

Diamond—Ceramic Coating of the Future

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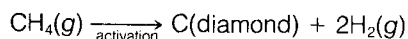
I. Introduction

THE unique properties of diamond are yet to be tapped for a large number of advanced materials applications. Fascination with this king of all gemstones has turned into excitement recently with the development of techniques for creating crystalline diamond films and coatings using low-pressure gases rather than the high pressures and temperatures previously considered essential. These developments herald a new era in diamond technology and offer the potential for exploiting the unique properties of diamond in applications ranging from coatings for bearings and cutting tools to free-standing windows and lens coatings for visible and infrared (IR) transmission, to thin films for high-temperature, high-power semiconductor devices.

Applications requiring advanced materials can uniquely utilize diamond because it (i) is the hardest known material; (ii) has the highest room-temperature thermal conductivity of any material; (iii) is resistant to heat, acids, and radiation; (iv) is a good electrical insulator, but can be doped to produce either *p*-type or *n*-type semiconductors; (v) has a small dielectric constant; (vi) has a large hole mobility; and (vii) is transparent to visible and IR radiation. (See Appendix B for more details on properties and applications of diamond.)

The high-pressure high-temperature (HPHT) synthetic diamonds developed by General Electric in the 1950s^{1,2} are now commonplace in cutting, grinding, and polishing, but many potential applications of diamond require thin films or coatings which cannot be produced from either natural or HPHT synthetic diamonds.

The diamond coating process which has generated the recent excitement utilizes temperature and pressure conditions under which graphite is clearly the stable form of carbon. However, kinetic factors allow crystalline diamond to be produced by the net chemical reaction



In addition to methane, a wide variety of carbon-containing reactant gases can be used. The typical process consists of a reactant gas at less than atmospheric pressure and containing >95% hydrogen which is activated by passing it through a plasma or past an $\approx 2000^\circ\text{C}$ filament before contacting an 800° to 1000°C substrate on which the diamond is deposited. Many questions must be answered concerning this deceptively simple-looking "metastable" process before the potential of the new coating technology can be achieved. Our understanding of the basic science must be extended far beyond our present knowledge, a challenge currently being met by laboratories around the world.

The purpose of this paper is to present a review of diamond-coating science and technology and to summarize the properties of diamond and a number of applications which can uniquely utilize these properties.



Karl E. Spear is the chair of the Ceramic Science and Engineering Program in the Department of Materials Science and Engineering at The Pennsylvania State University. Dr. Spear earned a B.S. in mathematics from Baker University in 1961 and a Ph.D. in chemistry from the University of Kansas in 1967. Before joining the Penn State faculty in 1970, he was at Oak Ridge National Laboratory. During 1978-79, Dr. Spear was on sabbatical leave at the United Kingdom Atomic Energy Research Establishment at Harwell and at Oxford University. He has broad research interests in the high-temperature thermochemistry and phase behavior of ceramic and metal systems. Dr. Spear is a member of the American Ceramic Society Basic Science and Nuclear Divisions, is the secretary-treasurer of the Ceramic Educational Council, and is chair of the Advisory Committee for the Phase Equilibria Data Center.

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review

II. Historical Perspective on Vapor-Deposited Diamond

A thorough review of previous investigations on the "Synthesis of Diamond Under Metastable Conditions," including the history of vapor-deposited diamond, was recently written by DeVries.³ This review and a paper by Badzian *et al.*⁴ also include patent literature on this topic. An excellent review of "Carbon Thin Films," which includes non-crystalline and microcrystalline hard carbon films, was jointly written by Angus, Koidl, and Domitz,⁵ and another very recent review was written by Angus and Hayman.⁶ This section presents only a brief historical perspective on the early work on the vapor synthesis of crystalline diamond

primarily in the 1950s in the Soviet Union and the United States. The major Japanese effort began in the 1970s.

The first two decades of research on vapor-deposited diamond in the Soviet Union was summarized in a 1975 article in *Scientific American* titled "The Synthesis of Diamond at Low Pressures."⁷ The reported diamond growth rates were low (angstroms per hour) and the simultaneous codeposition of graphitic carbon was always a problem. The early research primarily involved the thermal decomposition of hydrocarbons and hydrogen-hydrocarbon gas mixtures, with no additional activation of the gas.

Similar research was also being conducted in the United States during this early time period. In 1958, Eversole⁸ filed a patent on a low-pressure vapor synthesis process, but again the growth rates were very low and graphitic carbon was deposited simultaneously. The synthesis process required many cycles of growth followed by hydrogen etching to remove excessive graphitic deposits. Angus and co-workers⁹⁻¹¹ continued to pursue these techniques during the 1960s and early 1970s, and they obtained results similar to those of Eversole.

As in the early 1900s, most of the scientific community viewed the results of the 1950s through the mid-1970s with great skepticism, more of a curiosity than as a technological break-through. However, these results began laying the groundwork for our scientific understanding of vapor processes leading to diamond growth.

Soon after the *Scientific American* article,⁷ Deryagin's group reported the use of gas activation techniques which resulted in dramatic increases in diamond growth rates while eliminating much of the graphite codeposition.¹²⁻¹⁵ Starting in the early 1980s, Japanese researchers began reporting dramatic successes in low-pressure diamond growth using a variety of new gas activation techniques (see Appendix C).

A major increase in activity around the world on both the science and the technology of vapor-deposited diamond is quite apparent today. This activity is a result of a combination of demands from product designers for new super materials, decades of unheralded research on low-pressure diamond growth, and the breakthroughs of the 1970s which dramatically increased diamond growth rates while decreasing the codeposition of graphite. A stream of popular reports on diamond coatings¹⁶⁻²² is a reflection of the strong commercial interest.

Industries in the United States with activities in low-pressure diamond growth include large companies, such as Air Products, Alcoa, Amp, Armstrong, DuPont, Exxon, Ford, General

