

High temperature chemistry of CVD (chemical vapor deposition) diamond growth

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Abstract: Understanding the high temperature chemistry of diamond deposition is the key to turning recently developed CVD techniques for synthesizing diamond coatings into technological applications utilizing its unique combination of properties. This paper reviews the state of our knowledge for diamond deposition from carbon-hydrogen systems, a knowledge that has benefited greatly from combustion research over the past several decades. Generic kinetic considerations have generated useful limits on and trends in deposition behavior, and proposed mechanisms have provided insights into our thinking about molecular processes which transform hydrocarbons into a diamond structure. The type of information and research thought to be of most use in furthering our understanding of the high temperature chemistry of diamond deposition is summarized at the end of this paper.

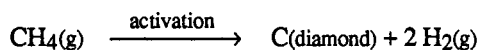
INTRODUCTION

High temperature chemistry plays an important role in the chemical vapor deposition (CVD) synthesis of coatings and powders (1,2), including the newly developed methods for vapor depositing diamond films at reasonable rates. Diamond CVD has opened many potential uses of this unique material, as is discussed in a recent comprehensive book (3) which traces the emergence of CVD diamond science and technology, reviews our current understanding of its synthesis, examines its properties and characterization, and then surveys current and potential applications, including an economic and market analysis. Additional reviews can also be found on the history, science, and technology of CVD diamond (4-6).

This paper on the high temperature chemistry of CVD diamond from carbon-hydrogen systems briefly describes background information on observed chemistry and useful concepts and ideas which have developed (6), and then delves into knowledge of limiting behavior gained from generic kinetic considerations (7-9), and mechanisms which have been proposed for incorporating carbon-containing species into specific diamond surface sites (10). The paper concludes with a general summary of the type of information thought to be most needed to enhance our understanding of the high temperature chemistry of CVD diamond growth.

GENERAL BACKGROUND ON CVD DIAMOND GROWTH CHEMISTRY

A typical process for depositing diamond films at reasonable rates of 0.1 to 1 $\mu\text{m/hr}$ consists of reactant gases at one atmosphere or less total pressure which are activated before contacting a 500 to 1000°C substrate onto which diamond is deposited. The coating process utilizes conditions under which graphite is clearly the stable form of carbon, but diamond surface stabilization during growth along with kinetic factors allow crystalline diamond to be produced by a typical net reaction of



where the gas is usually activated by either plasmas, discharges, or temperatures greater than 2000°C. In addition to methane, typically diluted to 0.05 to 2% in hydrogen, a wide variety of carbon-containing substances including saturated and unsaturated hydrocarbons, alcohols, ketones, halides, and carbon monoxide have been used as precursor gases. This paper concentrates only on hydrocarbon precursors.

The chemistry of diamond nucleation and growth is more complex than in most deposition systems because of: (i) the unique competition for deposition among sp^2 and sp^3 types of carbon, and (ii) the many possible chemical reactions resulting from the complexity of organic systems in comparison to typical inorganic CVD systems. In contrast to silicon, which does not exhibit sp^2 hybridized structures, the competitive co-deposition of non-diamond carbon is always a concern in diamond CVD. Controlling the simultaneous deposition of diamond and non-diamond carbon requires an understanding of the competitive

molecular processes, a task which has been greatly aided by chemical information developed over the past several decades through studies of combustion processes (see Appendix in ref. 10 for details). An early attempt to examine the complexities of diamond CVD by kinetic calculations was made by Frenklach and Wang (7). They calculated the competitive rates of deposition of sp^2 and sp^3 carbons, the conversion of sp^2 to sp^3 carbon and the reverse, etching of the various forms of carbon, and other such processes to determine net deposition rates and quality of diamond deposits.

Experimental Observations of Diamond Growth Chemistry

Selective experimental "facts" concerning CVD diamond growth chemistry are listed below; more detailed and extensive discussions were given previously (6,8,10).

- 1) *Gas Activation*: required for achieving appreciable diamond growth rates of A/hr to $\mu\text{m/hr}$.
- 2) *Independence of Activation Method*: various activation methods produce good quality CVD diamond.
- 3) *Independence of Carbon-Containing Precursor*: diamond of similar quality and morphology has been grown using a variety of carbon-containing species.
- 4) *Hydrogen is Required for Efficient Growth*: not necessarily in excess to that introduced as part of a hydrocarbon precursor.
- 5) *Co-deposition of Diamond and Non-diamond Carbon*: graphite and other non-diamond carbons usually deposit simultaneously with diamond.
- 6) *Diamond Growth Rate Maximum with Temperature Change*: maximum $\sim 1000^\circ\text{C}$ in typical systems.
- 7) *Crystallite Morphology*: octahedral {111}, cubic {100}, twinning on {111} surfaces, and cubo-octahedral composed of both {111} and {100} surfaces are most common.

