

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

M. P. D'Evelyn, C. J. Chu,<sup>a)</sup> R. H. Hange,<sup>a)</sup> and J. L. Margrave<sup>a)</sup>

Department of Chemistry and Rice Quantum Institute, Rice University, Houston, Texas 77251-1892

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Previous <sup>13</sup>CH<sub>4</sub>/<sup>12</sup>C<sub>2</sub>H<sub>2</sub> 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 <sup>13</sup>C mole fraction. The new Raman data imply a <sup>13</sup>C 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 <sup>13</sup>C 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,<sup>1</sup> 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<sup>2,3(e)</sup> and acetylene<sup>3</sup> 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 films<sup>4</sup> and homoepitaxial films grown on (100), (111), and (110) natural diamond substrates<sup>5</sup> through isotopic competition experiments involving growth from a mixture of <sup>13</sup>CH<sub>4</sub> and <sup>12</sup>C<sub>2</sub>H<sub>2</sub>. Martin and co-workers<sup>6</sup> have shown that diamond grows more readily when CH<sub>4</sub> 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.*<sup>7</sup> have very recently grown polycrystalline diamond films from a mixture of <sup>13</sup>CH<sub>4</sub> and <sup>12</sup>C<sub>2</sub>H<sub>2</sub> by microwave plasma CVD, avoiding complete isotopic scrambling by operating at high flow rates. They found that the <sup>13</sup>C 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,<sup>8</sup> while indirect evidence suggesting growth predominantly by acetylene or from a combination of both precursors has also been seen.<sup>9</sup>

Our experiments, carried out under conditions where complete isotopic scrambling between <sup>13</sup>CH<sub>4</sub> and <sup>12</sup>C<sub>2</sub>H<sub>2</sub> 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.<sup>4,5</sup> The isotopic composition of the diamond films was derived from the first-order Raman shift frequency, which we determined<sup>4</sup> to be approximately linear in <sup>13</sup>C mole fraction. However, recent experiments by Hass *et al.*,<sup>10</sup> Banholzer *et al.*<sup>11</sup> and by Nisida and Kanda<sup>12</sup> have shown that the dependence of Raman frequency on <sup>13</sup>C 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 Chrenko<sup>13</sup> showed a similar effect but the <sup>13</sup>C compositions were subsequently found to be slightly inaccurate.<sup>14</sup> The cubic fit is seen to fit all the data rather well. Hass *et al.*<sup>10</sup> have shown that the curvature results from isotopic disorder in diamond as a consequence of the nonsymmetric way that <sup>12</sup>C and <sup>13</sup>C 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.<sup>4</sup> The apparent linear dependence was discussed<sup>4</sup> in a framework equivalent to the virtual crystal approximation described by Hass *et al.*<sup>10</sup> The relative flow rates of <sup>13</sup>CH<sub>4</sub> and <sup>12</sup>CH<sub>4</sub> 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 <sup>13</sup>CH<sub>4</sub>/<sup>12</sup>CH<sub>4</sub> 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,<sup>5</sup> our analysis presumes that the incorporation rates of <sup>12</sup>CH<sub>3</sub> and <sup>13</sup>CH<sub>3</sub> (or the carbon isotopes of C<sub>2</sub>H<sub>2</sub>) into the growing diamond film are identical. Derjaguin and Fedoseev<sup>15</sup> have claimed that carbon-13 is preferentially incorporated into diamond, but recent preliminary results of Banholzer<sup>16</sup> indicate no significant <sup>13</sup>C/<sup>12</sup>C kinetic isotope effect.

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

<sup>a)</sup> Also affiliated with Houston Advanced Research Center, 4802 Research Forest Dr., The Woodlands, TX 77381.

