STUDIES OF AMORPHOUS HYDROGENATED “DIAMONDLIKE” HYDROCARBONS AND CRYSTALLINE DIAMOND

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The relationship between crystalline diamond, the “diamondlike” hydrocarbons (a-C:H) and diamond carbons (a-C) can be conveniently shown using a plot of atom number density vs. atom fraction hydrogen. For a-C:H the sp³/sp' ratio, the average coordination number and the composition limits are close to the values predicted for a random covalent network. The “diamondlike” carbons (a-C) appear to be a separate class of material (or materials). Twin planes and stacking faults observed in crystalline diamond grown from vapor can arise from the formation of hexagonal nuclei on [111] planes followed by layer growth through the addition of single and two-carbon-atom species. Intersections of re-entrant [111] surfaces on crystals with two or more parallel twin planes act as nucleation centers which are continuously regenerated as growth proceeds. Three-carbon-atom and four-carbon-atom nucleation events on smooth [111] surfaces are not necessary for the extension of these multiply twinned crystals, and hence they should be dominant growth forms. The smallest hydrocarbon molecules with this unusual property are two of the “boat-boat” conformers of bicyclooctane. These molecules, and other polycyclic hydrocarbons with two or more parallel twin planes, are proposed as the precursor nuclei for the growth of diamond from vapor.

1. Diamondlike hydrocarbons

Structure of diamond-like hydrocarbons (a-C:H)

The elemental composition and properties of amorphous hydrogenated “diamondlike” hydrocarbons (a-C:H) have been studied by numerous workers and are reviewed elsewhere.¹⁻⁴ These hydrocarbons can be easily prepared as thin films on Si, quartz, polymers and other substrates by rf self-bias deposition from hydrocarbon gases. They can also be formed by direct deposition from low energy (=100 eV) hydrocarbon ion beams and by other energetically assisted deposition methods.

The hydrocarbon films obtained by these methods are unlike any conventional polymer. They are much denser than other hydrocarbons and can be made harder than silicon carbide. They may be thought of as a “hydrocarbon ceramic.” The relationship between crystalline diamond, the diamondlike hydrocarbons (a-C:H) and conventional hydrocarbons may be conveniently shown on a plot of atom number density vs. atom fraction hydrogen⁵⁻⁶ (see Fig. 1). The a-C:H fall between crystalline diamond (DI) and the adamantanes.

![Graph](image)

Fig. 1. Atom number density (gram atom per cubic centimeter) vs. atom fraction hydrogen. Legend: DI, diamond; a-C, diamondlike carbon; a-C:H, diamondlike hydrocarbons; AC, oligomers of acetylene; AD, adamantancne; AL, n-alkanes; AM, amorphous trigonally bonded carbon; AR, polynuclear aromatics; GR, graphite. Citations for the a-C:H data are given in reference 4). The dashed vertical lines are the theoretical composition limits predicted by Eq. (3).

(AD) at number densities greater than any other hydrocarbon. The atom number density of a–C:H increases with hydrogen concentration, in contrast to the behavior of other hydrocarbons. Thus unusual behavior results from an increase in the average coordination number of the carbon atoms from 3 to 4 as the amount of hydrogen increases.

The a–C:H films likely form by quenching by the cold substrate of the hot surface layer in contact with the plasma phase. The introduction of hydrogen into the network at the moment of formation reduces strain and permits a greater fraction of the carbon sites to assume the four-fold (sp³) coordination.

The critical role that hydrogen plays in the stabilization of these materials is discussed in terms of the constraint counting arguments first used by Phillips for describing random covalent networks. The optimum coordination number is reached when the number of directed covalent bonds between nearest neighbors in the network introduces constraints just equal to the number of mechanical degrees of freedom of the network. An alternative, qualitative argument based on energy minimization is instructive. In this view, increasing the average number of bonds in the carbon network contributes to stability by virtue of the bond energy. However, since the network of atoms is randomly distributed in space, increased bonding also leads to increased strain energy because of bond stretching and bond angle distortion. The average coordination number that just uses up the allowable degrees of freedom can be thought of as the optimal coordination number balancing these two effects.