Growth Species

Methyl radicals and acetylene are the most abundant hydrocarbon species reaching diamond growth surfaces in typical microwave plasma and hot-filament activated diamond reactors (11). The mechanisms discussed in this paper primarily involve these species, but in some high energy reactors such as one atmosphere arcjets, species such as CH_2 , C_2H , and even C atoms may attain significant concentrations (12-14). Matsumoto and Matsui (15) and Angus and Hayman (5) considered using large hydrocarbon species with structures similar to diamond fragments, such as adamantane, but such species are typically not stable at diamond growth conditions. Deducing which chemical species could be mechanistically important in diamond growth should take into account species concentration, adsorption and desorption coefficients, only elementary surface reactions leading to diamond growth which exhibit low activation energies, and an overall net growth reaction with a negative Gibbs free energy.

PROPOSED CONCEPTS AND IDEAS ON DIAMOND GROWTH

Studies of Deryagin, Fedoseev, Spitsyn, Varnin, and co-workers

These scientists developed a global kinetic theory for diamond nucleation and growth (16), but did not identify either potential growth species or specific reactions taking place at the surface. However, they suggested the insightful concept that despite the fact that diamond is metastable with respect to graphite at low pressures, the CVD growth of diamond can occur because it is controlled by kinetics and not thermodynamics. The "kinetic advantage" was explained by Deryagin and co-workers, along with Angus (see ref. 5), as the preferential etching of graphite over diamond by hydrogen atoms. This "etching theory" assumes that graphitic carbon and diamond are formed simultaneously, but the graphitic phases are more readily etched than diamond by H atoms which are present in super-equilibrium concentrations.

Postulate of Chemical Similarity

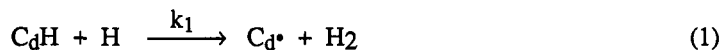
CVD diamond surface reactions have been assumed to be similar to reactions with large alkane molecules. This is the essence of the postulate advanced several years ago of the chemical similarity between analogous surface and gas-phase reactions (8,17,18). This postulate is founded on the premise that the chemical reactivity of solid carbonaceous materials is localized at the carbon sites in a manner similar to that of corresponding gaseous alkane species. Two immediate conclusions follow: (i) surface reactions in diamond CVD are similar to those typical of hydrocarbon gas-phase chemistry, and (ii) the kinetics of analogous elementary chemical reactions on a per site basis are the same for all forms of carbon. Based on these considerations, surface processes can be modeled in terms of elementary chemical reactions at specific surface sites. Many proposed reaction mechanisms of diamond growth have assumed this postulate of chemical similarity (7,8,19-23), in that most of the surface reactions used were founded on analogous gas-phase reactions, and their rate parameters were estimated from closely related prototype gas-phase reactions. Although most mechanistic modeling studies have met with apparent "success", it should be remembered that the postulate of chemical similarity is just an ad hoc hypothesis advanced initially to provide a rational means for semi-quantitative thinking on the fundamental aspects of diamond chemistry.

Aromatics Theory

Along with generating molecular precursors for diamond growth, gas-phase reactions produce higher molecular weight compounds. Among them are particularly stable and "sticky" aromatic hydrocarbons, the smallest of them being benzene. When present in the deposition zone at typical substrate temperatures, aromatic species can condense on the growing surface, thereby covering the diamond sp^3 carbon with sp^2 carbon phases and poisoning the sites for diamond growth (17,24). The condensing aromatic molecules could serve as nuclei for sp^2 carbon growth, pyrolyze to smaller hydrocarbon fragments which gasify or produce various forms of solid carbon, or hydrogenate to become part of a diamond or an amorphous sp^2/sp^3 carbonaceous network. Although no experimental information is available for condensation of aromatics on diamond surfaces, inclusion of the aromatics model into detailed kinetic simulations of diamond CVD appears to correctly reproduce experimental effects of temperature, pressure, hydrocarbon concentration, and the addition of oxygen on the quality of diamond deposits (7,25).