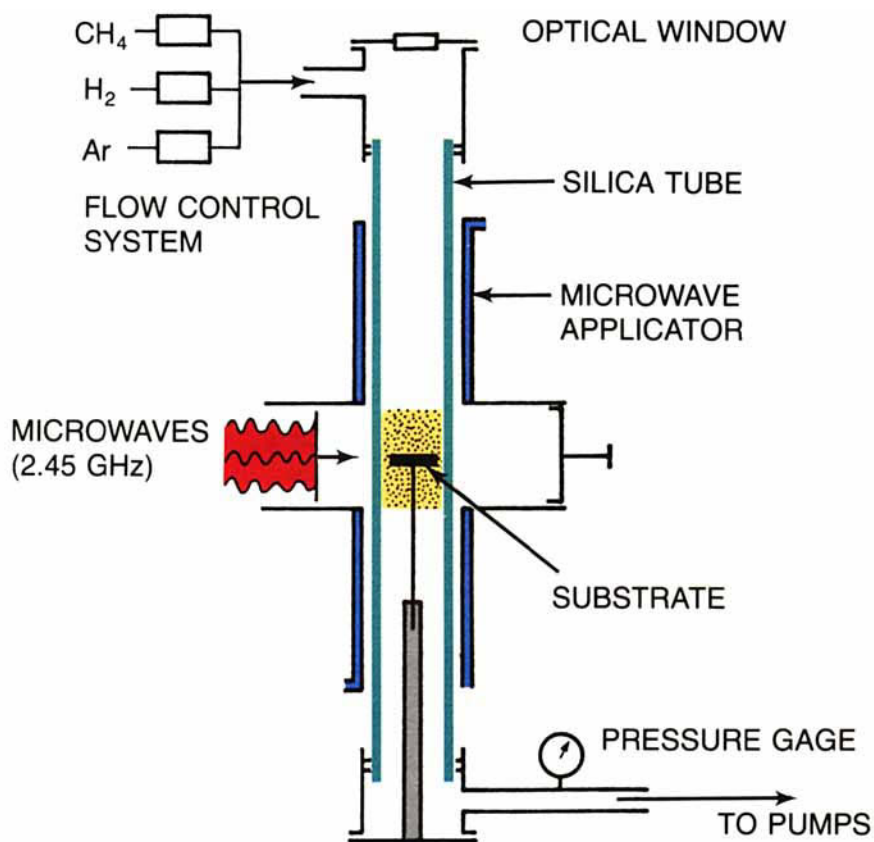


Fig. 1. Schematic diagram of microwave-plasma-assisted chemical vapor deposition (MPACVD) diamond growth system.

without attempting to duplicate these above comprehensive literature reviews. Indications of the current commercial interest in this process are also mentioned.

The production of synthetic diamonds from low-pressure gases was first reported in 1911 by von Bolton (from Ref. 3). He claimed to have achieved growth on diamond seed crystals from illuminating gas (acetylene) decomposition at 100°C in the presence of mercury vapor. However, little attention was given to these claims. Systematic studies of diamond vapor deposition techniques began pri-

Electric, General Motors, GTE, Hercules, IBM, Kennametal, Martin Marietta, Philips, PPG, Raytheon, Sandvik, Texas Instruments, and Westinghouse, as well as startup companies, such as Crystallume (Palo Alto, CA) and Diamond Materials Institute (DMI) (State College, PA). The interest in Japan has swelled over the past decade to well over 40 industrial firms that are actively involved in this area. They include Fujitsu, Hitachi, Kobe Steel, Kyocera, Matsushita Electric, Mitsubishi, NEC, Seiko, Showa Denka, Sumitomo Electric, and Toshiba. More than 500 patents have been filed in Japan related to diamond-coating processes.²¹

On September 14, 1986, the front page of the Sunday *New York Times* announced a "New Era of Technology Seen in Diamond Coating Process."²³ Current activities strongly support the optimism of this headline.

III. Growth and Characterization of Crystalline Diamond

In the vapor deposition growth of crystalline diamond, the two most common methods for achieving the required activation of the precursor gases are the use of a microwave plasma and an $\approx 2000^\circ\text{C}$ heated filament located about 1 cm above the growth surface. Schematic diagrams of such systems are shown in Figs. 1 and 2. Typical ranges of growth conditions are shown in Table I. Most of the experiments which led to the conditions in Table I were performed with methane as a hydrocarbon source, but other hydrocarbon sources have yielded similar results. Typical growth rates range from 0.1 to 10 $\mu\text{m}/\text{h}$.

The crystalline diamond coatings grown from low-pressure gases are different from the "diamond-like carbon" (DLC) films first reported by Aisenberg and Chabot.²⁴ The term DLC is often used to indicate a variety of noncrystalline carbon materials, ranging from amorphous to microcrystalline and typically containing from a few to about 50 at.% hydrogen. An excellent review of the extensive literature on noncrystalline carbon coatings has been given by Angus, Koidl, and Domitz.⁵

A working definition of "crystalline diamond material" was recently suggested by Messier *et al.*²⁵ in a paper discussing the differences between crystalline diamond and DLC coatings. The present review concerns crystalline diamond produced by vapor deposition techniques and defined by the following properties: (i) a crystalline morphology visually discernible by microscopy, (ii) a single-phase crystalline structure identifiable by X-ray and/or electron diffraction, and (iii) a Raman spectrum typical for crys-

talline diamond. Of all these characterization techniques, the Raman spectrum is the most sensitive for identifying the presence of crystalline diamond in mixtures of various forms of carbon. The Raman scattering efficiency for the sp^2 -bonded graphite is more than 50 times greater than that for the sp^3 -bonded diamond; therefore, small amounts of sp^2 -bonded carbon in the diamond deposits can be readily detected.

Figure 3 shows three typical Raman spectra for diamond films deposited

Fig. 2. Schematic diagram of heated-filament-assisted chemical vapor deposition (HFCVD) diamond growth system.