Angus and Jansen applied this theory to the special case of a random hydrocarbon network containing only sp³ and sp² carbon sites and hydrogen. They obtained an expression for the optimal value of the average coordination number, m, which is a defined quantity given, in this case, by

\[ m = x_1 + 3x_3 + 4x_4, \]  

(1)

where \( x_1 \) is the atom fraction hydrogen and \( x_3 \) and \( x_4 \) the atom fractions of sp² and sp³ carbon, respectively. When all sp² carbon sites are present as \( \pi \) bonded pairs, Angus and Jansen found the optimal coordination number to be

\[ m = \frac{1}{7} [20 - 8x_1]. \]  

(2)

They also showed that the optimal coordination number of the carbon skeletal network alone, \( m_C \), was equal to 2.4, the value given by Phillips for a monatomic random network. Angus and Jansen also obtained an expression for the sp³/sp² ratio at the optimal coordination number:

\[ \frac{x_4}{x_3} = \frac{6x_1 - 1}{8 - 13x_1}. \]  

(3)

The upper composition limit (\( x_1 = 8/13 \)) predicted by Eq. (3) is reached when the network is comprised only of four-coordinated carbon atoms with a sufficient concentration of hydrogen to lower the average coordination number to the optimal value. The lower limit (\( x_1 = 1/6 \)) depends on the assumption that the network is comprised of both three- and four-coordinated carbon. If doubly coordinated (sp³) carbon sites are present, random networks with hydrogen atom fractions less than 1/6 are possible.

Comparisons of the predicted values of the average coordination number and the sp³/sp² ratio with the available data are given in Figs. 2 and 3, respectively. The agreement is quite remarkable. In Fig. 1 the predicted composition limits as given by Eq. (3) are shown as vertical dashed lines. Again, agreement between experiment and theory is good.

Formation of medium or long range order is another means by which network strain can be relieved and, in fact, this appears to be the situation in the related material, a–Si:H. Some medium-range ordering may also be occurring in a–C:H. From Fig. 2 one can see that the average coordination number of a–C:H at the lower hydrogen concentrations is somewhat greater than that predicted by the theory. This may arise from the presence of small clusters. The measured values of the sp³/sp² ratio shown in Fig. 3 indicate that there is an excess of sp³ sites. However, the data are not
sufficiently precise to support such an interpretation. In fact, a structure comprised of small isolated clusters with sp² carbon sites is consistent with the optical properties of a–C:H, which are dominated by π-π* transitions, as well as with theoretical arguments. It should be emphasized that the theory of random networks says nothing about what type of clustering might occur. Films grown under other conditions could contain clusters dominated by sp³ carbon sites, perhaps even microcrystalline diamond.

**Properties of diamondlike hydrocarbons**

The properties of a–C:H depend strongly on the hydrogen concentration, which in turn can be controlled by controlling the impact energy of the ions. Variations in refractive index and optical band-gap with composition are well known and have been described by many workers. The mechanical properties and wear resistance also vary with composition, with the hardest, most wear-resistant materials found at the lower hydrogen concentrations, i.e., where the ratio of sp³ to sp² carbon sites is the lowest.

Here we show the internal compressive stress of a series of a–C:H films as a function of hydrogen concentration (Fig. 4). These measurements were obtained by measuring the deflection of silicon and quartz wafers both before and after deposition of the a–C:H films. The hydrogen content was
determined by $^{15}$N nuclear reaction analysis. The high compressive stresses are consistent with a constrained, continuous network structure.