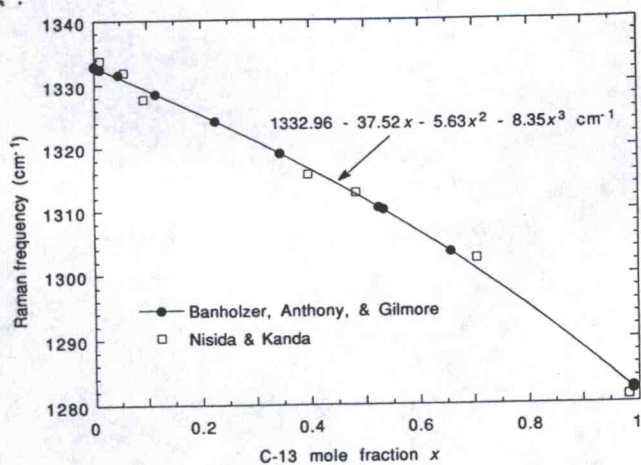


FIG. 1. Dependence of first-order Raman shift of diamond on carbon-13 mole fraction. Data are shown from Banholzer *et al.* (see Ref. 11) and Nisida and Kanda (see Ref. 12).

Also included in Table I are the  $^{13}\text{C}$  mole fraction of methane and acetylene determined previously<sup>4,5</sup> by matrix isolation infrared spectroscopy after collection via a probe located immediately adjacent to the substrate. The  $^{13}\text{C}$  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,<sup>4</sup> the  $^{13}\text{C}$  mole fraction of  $\text{CH}_3$  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,<sup>17</sup> interconversion of  $\text{CH}_3$  and  $\text{C}_2\text{H}_2$  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<sup>4,5</sup> 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  $\text{CH}_3$  and  $\text{CH}_4$ , via  $\text{CH}_4 + \text{H} \rightleftharpoons \text{CH}_3 + \text{H}_2$ , has been calculated by Goodwin and Gavillet<sup>18</sup> to remain in quasiequilibrium to within a few mm of the substrate. The quasiequilibrium will insure that  $\text{CH}_3$  and  $\text{CH}_4$  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<sup>18(b)</sup> and observed by Hsu.<sup>19</sup>  $\text{CH}_3$  and  $\text{CH}_4$  will nonetheless remain in isotopic equilibrium unless reactions interconverting  $\text{C}_1$  and  $\text{C}_2$  species occur at a significant rate within the boundary layer or on the diamond surface. The preponderance of evidence, including detailed modeling calculations,<sup>18</sup> 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  $^{13}\text{C}$  mole fractions in methane and acetylene with and without a diamond substrate, suggesting that surface-catalyzed interconversion is insignificant. However, both Harris *et al.*<sup>20</sup> and Wu and co-workers<sup>9(a)</sup> 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,<sup>20</sup> as the ap-

TABLE I. Comparison of  $^{13}\text{C}$  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)	$\text{CH}_4^a$	$\text{C}_2\text{H}_2$	$\text{CH}_4/\text{C}_2\text{H}_2$
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:						
$58.2 \pm 3.6$				$61.6 \pm 5.5$	$32.4 \pm 5.6$	$3.8 \pm 0.6$
	57.6			53.9	34.8	2.8
		55.5		61.1	36.0	1.8
			55.3	58.5	30.5	2.6
	57.0	57.6	57.8	61.1	38.4	2.9
		Mean:				
		$56.8 \pm 1.2$		$58.6 \pm 5.4$	$34.9 \pm 5.3$	$2.5 \pm 0.8$

<sup>a</sup>The  $^{13}\text{C}$  mole fraction of  $\text{CH}_3$  is assumed to be equal to that of  $\text{CH}_4$ .

parent carbon balance was low near the filament,<sup>9(a),20</sup> and perturbation of the gas phase temperature profile and chemistry by the probe is probably significant.<sup>20</sup> In any case, our sampling probes were located at a distance from the filament within  $\approx 1$  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  $^{13}\text{C}$  mole fractions of  $\text{CH}_3$  and  $\text{CH}_4$  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  $^{13}\text{C}$  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.<sup>4</sup> We think it is very unlikely, however, that the  $^{13}\text{C}$  mole fraction of  $\text{CH}_3$  at the substrate surface differed from our measured value for  $\text{CH}_4$  (59–62%) by more than 5–10%. Given the magnitude of the difference in  $^{13}\text{C}$  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  $^{13}\text{C}$  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,<sup>3</sup> while not disproved by our experiments, are shown not to be dominant, at least under the growth conditions employed here. As discussed elsewhere,<sup>5,21</sup> 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.

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

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