GENERAL KINETIC FEATURES OF CVD DIAMOND GROWTH

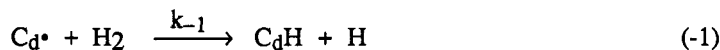
Independent of specific growth mechanisms, there appears to be growing consensus on two general features of diamond growth reaction kinetics. The *first* is that the principal element of diamond growth is the formation of an active diamond growth site, a surface carbon sp^3 radical C_d^* , followed by the addition of a carbonaceous gaseous species to this surface radical (8,18,26,27). The *second* feature is that under typical growth conditions, the number density of carbon surface radicals, defined as $\chi_{C_d^*}$ = number of diamond carbon surface radicals per unit area, is determined primarily by the balance between the abstraction of hydrogen from surface C-H bonds by gaseous hydrogen atoms,



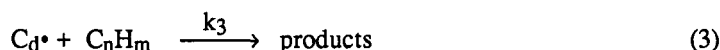
and the combination of the carbon surface radicals with free gaseous hydrogen atoms,



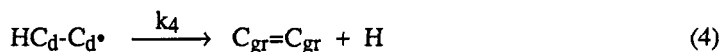
where C_dH and C_d^* denote the diamond surface sites of C-H bond and carbon surface radicals, respectively. These kinetic features were first revealed in the analysis of Frenklach and Wang (7). The reverse of reaction (2), the thermal desorption of chemisorbed hydrogen atoms, can be neglected under typical growth conditions because of the strong C-H bond strength. The reverse of reaction (1),



is too slow to compete with reaction (2) under typical CVD diamond conditions. In addition to reactions (1) and (2), the number density of the surface radicals, $\chi_{C_d^*}$, is determined by the addition of the growth species to the surface radicals,



and the thermal decomposition of the diamond structure surface radicals to sp^2 surface carbons (and its reverse),



where C_{gr} denotes an sp^2 -hybridized carbon site.

Under steady state conditions for C_d^* (see ref. 7),

$$\chi_{C_d^*} = \frac{k_1[H] \chi_{C_dH} + k_{-4}[H] \chi_{C_{gr}}}{k_{-1}[H_2] + k_2[H] + k_3[C_nH_m] + k_4} \quad (5)$$

where χ denotes the number density of the corresponding carbon surface sites, square brackets the concentrations of gaseous species, and k_i the rate coefficients of the corresponding reactions. Note that the products formed in reaction (3) contribute to the formation of C_dH and C_d^* sites, so would minimize the decrease in growth sites caused by reaction (3).

The above general kinetic analysis (7) has been recently used by others in explaining kinetic behavior and scaling laws for optimizing diamond CVD systems (9,22,28). The following illustrates how observed experimental trends can be explained using such an analysis (6-8,10):

A. *Under typical deposition conditions (high H atom concentrations),* the term $k_2[H]$ dominates the denominator and $k_1[H] \chi_{C_dH}$ dominates the numerator of Equation (5), which leads to expression

$$\chi_{C_d\bullet} = \frac{k_1}{k_2} \chi_{C_dH} \quad (6)$$

From Equation (6) follows that the number density of carbon surface radical sites, $\chi_{C_d\bullet}$, and hence the rate of diamond growth: (i) should not depend on the gas-phase concentration of hydrogen atoms, and (ii) increases with temperature because reaction (1) has a significant activation energy whereas reaction (2) does not. Equation (6) shows that $\chi_{C_d\bullet}$ is proportional to χ_{C_dH} . The total number density of surface sites is governed by the equation, $\chi_{C_{total}} = \chi_{C_d\bullet} + \chi_{C_dH} + \chi_{C_{gr}}$, where $\chi_{C_{gr}}$ is the number density of the graphitic (non-diamond in general) carbon sites. Even if the term $k_1 \cdot \chi_{C_dH}$ were not substantially larger than $k_4 \cdot \chi_{C_{gr}}$ in equation (5), the number density of carbon surface radical sites would still be independent of hydrogen atom concentration. This behavior is expected in the main growth regime under typical deposition conditions: hot-filament, microwave-plasma, or thermal-plasma reactors, highly-diluted hydrocarbon in hydrogen mixtures, about 800 to 1000°C substrate temperature, and a large super-equilibrium of H atoms.

B. *At low hydrogen atom concentrations,* the term $k_{-1}[H_2]$ dominates the denominator and $k_1[H]$ still dominates the numerator of Equation (5), which leads to expression

$$\chi_{C_d\bullet} = \frac{k_1 [H]}{k_{-1}[H_2]} \chi_{C_dH} = K_1 \frac{[H]}{[H_2]} \chi_{C_dH} \quad (7)$$

where K_1 is the equilibrium constant of reaction (1). From Equation (7) follows that the number density of carbon surface radical sites, $\chi_{C_d\bullet}$, and hence the rate of diamond growth, is determined by the "equilibrium position" of reaction (1), and hence by the concentration of H atoms. Early experiments of Angus and co-workers (29) were probably in this regime, since the gas was not activated and the concentrations of H atoms were low. The lack of hydrogen atom etching of the non-diamond surface carbons also reduces the total number of diamond growth sites.