In summary, the properties of a-C:H appear to be consistent with a structure comprised of an approximately random network with $sp^3$ and paired $sp^2$ carbon sites. Within this network, patches of medium range order may develop. At the lower hydrogen concentrations, these clusters will have average coordination numbers greater than the optimal value, e.g., small graphitic-like clusters with $m_c=3$ or diamond crystallites with $m_c=4$. At the higher hydrogen concentrations, regions of polymeric hydrocarbons ($m_c=2$) develop, leading to softer, optically transparent films. When these polymeric regions percolate through the entire structure, the film becomes soft and unable to support compressive stresses.

Diamondlike carbon

The diamondlike carbons (a-C) contain much less hydrogen than the diamondlike hydrocarbons (a-C:H) and yet can have $sp^3/sp^2$ ratios greater than $2/1^{17-23}$. They may be viewed as a separate class of material (or materials) distinct from the hydrogenated films. Since there is no hydrogen to provide strain relief, these films likely exhibit medium range order or micro-crystallinity. The a-C are of great interest because of their extreme hardness, which in some cases is greater than that of diamond.

2. Vapor growth of crystalline diamond

Role of surface structure in the vapor growth of crystalline diamond

The energetics of attachment and consequently the attachment rate of carbon atoms to the surface depend on the nature of the surface sites and the chemical species participating in the reaction. A comprehensive study of this problem will require detailed quantum-mechanical calculations of the energies of the transition states during the attachment process. Nevertheless, insight into the role of surface structure on reaction rate can be obtained by simple bond-counting arguments. This procedure has been used with remarkable success in predicting the orientation of the pyramidal etch pits (trigons) on diamond$^{24,25}$ and in the growth of group IV and III-V materials$^{26}$. Implicit in our discussion is the role of chemisorbed hydrogen in keeping the diamond surfaces from reconstructing. We also assume that vacant surface sites for attachment of reactive species are generated either by abstraction reactions with atomic hydrogen or other radical species, or by spontaneous thermal desorption.

Unreconstructed {100} surfaces provide vacant surface sites with two unsatisfied valencies. Addition of a single carbon atom to these sites will be energetically favored over processes where the carbon ad-atom makes only one bond with the surface. Furthermore, repeated addition of single atoms to these sites will cause the crystal to grow without error to smooth {111} faces, upon which less probable three-carbon-atom and four-carbon-atom nucleation events must occur for further growth to proceed. (An important exception in which the necessity of these three-atom and four-atom events is mitigated is discussed later in this paper).

The nucleation events on the smooth {111} faces can give rise either to cubic nuclei or hexagonal nuclei$^4$. These choices are shown in Fig. 5. Once a nucleus of either type is formed on a {111} surface (see Fig. 6), it may be extended across the surface by addition of single-carbon-atom or two-carbon-atom species. If these addition reactions are more probable than the nucleation event, extension of the lattice will proceed by layer growth across the {111} surface. The nearest neighbor configurations of the surface step sites are identical whether a layer is growing from a cubic or a hexagonal nucleus. However, layer growth from a cubic nucleus leads to correct extension of the lattice, while extension of a hexagonal nucleus leads directly to a single twin plane. The energy difference between the two nuclei is small, approximately 0.1 electron volt per carbon atom. Consequently, twins and stacking faults are prone to occur, especially at high supersaturations.

Nuclei on {111} surfaces are bounded by two different types of step sites. Along the $\langle 110 \rangle$ steps that face outward in $\langle 112 \rangle$ directions, all atoms on the step are bonded three times to the surface. A kink site can be formed by the addition of two
In a growth environment dominated by single-carbon-atom addition processes, the \(\langle 112 \rangle\) directions will be faster growing than the \(\langle 112 \rangle\) directions. A nucleus of arbitrary shape will grow out until it is bounded by the three-bonded \(\langle 110 \rangle\) steps facing outward along \(\langle 112 \rangle\) directions. After this condition is reached, layer growth can proceed only after a kink site is formed.