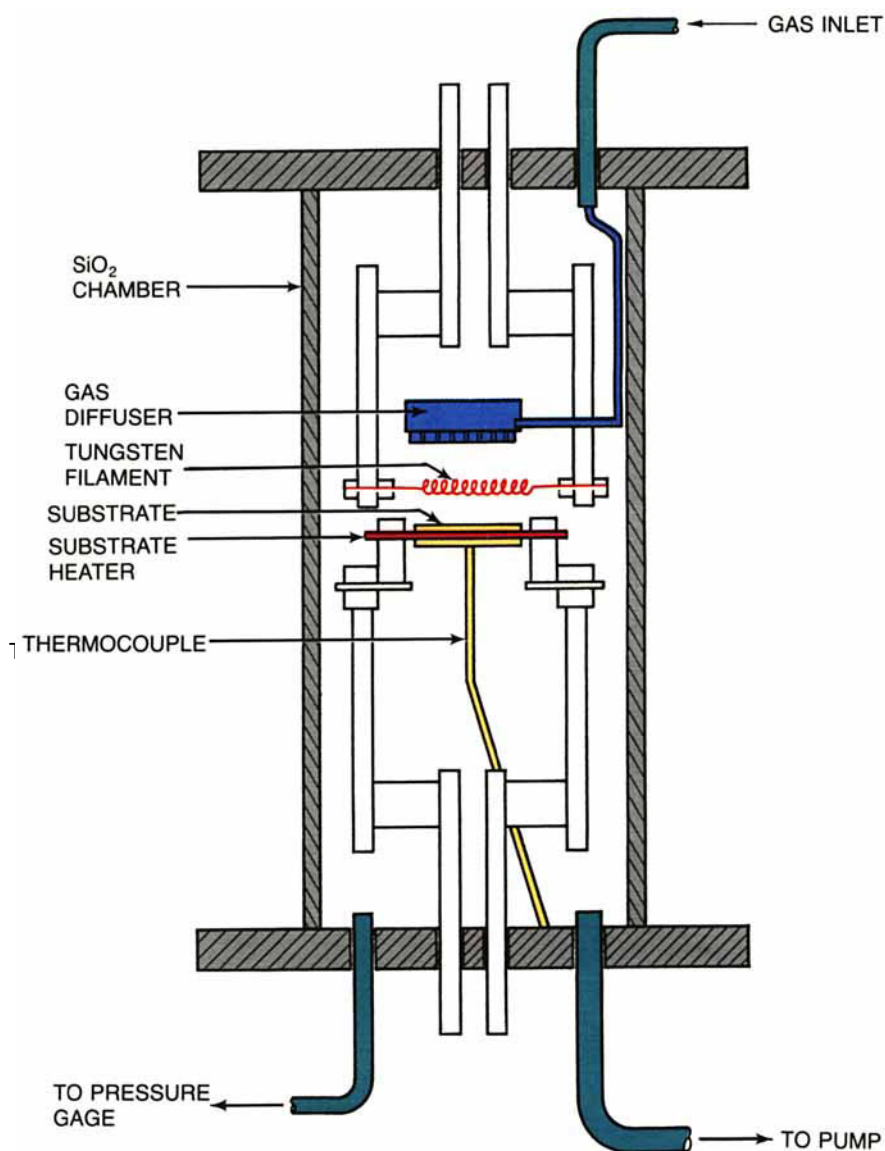


Table I. Growth Conditions of Vapor-Deposited Diamonds

| | Typical conditions | Best crystals |
|---|--------------------|---------------|
| Substrate | | |
| temperature ($^\circ\text{C}$) | 700–1000 | 950–1050 |
| Total pressure (kPa) | 0.013–12 | 5.3–12 |
| CH_4 (in H_2) (mol%) | 0.1–5.0 | 0.1–1.0 |
| Total flow (sccm)* | 20–200 | 50–100 |
| Filament | | |
| temperature ($^\circ\text{C}$) | 1800–2500 | 2000–2500 |

*Standard cubic centimeter per minute.

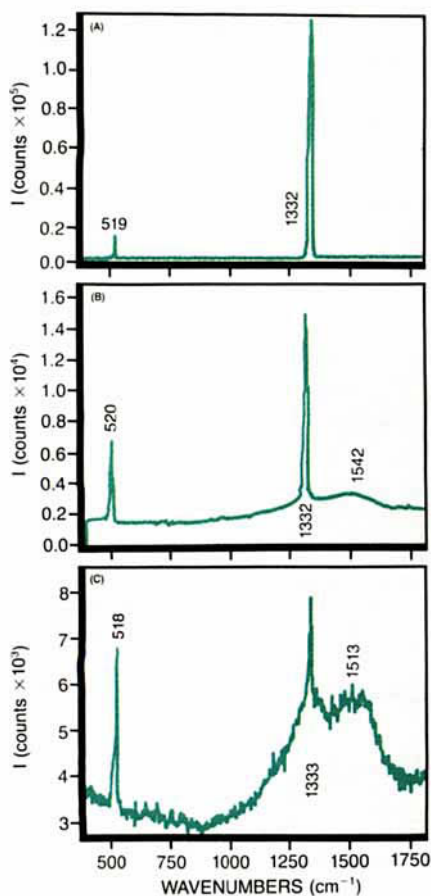


Fig. 3. Raman spectra for three typical diamond samples vapor deposited on single-crystal silicon: (A) highly perfect diamond film, (B) film of intermediate perfection, and (C) film containing appreciable amounts of sp^2 carbon. Note the intensity scale change in each of the three spectra. The 519 cm^{-1} line is from the silicon substrate, the 1332 cm^{-1} line is characteristic of diamond, the broad peak in the 1500 to 1600 cm^{-1} range is characteristic of sp^2 -type disordered carbon.

on silicon substrates. The peak at 519 cm^{-1} is from the silicon substrate, whereas the peak at $1332 \pm 1\text{ cm}^{-1}$ wave number is characteristic of diamond. The broad peaks occurring in the 1500 to 1600 cm^{-1} wave number range are characteristic of disordered sp^2 -type carbons in the deposit. The Raman spectra labeled (A) is a typical pattern for a highly perfect diamond film. The pattern labeled (C) is typical for an imperfect film of crystalline diamond with appreciable amounts of sp^2 carbon present as defects or in a separate phase. The pattern labeled (B) is for a film of intermediate perfection. Noncrystalline carbon such as DLC would not show the 1332 cm^{-1} wave number peak.

Knight and White²⁶ have written a comprehensive paper and review on the Raman spectroscopy of vapor-deposited diamond films and of other forms of carbons. In addition to the various vapor-deposited films, they have included spectra for natural diamond, a General Electric HPHT diamond, lonsdaleite, carbonado (natural polycrystalline diamond), three forms of graphite (polycrystalline, highly oriented pyrolytic, and a natural graphite crystal), glassy carbon, diamond-like carbon, coke, and charcoal. Both the peak position and the width provide information on the type of carbon deposited.

Tsai and Bogy²⁷ have written a detailed review on the characterization of diamond-like carbon films, and they include a section on Raman spectroscopy. They also include other characterization methods and property measurements that can be used for characterizing DLC thin films.

X-ray and/or electron diffraction can be used to identify the crystalline carbon phases of graphite, diamond, lonsdaleite, and the various carbynes, but not coexisting amorphous carbon phases, even when they dominate the deposits. A sharp diffraction pattern may sometimes be interpreted as "proof" that a high-quality crystalline diamond film has been grown, when

in fact, a large percentage of the film may be noncrystalline carbon that codeposited with the highly crystalline grains.

Hydrogen impurity contents from a few percent to greater than 30 at.% are common in the vapor-deposited DLC films. These films are often grown from pure hydrocarbons in low-pressure plasma systems. The crystalline diamond films, on the other hand, are typically grown from hydrogen–1 mol% methane mixtures and usually contain only small amounts of hydrogen impurity. Table II lists the average hydrogen content²⁸ of four films grown at The Pennsylvania State University in the microwave-plasma-assisted system shown schematically in Fig. 1. Only the film grown from a gas mixture containing a large amount of methane (5 mol%) exhibited an appreciable amount of hydrogen (2500 ppm, atomic). In general, the experimental information indicates that greater amounts of hydrogen in the feed gas lead to less hydrogen impurity in the diamond deposit.

Discussions later in this paper on mechanisms of growth include hypotheses on the major roles of atomic hydrogen in the precursor gas. One role of the atomic species is to abstract hydrogen from C–H bonds on the growing surface of the diamond deposits. An argument can be developed that hydrogen bonded to the carbons on the growing surface cannot be removed efficiently if the concentration of atomic hydrogen in the system is too small.

The diamond films that are currently being grown by vapor deposition evolve from small crystals, like those shown in the scanning electron microscope images in Fig. 4. When these crystallites grow together, dense diamond films such as the one shown in Fig. 5 can be prepared. The nucleation of diamond crystallites on substrate surfaces is not well understood. It is known that when the surface of the substrate is scratched with submicrometer diamond paste, nucleation occurs along the scratch. A high density of scratches helps to insure a high nucleation density. This is illustrated in Fig. 6, which shows the deposition of diamond crystallites on a portion of a single-crystal silicon wafer. Yugo *et al.*²⁹ and Chang *et al.*³⁰ have reported the effects of various substrate treatments on the diamond nucleation density.

The energy and mechanistic differences between growing "perfect" and defective crystals is apparently quite small. As a result, twinned and defective diamond crystals are often deposited, as is shown in the examples in Fig. 7. Other examples can be found among the crystals shown previously in Fig. 4.