C. *An increase in substrate temperatures* causes an increase in the rate coefficient k_4 , since it has a relatively high activation energy, and it eventually dominates the denominator of Equation (5). At these high temperatures, the thermodynamic stability of $C_d\bullet$ radicals becomes the limiting kinetic factor, and the sp^3 -hybridized $C_d\bullet$ sites decompose forming an sp^2 graphitic phase. This latter phase reduces the number density of sites capable of sustaining diamond growth. The graphitic-type phases are also more readily gasified (etched) by reactions with hydrogen atoms and oxygen containing species.

D. *At low substrate temperatures,* the condensation of aromatic molecules from the gas phase onto the growing surface can poison the growth of diamond by covering available sp^3 sites, i.e., decreasing both χ_{C_dH} and $\chi_{C_d\bullet}$. The condensing aromatic molecules are presumably converted by thermal decomposition or by the addition of hydrogen atoms into an amorphous sp^2/sp^3 carbonaceous network.

E. *An increase in the initial hydrocarbon concentration* can affect the deposition by: increasing the growth species concentrations and therefore deposition rates; increasing the formation of aromatics which reduces the film quality; and decreasing H atom concentrations that, among other things, shift the maximum in deposition rate to higher substrate temperatures (7). At high temperatures where surface radicals can react according to reaction (4) to produce non-diamond surface carbons, an increase in hydrocarbon concentration can enhance the rate of reaction (3) relative to that of reaction (4).

F. *The effect of pressure* on diamond deposition is essentially a concentration effect; the absolute concentrations of key hydrocarbon species are increased with an increase in pressure, thus enhancing the phenomena described in the preceding paragraph.

PROPOSED MECHANISMS FOR DIAMOND DEPOSITION

None of the mechanisms sited in this paper have been generally accepted as the likely path for incorporation of gas phase carbon into a bulk diamond structure. Testing of mechanistic pathways for diamond growth through kinetic calculations involving elementary reactions and then comparing predicted and observed growth rates has been of limited help since substantially different surface reaction mechanisms can yield essentially the same predicted growth rates. This is not surprising in light of the generic kinetic features discussed above. The most stringent testing of diamond growth mechanisms is currently checking for consistency with "known experimental facts" on diamond growth, trends in growth behavior with changing experimental parameters, and established thermodynamic and kinetic constraints.

Critical to developing a mechanistic knowledge of CVD diamond is understanding the surface processes occurring, the processes by which specific gaseous species chemically transform into diamond at specific growth sites on a diamond surface. Elementary chemical reactions, one-step chemical transformations which proceed via a single transition state, are used to describe the detailed mechanistic steps, and are the reactions used for kinetic calculations. In addition to the chemical reactions, surface bond lengths and angles, the non-nearest-neighbor environment, intermediate transition state configurations, and other factors effecting steric energies must be considered. Therefore, a knowledge of common surface structures and growth sites for diamond is required.

Diamond Surface Structures and Growth Sites

Although most mechanisms have been described in terms of $\{111\}$, $\{100\}$, or $\{110\}$ surfaces, a close examination of these diamond surface structures reveals only a few elementary sites for favorable hydrocarbon attachment. The diamond surface structure illustrated in Fig. 1 shows that atomic steps on $\{111\}$ surfaces (ledge sites) are identical to unreconstructed surface sites on either $\{110\}$ or $\{100\}$ surfaces. The horizontal $\{111\}$ layers being emphasized by different shadings of the carbons in this figure. The two respective sets of "zig-zag carbon chains," producing $\{100\}$ surfaces, extend in $\langle 110 \rangle$ directions that are oriented 90° to each other.

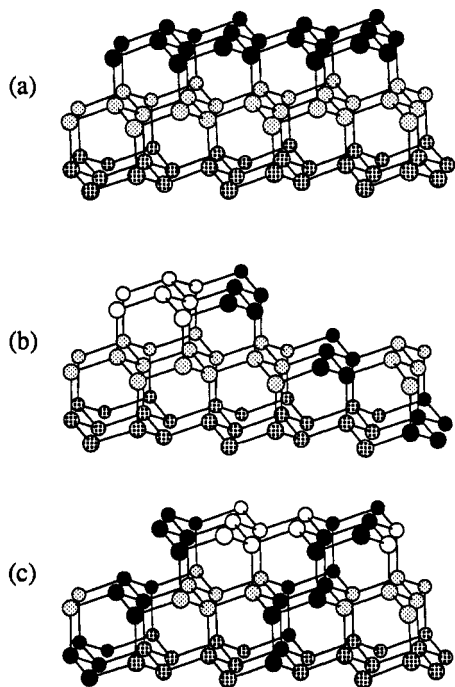


Fig. 1. Diagrams of diamond structure. All circles represent carbon atoms; the lighter shading or cross-hatching depict $\{111\}$ planes. Dark circles illustrate: (a) a $\{111\}$ plane, (b) a $\{110\}$ plane, and (c) two $\{100\}$ planes, rotated 90° with respect to each other.