Based on their abundance and reactivity, the most likely carbon-containing species that can add to the surface are methyl radical, \(\text{CH}_3\), and acetylene, \(\text{C}_2\text{H}_2\). Layer growth can proceed by repeated addition of \(\text{C}_2\text{H}_2\) molecules along three-bonded \(\langle 110 \rangle\) steps as proposed by Frenklach and Spear. Alternatively, one could form (double) kink sites by addition of a two-carbon acetylenic species to a step followed by growth through addition of single-carbon-atom species to the kink sites. Finally, growth by formation of a kink site by sequential addition of two single-carbon-atom species followed by addition of single-carbon-atom species to the kink sites is also feasible.

Data in support of any mechanism is limited. However, measurements of reaction order for the deposition of diamond on diamond powder by thermal chemical vapor deposition shows that the rate is first order with respect to methane and half order with respect to ethylene. These data support a mechanism involving addition of single carbon atoms, at least at these reaction conditions. However, the formation of kink sites on \(\langle 110 \rangle\) steps on \(\{111\}\) surfaces as well as four-carbon-atom nuclei from two-carbon-atom species is not ruled out by these data.

**Role of twin planes in crystal growth**

Multiple twin planes can have a profound effect on the rates of crystal growth, and consequently can have a dominant influence on the types of crystals that grow to macroscopic size. A diamond-cubic crystal containing two or more parallel twins on \(\{111\}\) planes can be extended indefinitely by addition of two-carbon-atom species. The intersections of re-entrant \(\{111\}\) surfaces arising from these twins are regenerated as growth proceeds and act as continuing sites for the nucleation of new layers. No three-carbon-atom or four-carbon-atom nucleation events are ever required. This
phenomenon has been exploited for the rapid growth of germanium dendrites from the melt$^{30-32}$. It can be easily visualized by manual or computer construction of a doubly twinned crystal. The possible role of turn planes on diamond growth has been mentioned by DeVries$^3$.

Multiply twinned crystals will be expected to be present in large numbers, simply because they can grow more rapidly than untwinned crystals. The multiplicity of growth forms actually observed arises from differences in the conformations of the initial nuclei (see below) and from the random, probabilistic nature of hexagonal nucleation events on \{111\} surfaces.

**Nucleation of diamond**

Most discussion of growth mechanisms of diamond from vapor have involved the extension of a diamond crystal presumed to already exist$^{28,33}$. Mechanisms for the *de-nova* nucleation of a diamond crystallite from the vapor phase have received less attention, although there has been at least one attempt to describe possible hydrocarbon molecules which can act as diamond nuclei$^{34}$. However, the essential connection between the small-molecule organic reactions taking place in the vapor phase and the large, macroscopic diamond crystals has not been made.

Experimental evidence from many workers indicates that diamond can spontaneously nucleate on a wide variety of substrates. Scratching the substrate with diamond powder or other abrasive increases the nucleation rate, but diamond can nucleate without this pre-treatment. There is, in fact, credible evidence from several sources that diamond nucleates in the gas phase$^{35-37}$. It is also observed that there appears to be little or no preferred orientation of the individual diamond crystals with respect to the various substrates. A further important observation is the astonishingly large number of processes which lead to nucleation and subsequent growth of diamond from vapor. Any proposed mechanism for diamond nucleation must fit within this general framework of observations.

It has been proposed that the diamond precursors are the polycyclic, saturated hydrocarbons containing two or more parallel twin planes$^{38}$. The smallest molecules with this unusual property are two of the "boat-boat" conformers of bicyclodecane, shown in Fig. 7. Each of these compounds can grow without limit within the planes of the twins, by the repetitive addition of two-carbon-atom species. No three-carbon-atom or four-carbon-atom nucleation events are required. One likely gas phase species for this repetitive addition process is acetylene, \( \text{C}_2\text{H}_2 \). Since no three-carbon-atom or four-carbon-atom nucleation events are required, the overall rate of this process is likely to be rapid. As the molecule grows, the total probability of forming three-carbon-atom or four-carbon-atom nuclei on one of the exposed planes increases. These nucleation events will ultimately lead to extension of the nucleus normal to the twin planes.