Table II. Hydrogen Content and Growth Parameters for Four Diamond Films*

| Parameter/property | Sample | | | |
|---|--------------|--------------|--------------|---------|
| | DD12 | DD17 | DD18 | #66 |
| Substrate | β -SiC | β -SiC | β -SiC | Si |
| T (°C) | 975 | 976 | 975 | 990 |
| P (kPa (torr)) | 10 (80) | 10 (80) | 10 (80) | 10 (80) |
| Thickness (μm) | 3.9 | 14.4 | 18.0 | 6.5 |
| Growth rate ($\mu\text{m}/\text{h}$) | 0.19 | 0.74 | 1.6 | 0.72 |
| CH_4 (in H_2) (%) | 0.37 | 1.78 | 5.0 | 1.0 |
| Average H-impurity [†] (ppm atomic) | 630 | 350 | 2500 | 435 |

*Grown by microwave-plasma-assisted vapor deposition at The Pennsylvania State University, University Park, PA. [†]Analysis performed by W. Lanford.²⁸

IV. Chemistry of the Chemical Vapor Deposition Diamond Growth Processes

A generally accepted understanding of chemical mechanisms which lead to low-pressure growth of either diamond-like carbon or crystalline diamond is still lacking, but kinetic data on the processes have been reported. Russian scientists Deryagin, Fedoseev, Spitsyn, and their co-workers^{7,12-15,31-33} developed an extensive experimental base of chemical and kinetic information and proposed global kinetic theories for diamond growth based on nucleation theory, Langmuir adsorption-desorption kinetics, and equilibrium. Reviews in English by Fedoseev *et al.*¹⁵ and recently by Badzian and DeVries³⁴ give excellent summaries of this Russian work. Chauhan, Angus, and Gardner¹¹ reported detailed kinetic data on diamond deposition from thermally activated methane and methane-hydrogen mixtures and included preliminary results from the use of ethylene as a hydrocarbon source. Some speculations on nucleation and growth mechanisms were also given.

(1) Summary of Experimental Observations

Among a continuous "flood" of papers on low-pressure chemical vapor deposition (CVD) growth of diamond films, the following facts appear to be prominent:³⁵

(i) Activation of the gas is required. Some form of gas activation is absolutely necessary for achieving appreciable CVD diamond growth rates.

(ii) Independence on the method of activation. Good quality diamond films have been produced under a variety of different methods: microwave-, rf-, UV-, laser-, and hot-filament-activated gas mixtures. The method of activation influences the ease with which diamond is grown; however, an explanation for this influence has not been established.

(iii) Independence of starting material. The chemical nature of the hydrocarbon precursor does not appear to be critical. Crystalline diamond has been grown using aliphatic and aromatic hydrocarbons as well as alcohols and ketones.

(iv) Hydrogen is required for efficient growth. The Russians proposed that it is atomic hydrogen that has to be present in the gas phase in super-equilibrium concentration. Activated hydrogen etches graphite at a much higher rate than it does diamond.

(v) Effect of oxygen. Small amounts of O₂ added to the precursor gas accelerate the growth rate of diamond films. Diamond can also be grown from hydrogen-hydrocarbon gas mixtures which contain larger amounts of

oxygen (as in an oxygen-acetylene flame).

(vi) Plasma species. A number of ongoing spectroscopic studies of activated gas environments under the conditions of diamond film growth indicate the predominance of acetylene and methyl-radical growth species.

(vii) Formation of graphite usually accompanies the growth of diamond. A major problem in growing high-quality diamond films, including single-crystal films, is the codeposition of graphitic carbon.

(viii) Effect of temperature. The temperature dependence of the rate of diamond growth exhibits a maximum; that is, it initially increases with temperature and then decreases. This behavior is a manifestation of the competition between the growth of diamond and graphite.

(ix) Surface treatment. Various substrate surface treatments such as scratching, seeding, and etching affect primarily the induction time (nucleation rate), but not the rate of subsequent growth.³⁶

(x) Crystallite morphology. {111} and {100} surfaces dominate. Cubo-octahedral crystals composed of both of these surfaces are common. Twinning frequently occurs on {111} surfaces.

Although mechanistic reasons which favor the growth of crystalline diamond rather than graphite in low-pressure CVD processes are not well established, proposed mechanisms must be consistent with these ten reported experimental observations.

(2) Role of Atomic Hydrogen

A major breakthrough in developing both the science and the technology of low-pressure diamond growth occurred when the Russian scientists experimentally determined the importance of atomic hydrogen for enhancing the rates of diamond growth and reducing or eliminating codeposition of graphite. They found that the addition of excess hydrogen to the hydrocarbon precursor gas led to less graphite codeposition, just as Chauhan *et al.*¹¹ had determined, but the Russian scientists also discovered that "activating" the gas prior to deposition increased the diamond growth rates from Å/h to μm/h. Two mechanisms were used to activate the gas: an electric discharge in the system and a hot tungsten filament over which the gas flows before encountering the lower-temperature deposition region.

Deryagin and Fedoseev¹² proposed that a superequilibrium concentration of atomic hydrogen at the growth surface is responsible for the major reduction in graphite codeposition. They argued that atomic hydrogen behaves like a "solvent" for graphite. Their studies of the relative etching rates of diamond and graphite showed that the

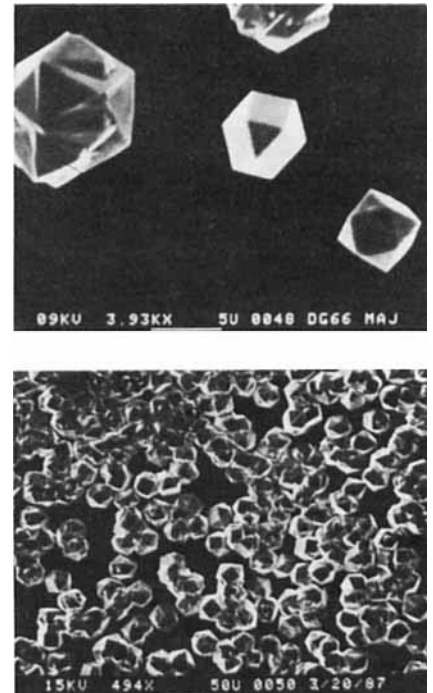


Fig. 4. Scanning electron microscope images of microwave-plasma vapor-deposited diamond crystals.

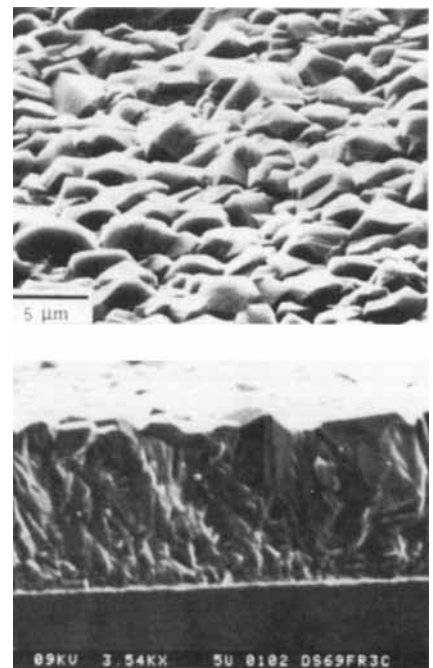


Fig. 5. Scanning electron microscope images of the surface and a cross section of a diamond film vapor-deposited on a silicon substrate.

removal of graphite by activated hydrogen was orders of magnitude faster than that for diamond. As a part of their diamond growth studies, Angus *et al.*⁹ had previously determined that molecular hydrogen would thermally etch graphite at a rate almost 500 times faster than it would etch diamond, but this graphite removal process was performed in a separate cycle from the diamond growth process.