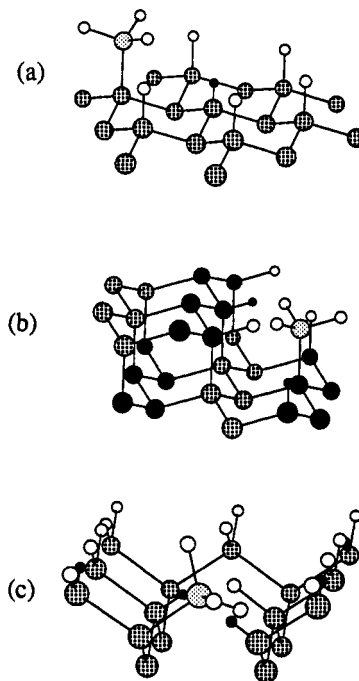


Fig. 2. The attachment of methyls by one bond to: (a) $\{111\}$, (b) $\{110\}$, and (c) $\{100\}$ surface sites to illustrate the effect of neighboring surface environment on steric repulsion.

A unique nomenclature for diamond surface sites has not yet been established, only whether the gas phase carbon attaches to the surface through one, two, or three C-C bonds. Next-nearest neighbor interactions with attached species at a given growth site can also play an important role, as is illustrated in Fig. 2 by a methyl group attached to $\{111\}$, $\{110\}$, or $\{100\}$ surface sites. Although carbon additions can be mechanistically described as involving specific $\{hkl\}$ -type sites, a comparison of proposed mechanisms should not focus on specific $\{hkl\}$ surfaces, but on the details of an attachment site, including at least its first and second nearest neighbor environments. The carbon atoms on a growth surface typically have their "dangling bonds" satisfied by hydrogen, C_nH_m , or species containing oxygen or a halogen. In most cases, these surface species must be removed to create active radical growth sites.

CH₃-Based Mechanisms

The first proposed reaction mechanism based on CH₃ was that of Tsuda et al. (26,27). They assumed a hydrogenated diamond $\{111\}$ surface, and used a series of semi-empirical quantum chemical computations in searching for the lowest energy path of diamond growth. Based on these computations, they reported a two-step reaction sequence: (i) a $\{111\}$ surface is covered by methyl groups, and (ii) three neighboring methyl groups become bonded together by a gaseous CH_3^+ cation to form part of the diamond lattice while releasing three H₂ molecules. Tsuda et al. (27) later presented a similar reaction sequence accomplished entirely by reactions of CH₃ radicals with surface complexes which maintain a positive electric charge. Difficulties with both proposals include: (i) bringing a charge to the surface encounters a higher potential energy barrier than surface activation by hydrogen atom abstraction, (ii) maintaining a charge on the growing surface is unlikely in ion-producing environments, (iii) a significant repulsion exists between adjacent methyl groups on the diamond $\{111\}$ surface (30).

Most other proposed methyl addition mechanisms involve $\{100\}$ diamond surfaces. These $\{100\}$ surfaces stabilized by hydrogen atom terminations exhibit significant steric energies caused by neighboring hydrogens, as can be seen in Fig. 3(a) (30). This "dihydride" surface can reconstruct into a lower surface energy form as shown by Fig. 3(b), which is commonly known as the "monohydride" since it exhibits only one terminating hydrogen per surface carbon. Although the restructuring reduces much of the steric energy, it introduces distorted bond angles and thus larger energies for the tetrahedral surface carbons. A lower energy structure intermediate between (a) and (b) was suggested by Yang and D'Evelyn (31), in which alternating rows of dihydride and monohydride exist at the $\{100\}$ surface.

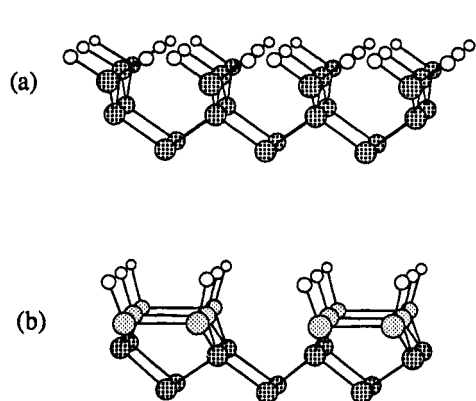


Fig. 3. Illustrations of $\{100\}$ diamond surfaces with hydrogen terminations: (a) unreconstructed dihydride, (b) reconstructed monohydride surface.

