed out by Frenklach,¹⁷ interconversion of CH_3 and C_2H_2 is well out of quasiequilibrium away from the filament. It is readily seen that Eq. (1) is also approximately valid in the oppo-

site limit, irreversible conversion of $^{13}\text{CH}_3$ and $^{12}\text{CH}_3$ to $^{13,13}\text{C}_2\text{H}_2$ and $^{12,13}\text{C}_2\text{H}_2$. In the latter limit the concentration of $^{13,13}\text{C}_2\text{H}_2$ would be proportional to a cross section times a collision number multiplied by $[^{13}\text{CH}_4]^2$, while $[^{12,13}\text{C}_2\text{H}_2]$ would be proportional to twice (the factor of two results from the inversion symmetry present in $^{13,13}\text{C}_2\text{H}_2$ but lacking in $^{12,13}\text{C}_2\text{H}_2$) the same cross section and collision number multiplied by $[^{12}\text{CH}_4][^{13}\text{CH}_4]$, resulting in Eq. (1). However, irreversible acetylene formation from methyl radicals is contradicted by the observation^{4,5} of partial conversion of $^{12}\text{C}_2\text{H}_2$ to $^{12,13}\text{C}_2\text{H}_2$, presumably via $^{12}\text{CH}_3$. Equation (1) is likely to be reasonably accurate given its validity in either limit but is clearly subject to uncertainty.

On the other hand, interconversion of CH_3 and CH_4 , via $\text{CH}_4 + \text{H} \rightleftharpoons \text{CH}_3 + \text{H}_2$, has been calculated by Goodwin and Gavillet¹⁸ to remain in quasiequilibrium to within a few mm of the substrate. The quasiequilibrium will insure that CH_3 and CH_4 remain in isotopic equilibrium. Near the substrate, however, quasiequilibrium fails due to surface-catalyzed H recombination (via abstraction of surface hydrogen), as predicted by Goodwin and Gavillet^{18(b)} and observed by Hsu.¹⁹ CH_3 and CH_4 will nonetheless remain in isotopic equilibrium unless reactions interconverting C_1 and C_2 species occur at a significant rate within the boundary layer or on the diamond surface. The preponderance of evidence, including detailed modeling calculations,¹⁸ indicates that $\text{C}_1 \rightleftharpoons \text{C}_2$ interconversion is much slower than $\text{CH}_3 \rightleftharpoons \text{CH}_4$ interconversion. We observed essentially identical ^{13}C mole fractions in methane and acetylene with and without a diamond substrate, suggesting that surface-catalyzed interconversion is insignificant. However, both Harris *et al.*²⁰ and Wu and co-workers^{9(a)} observed, using a quartz probe, a $\text{CH}_4/\text{C}_2\text{H}_2$ ratio that continually increased with increasing distance from the hot filament, which might be interpreted as implying non-negligible $\text{C}_1 \rightleftharpoons \text{C}_2$ interconversion chemistry. These spatial variations in the $\text{CH}_4/\text{C}_2\text{H}_2$ ratio are probably due primarily to thermal diffusion,²⁰ as the ap-

TABLE I. Comparison of ^{13}C mole fractions (%) in diamond films and gas phase reactants using a $^{13}\text{CH}_4/^{12}\text{C}_2\text{H}_2$ input ratio of 2:1. The uncertainties listed are calculated at the 95% confidence level and include statistical contributions only.

Polycrystalline	Diamond homoepitaxial			Gas phase reactants		
	(100)	(111)	(110)	CH_4^a	C_2H_2	$\text{CH}_4/\text{C}_2\text{H}_2$
57.7				57.7	32.4	4.1
61.0				64.8	27.7	3.9
58.4				64.2	33.5	3.3
55.6				59.8	36.1	4.0
Mean:						
58.2 ± 3.6	57.6	55.5	55.3	61.6 ± 5.5	32.4 ± 5.6	3.8 ± 0.6
			57.8	53.9	34.8	2.8
				61.1	36.0	1.8
	57.0	57.6		58.5	30.5	2.6
		Mean:		61.1	38.4	2.9
		56.8 ± 1.2		58.6 ± 5.4	34.9 ± 5.3	2.5 ± 0.8

^aThe ^{13}C mole fraction of CH_3 is assumed to be equal to that of CH_4 .

parent carbon balance was low near the filament,^{9(a),20} and perturbation of the gas phase temperature profile and chemistry by the probe is probably significant.²⁰ In any case, our sampling probes were located at a distance from the filament within ≈ 1 mm of the filament-substrate distance, and therefore sampled a $\text{CH}_4/\text{C}_2\text{H}_2$ ratio representative of that at the substrate surface. Any further reactions of stable hydrocarbon species within the water-cooled probe would be quenched. We thus conclude that the ^{13}C mole fractions of CH_3 and CH_4 at the substrate should be very nearly equal, and the proximity of the gas-sampling probes to the substrate should assure a reasonably accurate determination of the isotopic compositions of methane and acetylene.

Clearly, a true *in situ* determination of the ^{13}C mole fractions of the gas phase species above the surface, by molecular beam sampling mass spectrometry, for example, would be preferable to our *ex situ* measurements, as noted previously.⁴ We think it is very unlikely, however, that the ^{13}C mole fraction of CH_3 at the substrate surface differed from our measured value for CH_4 (59–62%) by more than 5–10%. Given the magnitude of the difference in ^{13}C mole fractions between diamond (57–58%) and acetylene (32–35%), it seems quite clear that methyl radicals were the predominant growth precursor. We cannot exclude contributions to growth by acetylene, however. If the differences between the ^{13}C mole fractions of diamond and methane (methyl radical) are real, then $\approx 90\%$ of the diamond originated from methyl radicals and the remainder from acetylene.

Acetylene-based growth mechanisms,³ while not disproved by our experiments, are shown not to be dominant, at least under the growth conditions employed here. As discussed elsewhere,^{5,21} existing methyl radical mechanisms have shortcomings as well. Considerably more experimental and theoretical work, particularly on surface intermediates and surface rate processes, will be necessary in order to elucidate the details of the adsorption, decomposition, and incorporation of methyl radicals into the diamond lattice.

The authors acknowledge the National Science Foundation for support of this work by Grant CHE-8807546 and the Office of Naval Research for additional support. The authors thank Dr. Mike Tamor for bringing the new ^{13}C Raman data to our attention and Dr. Bill Banholzer, Dr. Curtis Johnson, Dr. Barbara Garrison, Dr. Michael Frenklach, and Dr. Steve Harris for providing us with manuscripts prior to publication. MPD also thanks Dr. Bill Banholzer, Dr. Steve Harris, Dr. Dave Goodwin, Dr. Ching-Hsong (George) Wu, and Dr. Mike Tamor for useful discussions.

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¹⁶ W. F. Banholzer (private communication to MPD). Diamond grown from commercial methane (presumably 1.08% ^{13}C) was found to have a ^{13}C mole fraction of 1.037%. He indicated that further studies are underway.

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