Setaka³⁷ has recently reported etching rates of graphite, glassy carbon, and diamond in a hydrogen plasma under typical activated growth conditions for diamond to be 0.13, 0.11, and 0.006 mg/(cm² · h), respectively. Saito *et al.*³⁸ also showed much greater etching rates for graphite than for diamond when subjecting the materials to microwave plasmas of either hydrogen or hydrogen–1.6 mol% water mixtures.

Oda *et al.*³⁹ studied the role of H atoms in the deposition of amorphous silicon and related alloy phases. The H atoms generated by a microwave plasma remote from the deposition region enhanced both the growth rates and quality of the films. They noted that impurities such as C and O were efficiently removed by active H-atom reactions and that dangling bonds on the surface of epitaxial films were effectively passivated by H atoms. Both of the observations in this study help to support hypotheses on the role of H atoms in diamond deposition.

(3) Role of Hydrocarbon Precursor

Another experimental observation of the Russian scientists was that the nature of the precursor hydrocarbon gas had little effect on the deposition behavior. Sato *et al.*⁴⁰ have grown diamond from gaseous mixtures of various hydrocarbons and hydrogen by plasma-assisted deposition and found similar results. Both saturated and unsaturated hydrocarbons were used, and similar growth features were noted for all the hydrocarbons when comparisons were made as a function of the C/H ratio in the input gas. The density of nucleation and the growth rates were found to be essentially the same as those observed with the more commonly used methane in previous studies.

This relative independence of diamond growth on the nature of the input hydrocarbon species is consistent with the fact that most hydrocarbon sources tend to chemically transform to common product species (such as acetylene, one of the most stable of such gaseous products) under harsh environments such as those found in high-temperature pyrolysis,⁴¹ combustion,⁴² plasmas,⁴³ and the other typical methods used for activating precursor gases in diamond deposition. Sup-

porting this is the observation that approximately the same growth conditions (temperature, pressure, concentrations of precursors) are needed for crystalline diamond growth, regardless of the method of activation. The method of activation influences the rate of diamond growth, but not the general structure of the deposited crystallites. This also supports the conclusion that the same general growth species are produced by all activation methods that produce crystalline diamond.

(4) Diagnostics of Activated Gas

Recent in situ measurements of species concentrations in activated methane–hydrogen gas mixtures above diamond growth surfaces have been made. Although a number of species have been detected, indications are that the primary species are methyl radicals and acetylene. Such diagnostic measurements are needed as a function of growth conditions and activation method, and the results then need to be correlated with growth rates, crystallite morphology, and the relative amounts of codeposited diamond and non-diamond carbon. These data will be a critical portion of the basic information needed for building a mechanistic understanding of the vapor deposition of crystalline diamond films.

Matsumoto *et al.*,^{44,45} Saito *et al.*,⁴⁶ Mitsuda *et al.*,⁴⁷ and Hartnett⁴⁸ have all performed emission spectroscopic analyses of microwave-plasma-activated hydrogen–hydrocarbon gas mixtures above substrate growth surfaces. Hartnett has reviewed these previous studies in his thesis. Only a limited number of species of interest are detected by this technique: H₂, atomic H, C₂, and CH.

Matsumoto⁴⁵ examined a hydrogen plasma with no hydrocarbon in the gas and no substrate. As expected, only the molecular and atomic hydrogen emissions were observed. Upon placing a graphite substrate in the hydrogen plasma, CH, C₂, and H were all observed. Mass spectroscopy measurements of the plasma showed C₂H₂ to be the main reaction product of the chemical etching of the carbon.

Attempts have been made by Mitsuda *et al.*⁴⁷ to correlate the emission spectroscopy intensity ratio of CH–H radicals to diamond formation and C₂ radical concentrations to graphite formation. However, other species, such as CH₃ radicals and C₂H₂, which cannot be detected by the emission spectroscopy techniques, are probably the main precursors to diamond growth. Therefore, correlations between CH and C₂ emission spectroscopy intensities and the relative concentrations of CH₃ and C₂H₂ in the activated gas

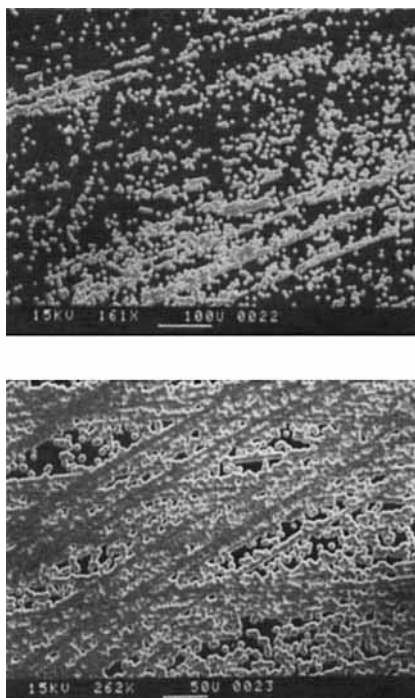


Fig. 6. Scanning electron microscope images showing the effect on the nucleation of vapor-deposited diamond of scratching a silicon substrate with submicrometer diamond grit. The diamond films are a result of the growing together of the crystallites.

are needed.

In addition to these emission spectroscopy measurements, two studies have been reported on other spectroscopic measurements of hydrocarbon species present in typical gas mixtures activated in filament-assisted diamond growth systems. Both sets of results indicated acetylene and methyl radicals are the most abundant vapor species near the growth surface.

IR diode laser absorption spectroscopy was employed as an in situ method to examine gas-phase species present during filament-assisted deposition of diamond films by Celii *et al.*⁴⁹ From a reactant gas mixture of 0.5 mol% methane in hydrogen, acetylene (C₂H₂), methyl radical (CH₃), and ethylene (C₂H₄) were detected above the growing surface, while ethane (C₂H₆), various C₃H_x hydrocarbons, and methylene (CH₂) radical were below their sensitivity levels. These authors noted that their findings were consistent with the Frenklach–Spear mechanistic growth model⁵⁰ for propagating (111) planes through the addition of acetylene to activated surface sites.

Mass spectral data were obtained by Harris *et al.*⁵¹ in a hot-filament-assisted diamond growth system as a function of filament to substrate distance. They used sampling techniques which were shown to be effective in sampling flames.⁵² The 2.6-kPa (20-torr) input gas in their diamond growth system was hydrogen containing about 0.3 mol% methane and 0.1 mol% Ne for calibration purposes. The tungsten carbide filament temperature in their system was estimated to be 2600 K. They stated that their results were consistent with those of Celii *et al.*⁴⁹ In addition to the mass spectral sampling of the gas, they also performed detailed chemical kinetic calculations using a model developed previously in studies of flames.⁵³ Their initial analysis suggested that diamond growth came mainly from acetylene and/or methyl-radical precursors, but that contributions from methane and ethylene could not be ruled out.