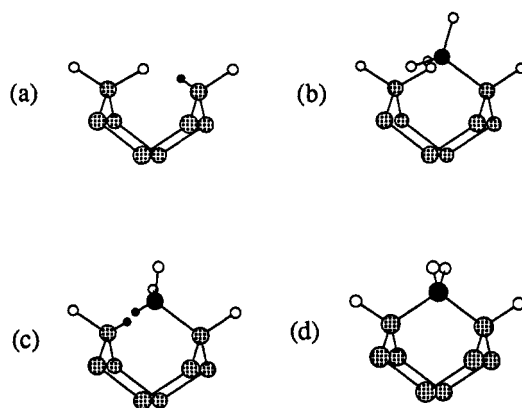


Fig. 4. Diagrams illustrating growth mechanism by methyl addition to an unreconstructed $\{100\}$ diamond surface (19).

Harris (19) proposed a specific reaction mechanism by which CH₃ incorporates into a diamond $\{100\}$ dihydride surface. Strong repulsions among adsorbed species pose a major difficulty with this mechanism (20,31-33). In the proposed reaction path of Harris (19) partially depicted in Fig. 4, a gaseous methyl radical combines with a dihydride surface radical formed by a H-abstraction, and the product undergoes first one and then an adjacent H-abstraction step forming a diradical surface intermediate (Fig. 4c).

These two radical sites combine into a C-C bond and complete a {100} surface carbon ring. However, the addition of a methyl radical to a dihydride surface radical is calculated to be as high as 80 kcal/mol (31-33), making the initial addition reaction very slow.

The above problem of steric repulsion may be resolved if CH₃ is added to a reconstructed monohydride {100} surface radical (see Fig. 3(b) for illustration of monohydride surface, which was shown by Hamza et al. (34) to exist only at higher temperatures). This CH₃ addition to the monohydride was proposed by Garrison et al. (32) and Huang and Frenklach (33). The mechanism of Garrison et al., revealed in molecular dynamic simulations, is schematically shown in Fig. 5. After a H-abstraction reaction, a CH₃ radical is added, Fig. 5(a). The abstraction of a hydrogen from the CH₃ creates the structure in Fig. 5(b), which transforms to create the double C=C bond shown in Fig. 5(c). (This (b)->(c) reaction is a β -scission type reaction.) The creation of the sp³ C-C bond in the final step (c)->(d) completes this mechanism. In the mechanism of Huang and Frenklach (33), the final structure in Fig. 5(d) is formed by a single, triangular transition state reaction from Fig. 5(b), but the potential energy barrier encountered in the two-step reaction of Garrison et al. (32) is lower than in the single, triangular transition state reaction, making the two-step path more plausible.

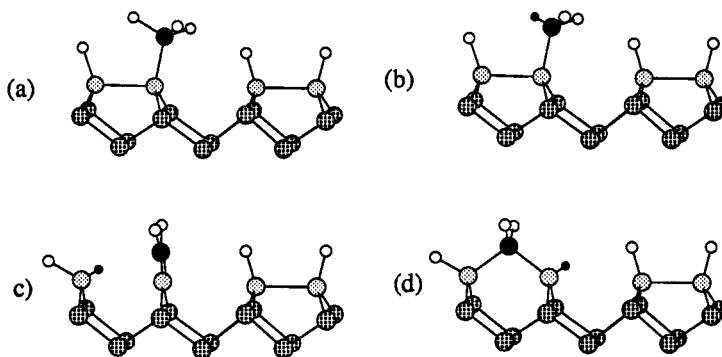


Fig. 5. Diagrams illustrating part of mechanism for methyl addition to a reconstructed {100} monohydride surface (32,33).

Other mechanisms for growth by CH₃ additions have been proposed, such as the combination of two adjacent CH₃ surface radicals (20,35), but these processes appear less likely under typical diamond growth conditions.

Acetylene Addition Mechanisms

The acetylene-addition reaction mechanism proposed by Frenklach and Spear (8) was partially inspired by a similar reaction mechanism identified for the formation and growth of polycyclic aromatic hydrocarbons (PAHs) in hydrocarbon pyrolysis and combustion, and by the realization that acetylene should be one of the main gaseous species present in an activated hydrocarbon gas or plasma. The latter prediction was later confirmed in experimental studies by several CVD diamond research groups (11). The initial mechanism (8) suggested the acetylene addition reaction takes place at C₁-H surface sites which have been activated by H-abstraction. First one gaseous acetylene molecule adds to the activated surface site, and this is followed by the addition of a second acetylene molecule. This sequence is partially illustrated in Fig. 6(a). The final state is the formation of a new fragment of diamond surface plus the regeneration of a hydrogen atom needed to initiate the first hydrogen abstraction reaction which created the initial active surface site. The acetylene addition process is achieved by a series of elementary reactions involving bond breaking and/or bond forming processes. Huang et al. (36), using semiempirical MNDO quantum-chemical calculations, later determined that fewer elementary reactions were needed than were proposed initially by Frenklach and Spear (8). A single reaction step via a complex transition state appears to be favorable on energetic grounds to the originally proposed sequence of two separate steps.