The "boat-boat" bicyclodecane conformers can be formed by the hydrogenation of naphthalene by atomic hydrogen, known to be present under diamond growing conditions.

![Diagram of boat-boat conformers of bicyclohexane](image)

All of the conformers of bicyclodecane will form at relative abundances determined by their energies. Simple molecular mechanics estimates indicate that the difference in energy between the most energetic conformer (the cis "boat-boat" form shown in Fig. 7) and the least energetic conformer (trans-decalin) is no more than 10 Kcal/gmole. At 1300 K, this means that the most energetic, i.e.,

**BOAT-BOAT CONFORMERS OF BICYCLOHEXANE WITH TWO TWIN PLANES**

![Diagram showing boat-boat conformers of bicyclohexane](image)

Fig. 7. The two conformers of bicyclodecane that contain two parallel twin planes. These molecules are proposed as the precursor species for the nucleation of diamond.
least abundant, conformer which can act as a diamond nucleus is present in concentrations approximately two percent of that of trans-decalin.

The nucleation mechanism has been discussed in terms of the simplest hydrocarbons with parallel twin planes. However, there is an entire spectrum of saturated hydrocarbon ring compounds with the same property. These can be derived from higher molecular weight polynuclear aromatics, for example phenanthrene. All that is required is a hydrocarbon structure containing two or more parallel twin planes.

It should be noted that many hydrocarbon ring compounds contain either no twin planes, a single twin plane or non-parallel twin planes. An untwinned molecule such as adamantane has no sites for easy addition of two-carbon-atom species and therefore is an unlikely precursor for diamond growth. Examples of “boat-boat” conformers of cyclodecane with a single twin plane are shown in Fig. 8. These molecules can initially add two-carbon-atom species, but they ultimately grow out to a structure which requires three-carbon-atom nucleation events for growth to proceed. Similarly, tetracyclododecane has a single twin plane and has three sites for the addition of two-carbon-atom species. However, after addition of these species, a structure is obtained which contains no sites for easy addition of further two-carbon species. Hexacyclopentadecane, with five non-parallel twin planes, has five sites which can accept acetylenic species. After these are added, however, a structure without easy growth sites is formed. Furthermore, this molecule is likely to be present in extremely small amounts, if at all, under reaction conditions.

**Discussion of nucleation mechanism**

The proposed mechanism is speculative, but is in agreement with many observations. First, the proposed mechanism is consistent with the large number of methods which are known to produce diamond from vapor. The proposed mechanism suggests that each of these processes provides an energetically favored channel from acetylenic species to polynuclear aromatics and finally to the fully hydrogenated, multiply-twinned precursor molecules. The channel relies only on simple compounds known to be present under extreme reaction conditions. It is also consistent with the discovery that diamond can nucleate in a fuel-rich oxy-acetylene torch\(^{391-41}\). These conditions, close to the point of sooting, are known to produce polynuclear aromatic compounds.

The proposed mechanism is also consistent with the otherwise inexplicable observation that diamond can be readily nucleated directly on a graphite substrate. The graphite may provide fragments which can undergo hydrogenation to provide multiply-twinned saturated cyclic hydrocarbons. It also may explain the catalytic effect of some substrates on nucleation rate. For example, nucleation rates are greater when boron is present, and boron compounds are known to be catalysts for the hydrogenation of naphthalene.

The mechanism implies that most, if not all, crystals of macroscopic size should contain at least two twin planes. Two closely-spaced, parallel twin planes appear as a stacking fault and leave the morphology of the macroscopic crystal unchanged. Therefore, the mechanism appears consistent with the observation that isolated diamond octahedra are sometimes observed.

Finally, one may speculate that the molecules shown in Fig. 7 are the precursors to diamonds found in interstellar space, since polynuclear aromatics are thought to be present in this environment\(^\text{42}\).

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