(5) Effects of Oxygen on the Diamond Deposition Process

Hirose and Terasawa⁵⁴ reported on the growth of crystalline diamond films from a number of organic compounds, several of which contained oxygen. However, they did not discuss the role of oxygen in the synthesis process. A number of investigators have since studied the influence of oxygen additions in various forms on the growth of diamond: oxygen additions by Kawato and Kondo⁵⁵ and Chang *et al.*,³⁰ water additions by Saito *et al.*,³⁸ and CO and oxygen additions by Mucha *et al.*⁵⁶ More recently, 10⁵ Pa (1 atm) oxygen–acetylene flames have been used to

grow crystalline diamond.^{57–59} Experimental detail is currently quite sparse on these latter studies.

Kawato and Kondo⁵⁵ examined gas mixtures of CH₄–H₂ and CH₄–H₂–O₂ in growing CVD diamond by the heated-filament activation technique. They examined the exhaust gas by gas chromatography and found the major content of this gas to be methane (CH₄), ethylene (C₂H₄), acetylene (C₂H₂), hydrogen (H₂), and carbon monoxide (CO). Although the relative concentrations of these species were not given, their analyses concentrated on the CH₄ and C₂H₂ species. The data show that the additions of 0.4 mol% O₂ to hydrogen containing from 1.6 mol% to 4.0 mol% CH₄ cause the growth rate of diamond to increase over the oxygen-free system, particularly at higher CH₄ percentages. The addition of oxygen also decreased the quantity of non-diamond carbon as determined by the decrease in the ≈1550 cm⁻¹ Raman peak. At the same time, the addition of oxygen caused a larger decrease in the C₂H₂ than in the CH₄ concentration in the exhaust gas. The authors reached the following conclusions from these results: "(1) The addition of oxygen reduces the concentration of acetylene, which is probably produced by the pyrolysis of methane or hydrogenation of non-diamond carbon. (2) The deposition of graphitic or amorphous carbon is suppressed by a reduction of the acetylene concentration or the oxidation of non-diamond carbon, so that the quality of the deposited diamond is improved. (3) With the addition of oxygen, the growth rate of diamond increases, and the total pressure for diamond synthesis can possibly be extended."

Saito *et al.*³⁸ used water-vapor additions to their CH₄–H₂ precursor gases in their microwave-plasma-assisted synthesis of crystalline diamond. The growth rates of 1 to 5 μm/h represented an increase of several times those obtained without the water additions. Concentrations of input gases varied from 1 mol% to 10 mol% for CH₄ and 0 mol% to 7 mol% for H₂O, with the rest of the gas being hydrogen. Small additions of water to the input gases containing 3 mol% and 10 mol% CH₄ caused large increases in growth rate, but a maximum in growth rate was achieved when the H₂O/CH₄ ratio reached between one-third and one-half. The additions of water also resulted in greater crystallinity in the films, and less codeposited non-diamond carbon. The authors also examined the relative etching rates of diamond and graphite in hydrogen and in hydrogen–1.6 mol% water mixtures under the same plasma conditions as used in growth. Diamond showed little etching

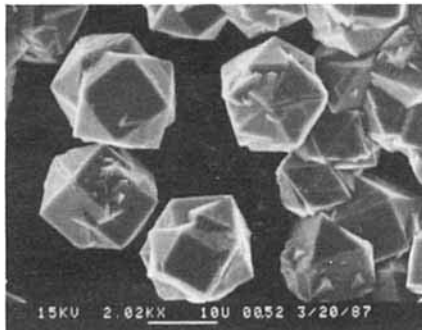
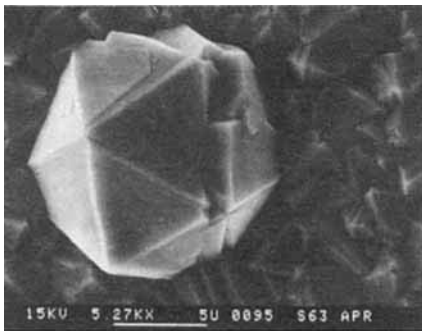


Fig. 7. Examples of highly twinned and defective vapor-deposited diamond crystals.

for both mixtures, but the etching rate of graphite was about twice as great when the water was added to the hydrogen.

Zaitsev *et al.*⁶⁰ measured the effect of water vapor on the dissociation of hydrogen in a glow discharge system and found a maximum in the hydrogen-atom concentration as more and more water was added to the 34-Pa (0.26-torr) gas. The hydrogen-atom concentration increased by about a factor of 5 when about 0.1% water was added, then decreased with higher percentages of water. The gas in this system contained no hydrocarbons, the pressure was lower, and the means of gas activation was different than that in the diamond growth system used by Saito *et al.*,³⁸ but the fact that Zaitsev *et al.* found the hydrogen-atom concentration to be enhanced by water vapor in the activated gas is consistent with the hypothesized important role of hydrogen atoms in the vapor growth of diamond.

(6) Deposit Morphologies

The morphology of vapor-deposited diamond crystallites is dominated by cubic {100} and octahedral {111} surfaces and {111} twin planes (stacking faults of the {111} planes). Cubo-octahedra exhibiting both {100} and {111} surfaces are common.

Matsumoto and Matsui⁶¹ utilized electron microscopy techniques to examine the structures of diamond crystallites grown in a hot-filament-assisted CVD system. The {100} and {111} surfaces dominated the crystallites. The typical crystal habits were cubo-octahedra and singly and multiply twinned particles. Examples of these common defective crystals can be seen in Fig. 7.

Kobashi and co-workers⁶²⁻⁶⁴ found that {111} faces dominated their 4-kPa (30-torr) microwave-plasma-assisted CVD crystals for substrate temperatures of about 800°C and methane concentrations of <0.4 mol%. When the CH₄ concentration was between 0.4% and 1.2 mol%, {100} surfaces dominated, but at higher concentrations the deposits were structureless.

Badzian⁶⁵ reports that, at temperatures of 900°C and lower, {111} faces dominate the crystallite morphology, and, at 1000°C and higher, {100} faces are predominant. At low CH₄ concentrations, {111} faces are predominant, and, at high concentrations, {100} faces are predominant. This observation is consistent with those of Kobashi and co-workers, and the earlier work reported by Spitsyn *et al.*¹³ The latter authors observed octahedral crystals with {111} faces with growth temperatures of 800°C and regular cubo-octahedra with {111} and {100} faces at 1000°C.

Haubner and Lux⁶⁶ observed morphological results that are not consistent with the above observations. They report that in their microwave-plasma-assisted deposition system, cubic crystals with {100} surfaces dominated at low CH₄ concentrations (0.3%), low substrate temperatures (600°C), and medium plasma intensity. At higher plasma intensities, but the same concentration and substrate temperature, cubo-octahedra ({100} and {111} surfaces) were observed. At 750° to 800°C and medium to high plasma intensities, octahedral crystals with {111} surfaces dominated. Low plasma intensities led to spherulitic crystallites at both lower and higher temperatures. (Note: the authors (private communication) estimate that the true substrate temperatures were about 200°C higher than the above uncorrected measured values they list in their paper.)

(7) Substrates for Deposition

Diamond has been vapor deposited on a wide variety of substrate materials, though the dominant substrate has been single-crystal silicon. Examples of substrate materials used are Si, Ta, Mo, W, SiC, WC, and diamond;⁶² Cu, Au, Si, Mo, W, and diamond;¹³ and diamond, graphite, Si, SiC, SiO₂, and Ni.⁶⁷ Studies on coating various oxide, carbide, and nitride cutting-tool materials are also underway around the world. The diamond nucleation rates and adhesions vary with the tendency to form intermediate carbide layers such as SiC or Mo₂C, but detailed systematic studies are yet to be reported.