A step on a diamond {111} plane was assumed as the starting position for the above acetylene growth sequence (8). However, Fig. 6 illustrates that such a step fragment can also be considered as part of either {110} or {100} surfaces. The first and last reaction steps illustrated in Fig. 6(a) are repeated in Fig. 6(b,c) with the shadings of the carbons varied to show a {111} surface step from the point of view of: (i) {110} surface sites in Fig. 6(b), and (ii) acetylene additions to <110> direction carbon chains in a {100} surface in Fig. 6(c). Also, this addition mechanism does not require the carbon containing species to be acetylene alone (8). This growth process can also be accomplished by other "acetylenic" species such as C₂H, C₂H₃, C₄H₂, etc. Their concentrations in the deposition zone of a typical CVD reactor, however, are expected to be much smaller than those of acetylene. However, the concentrations of C₂H are known to reach high levels in high-temperature acetylene flames (12), a seriously explored diamond growth environment.

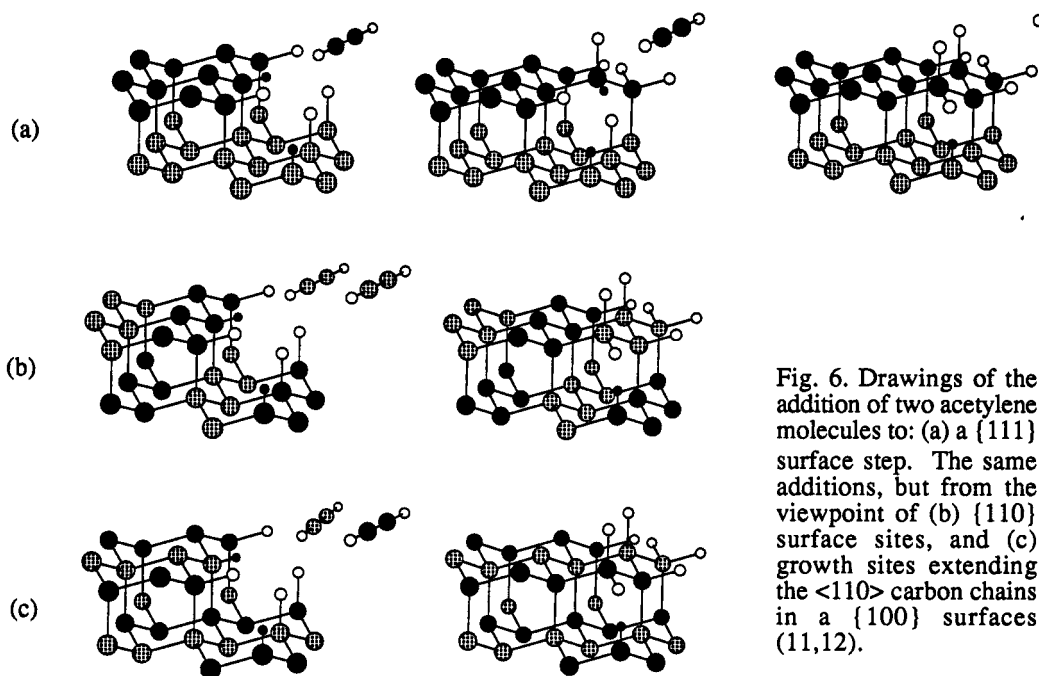


Fig. 6. Drawings of the addition of two acetylene molecules to: (a) a {111} surface step. The same additions, but from the viewpoint of (b) {110} surface sites, and (c) growth sites extending the $\langle 110 \rangle$ carbon chains in a {100} surfaces (11,12).

The above acetylene addition mechanism of Frenklach and Spear (8) has been criticized by Belton and Harris (21,37) on the premise that the proposed acetylene addition reaction is "highly reversible" because it exhibits a large negative entropy change. It is true that the first bonding of the acetylene to one activated surface site does not produce a strongly adsorbed state, but none of the subsequent elementary reactions which transform the acetylene into the diamond structure are activated processes, so they can be expected to be rapid (36). Once the second acetylene carbon is bonded to a surface carbon under typical diamond growth conditions, the desorption of this species is unlikely. This process may be considered analogous in many ways to many condensation reactions, all of which occur with a net reduction in the number of moles of gas and thus have large negative entropy changes. Even condensation reactions which have relatively small negative enthalpy changes can still be of significant importance if activated kinetic barriers are not encountered in the process of incorporating the vapor into the bulk solid state.