V. Energetics of Gas-Solid Growth Interface

The pressure versus temperature phase diagram for carbon given in Fig. 8 clearly shows that graphite is the stable form of carbon under the conditions used in vapor-depositing crystalline diamond. Why is it then possible to grow diamond at less than atmospheric pressure in the temperature range of 750° to 1100°C?

Although an established *mechanistic* answer is not yet available for this question, one answer that is consistent with reported experimental facts can be given.^{68,69} The heart of the hypothesis on "metastable" diamond growth rests on the fact that the diamond growth process occurs at the gas-solid interface in the carbon-hydrogen system. The vapor-growth process does not involve just elemental carbon, the one component which is represented on the phase diagram, but it also involves hydrogen. A diamond carbon surface saturated with sp³ C-H bonds is more stable than a carbon surface free of hydrogen.

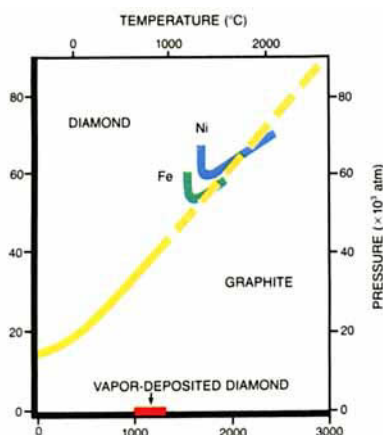


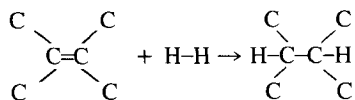
Fig. 8. Pressure versus temperature phase diagram for carbon. The lines labeled with metallic elements denote the HPHT conditions utilized for diamond growth using metallic solvents.

Once a surface carbon is covered by another diamond growth layer, then that covered carbon possessing four sp^3 C—C bonds is metastable with respect to a graphitic carbon. Thus, an upper temperature limit for the vapor growth of diamond is determined by the kinetics of the diamond-to-graphite solid-state transformation (and how these kinetics are influenced by structural imperfections).

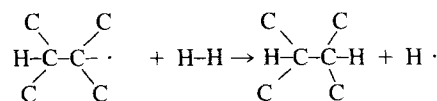
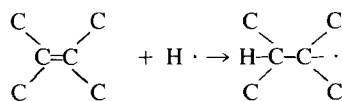
The close relationship among the diamond, lonsdaleite, and graphite crystal structures is described in Appendix A. A diamond structure with puckered {111} planes stacked in their ABCA... sequence is shown above the stacking of the hexagonal planes of graphite in Fig. 9. The diamond {111} planes are shaded to emphasize the relationship of the diamond structure to that of graphite. Hydrogen atoms are shown as satisfying the "dangling sp^3 bonds" of the carbons on the top diamond plane. Lander and Morrison⁷⁰ were the first to hypothesize that hydrogen can stabilize a diamond surface by forming sp^3 C—H bonds with the surface carbons. Without the hydrogens maintaining the sp^3 character of these surface carbons, it is easy to imagine the {111} diamond planes collapsing into the more stable planar graphite structure during the growth process. In fact, in the absence of hydrogen, it is well-known that the surface atoms on cleaned bulk diamond crystals will reconstruct from their bulk-related surface sites at about 900° to 1000°C.^{65,71(f),72,73} However, in hydrogen, the reconstruction reverses as dangling surface sp^3 bonds become satisfied by C—H bonding.⁷⁰

The question then arises as to why earlier thermal CVD studies utilizing hydrogen-methane mixtures for epitaxial growth on diamond surfaces were of very limited success. The pressure-temperature-composition conditions used by these researchers were quite similar to those used in later successful activated vapor growth of crystalline diamond, but growth rates were in the range of angstroms per hour, and, without periodically etching away the codeposited graphitic carbon, diamond growth would cease.⁹

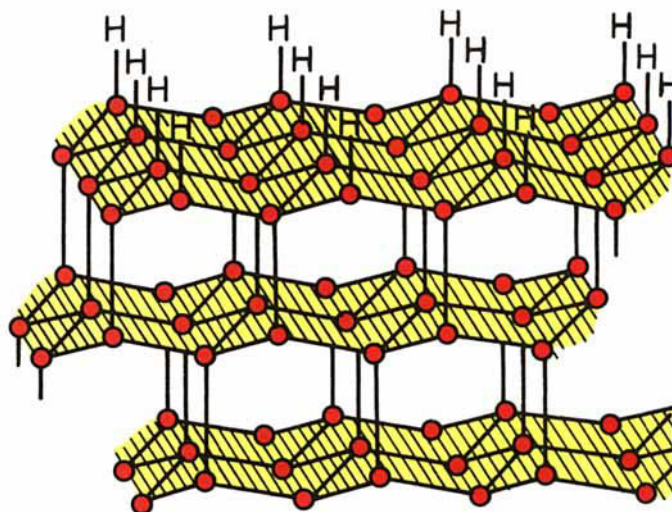
The net saturation of a C=C double bond with hydrogen has a



favorable negative enthalpy change (ΔH° (reaction) = -126 kJ). However, an activation energy to produce either a carbon or a hydrogen radical will be required to get the net reaction to proceed at a significant rate. Likely mechanistic radical reactions are



where a hydrogen radical attacks the C=C double bond to produce a carbon radical, which then reacts with a hydrogen molecule to complete the saturation and regenerate a hydrogen radical. This is in agreement with the fact that only when gas-activated



DIAMOND

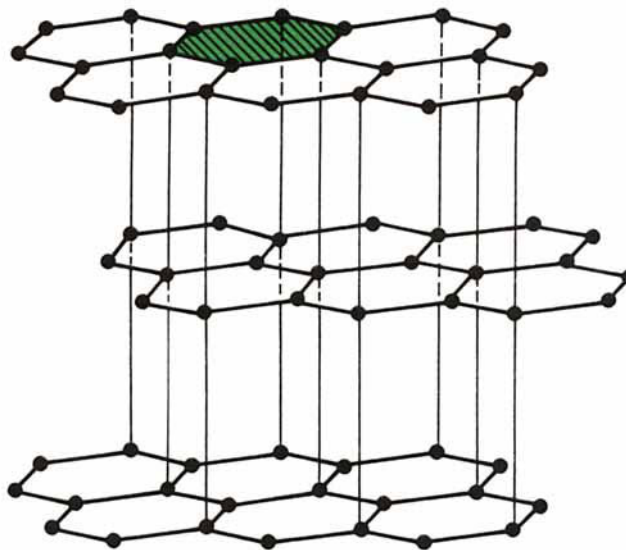


Fig. 9. Schematic diagrams showing the similarities in the crystal structures of diamond and graphite. The hydrogen atoms bonded to the surface carbons depict their role in stabilizing the diamond surface structure.

vapor deposition methods were first employed in the 1970s did the growth rates of crystalline diamond become large enough to be of technological interest.

As was presented in Section IV, atomic hydrogen etches graphitic carbon at a much higher rate than it etches sp^3 diamond carbon. Thus, the source of hydrogen atoms can serve the dual role of hindering graphite growth as well as etching away any that does nucleate on the growing diamond surface.