Another possibility for the involvement of acetylene in diamond growth was proposed by Belton and Harris (21). They described the mechanism as acetylene addition to a {110} surface, but the process is identical to adding this species to the {111} step site considered by Frenklach and Spear (8), as is shown by Fig. 6(b). The Belton and Harris mechanism basically involves the creation of a diradical site by two abstraction reactions on neighboring carbons, and the addition of an acetylene to this diradical to form an ethylene-like double-bonded group. Then, immediately adjacent to this attached ethylene group, two additional abstraction reactions must occur creating an adjacent diradical to which another acetylene is added. After a hydrogen atom addition to one of these ethylene groups occurs to create a vinyl-like radical, this radical reacts with the adjacent ethylene group to create a C₄-type radical, which is stabilized by another hydrogen atom addition reaction. These sequential steps are illustrated in ref. (10).

Two recent experimental papers have shown that using acetylene as the sole hydrocarbon source can produce high quality diamond at rates similar to those utilizing a methane source (38,39). These reports follow many papers which claim acetylene is not a major growth species in typical diamond CVD (40), a controversy that has been active since the first proposed mechanism for diamond growth by acetylene molecules (8). A very recent paper by Skokov et al. (41) provides detailed kinetic discussions in examining the feasibilities of a number of previously proposed mechanisms for diamond growth, and proposes a new type of mechanistic pathway for transforming acetylene molecules into a diamond structure. This mechanism uses a biradical with at least one of its sites being either a {100}-(2x1) dimer carbon, or a secondary carbon so that the adsorbed acetylene can undergo a series of H-additions, H-abstractions, and β -scissions leading to the incorporation of one or two carbon atoms into a diamond structure. Several possible reaction paths were examined in this paper (41) in searching for the path with the most favorable kinetic and thermodynamic parameters. Semiempirical quantum-chemical and transition-state-theory calculations were used to test these possible pathways.

Combined CH₃-C₂H₂ Mechanism

A diamond growth mechanism by the interdependent addition of both CH₃ and C₂H₂ was first invoked by Frenklach and Spear (8) for the nucleation of a new {111} diamond layer, and has been examined by sterically-resolved Monte-Carlo simulations by Frenklach (42). In this reaction model, the growth of diamond was assumed to be governed by additions of gaseous methyl radicals and acetylene molecules to surface radical sites, but only whenever these additions were sterically uninhibited. The dynamics of the radical sites were assumed to be controlled by the H-abstraction and H-combination reaction kinetics discussed above. In addition to the steric requirements for an initial C₂H₂ surface attachment, an additional demand was placed on an adjacent surface site so as to allow a low-energy reaction path for the acetylene attachment to a second surface carbon (33,35,36). A mechanism composed of elementary reactions along with their corresponding rate constants was proposed which creates results that are kinetically equivalent to the Monte-Carlo results (42). The equivalence is with regard to: (i) diamond film growth rate, (ii) steady-state surface fraction of chemisorbed CH₃, and (iii) the ratio of carbon atoms incorporated into the film from gaseous CH₃ and C₂H₂. This new mechanism implies that the formation of microscopically (atomic-level) perfect planes in diamond CVD is unlikely because CH₃ additions are not highly selective.

SUMMARY OF NEEDED INFORMATION

Synthesizing diamond films of desired uniformity and quality in a reproducible manner requires a better understanding of all competitive processes which deposit carbon. Only then can the simultaneous deposition of diamond and non-diamond carbon be controlled. This understanding must include not only the gas phase chemistry which determines precursor hydrocarbon concentrations, but also site-specific chemical reactions occurring on surfaces. Specific types of information needed include:

- (i) a clear and compact nomenclature for growth sites on diamond surfaces, both for perfect and imperfect surfaces,
- (ii) relationships between growth mechanisms and observed growth morphologies,
- (iii) development and/or the refinement of mechanisms which include:
 - a) all competitive deposition and etching processes (sp, sp², sp³, twins, defects, etc.), and
 - b) interconversions of hybridized states of carbon, and of different surface and defect sites,
- (iv) a refinement of kinetic models, including all the processes described in (iii) and their temperature and pressure dependent rate constants; and
- (v) development of innovative, sequential synthesis processes (e.g., sequential cycling of growth and etching periods) which will stringently test the mechanistic pathways postulated in (iii) and the deposition behavior calculated in (iv).

These interdependent tasks will provide a coherent direction and framework for research on diamond synthesis. Such a framework will enhance efficient comparison and synthesis of results from focused projects.

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