The thermodynamics of the deposition process may place a lower limit on the deposition temperature for given total pressures and gas concentrations. Without some type of surface activation, such as bombardment, the surface reactions for deposition may approach their equilibrium limits. The fact that faceted diamond crystals are produced during deposition is an indication that surface mobilities are large enough for surface reactions to reach equilibrium. Lander and Morrison⁷⁰ indicate the mobility of carbon on a (111) diamond surface is appreciable at 1000°C. Which reactions reach their equilibrium limits and which ones are kinetically limited is still an open question, but it is still of value to consider the thermodynamic limits for the deposition process.

Two plots of the output of equilibrium calculations are shown in Fig. 10 to illustrate how the deposition limits depend on experimental parameters.^{68,69} Such calculations have also been made by Bichler *et al.*⁷⁴ and Sommer *et al.*⁷⁵ The fraction of carbon deposited from methane–hydrogen mixtures is plotted versus temperature for several total pressures and compositions. The following important observations can be made:

(i) The fraction of carbon deposited changes from practically zero at lower temperatures to close to 100% over 200°C.

(ii) High pressures and/or low methane concentrations increase the lower temperature limit required to obtain any deposit.

Thus, thermodynamic considerations set a lower temperature limit on diamond growth of about 400° to 600°C, depending on specific pressure–composition conditions, unless “nonequilibrium” bombardment techniques are used. These techniques always produce some DLC (or similar highly defective form of carbon) along with crystalline or microcrystalline diamond.²⁵ Even small quantities of a defective form of carbon could render the deposited films useless for electronic applications.

Not shown on the above plots is the fact that the elemental gaseous carbon species of C, C₃, C₅, etc. have

negligible partial pressures at about 2000°C and lower. Also, at 2000°C, a typical temperature for the filament in the hot-filament-activated systems, the quantity of atomic hydrogen in equilibrium with about 1.3 kPa (10 torr) of molecular hydrogen is about 7 at.%, an appreciable amount to interact at the 800° to 1000°C substrate temperature.

VI. Mechanisms of Growth

In spite of a rapidly growing number of publications on the subject of low-pressure deposition of diamond, only a few concentrate on mechanisms of growth. The most extensive set of chemical information is from the Russian school of Deryagin, Fedoseev, Spitsyn, and co-workers and from work in the United States by Angus and co-workers (see Section IV). The Russian scientists argue, based on their experimental studies, that the growth of diamond is controlled by kinetic factors. For example, Varnin *et al.*³³ wrote that, “if the condensate as a whole under the regular conditions of crystallization mostly reveals properties close to those of graphite, then this is a consequence of not the energetic advantage of graphite (which, by the way, is quite insignificant), but the kinetic preferences in the growth of the graphite structure.” Thus, the Russians proposed that the formation of diamond competes kinetically with the formation of graphite.

Although the Russian school developed kinetic arguments using macroscopic concepts, such as classical nucleation theory and Langmuir adsorption–desorption on the surface, they did not make specific suggestions regarding the elementary chemical reactions and/or species involved in either gas-phase or surface processes, except for very brief statements that (i) “graphite grows via methyl radicals, while diamond, at least partially, via metastable radicals CH₅,”¹⁴ (ii) “complexes” of hydrocarbons form on the diamond surface,³¹ and (iii) homogeneously formed “nuclei and clusters of the new phase” are incorporated into the lattice of the crystal.³²

(1) Chemical Mechanisms of Surface Reactions

Tsuda *et al.*^{76–78} conducted quantum chemical computations in order to determine the lowest energy path for a proposed mechanism of diamond growth on {111} surfaces. They initially assumed⁷⁶ that only C₁H_{1–3} radicals and ions can be the growth species in CH₄–H₂ plasmas and reported the following two-step reaction sequence. In the first step, the {111} plane of the diamond surface is covered by the methyl groups via either methylene in-

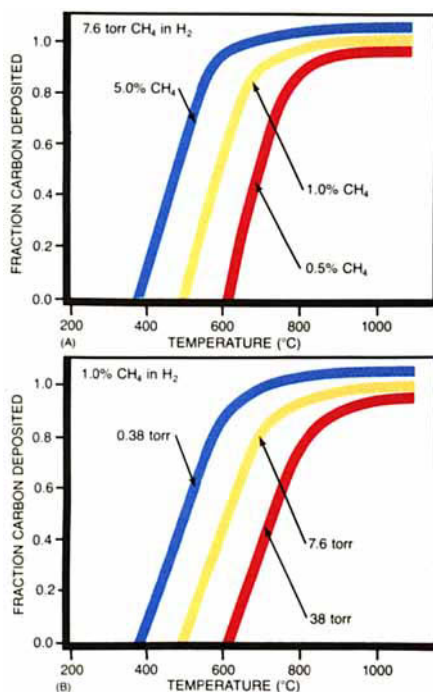
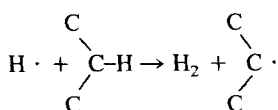


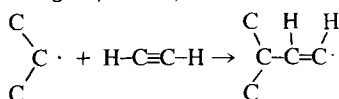
Fig. 10. Equilibrium plots of the fraction carbon deposited from methane–hydrogen mixtures as a function of temperature: (A) constant total pressure, varying CH₄ content in reactant gas and (B) constant CH₄ content, varying total pressure.

sertion or hydrogen abstraction followed by methyl radical addition. In the second step, following the attack of a methyl cation and the loss of three H₂ molecules, three neighboring methyl groups on the {111} plane are bound together to form the diamond structure. In the subsequent publication,^{77,78} they extended their analysis and concluded that the epitaxial growth of a diamond film is sustained, provided that the surface maintains a positive charge and that there is a supply of methyl radicals. This mechanism does not explain the critical effect of hydrogen atoms on the growth and relies on maintaining a positively charged surface or a precursor of CH₃⁺ cations, whose abundance in a plasma is questionable⁴³ and whose abundance in an ion-free environment, as is found in the hot-filament method of diamond growth, is doubtful.⁷⁹⁻⁸¹

A paper by Frenklach and Spear⁵⁰ proposes an alternative mechanism for the growth of {111} diamond surfaces. It basically consists of two alternating steps. The first step is the surface activation by H-atom removal of a surface-bonded hydrogen.



In the second step, this surface-activated carbon radical then acts as a site for adding more carbons to the structure by reacting with acetylene (or other carbon-hydrogen species in the gas/plasma).



The additional radical reactions for the mechanism of propagating a growth step on the {111} plane of diamond are given in the paper by Frenklach and Spear.⁵⁰ The propagation results in the addition of two acetylene molecules for one hydrogen abstraction step, with the resulting regeneration of the hydrogen atom which was consumed in forming the activated surface site.

Huang, Frenklach, and Maroncelli⁸² recently tested the Frenklach and Spear mechanism using quantum chemical computation techniques similar to those used by Tsuda *et al.*⁷⁶⁻⁷⁸ The following relevant results emanated from the work of Huang *et al.*: (i) Once the surface is activated by the 73 kJ/mol (17.4 kcal/mol) H-atom removal of a surface-bonded hydrogen, all other subsequent mechanistic steps occur with a decrease in energy; i.e., no activation energy is needed for any of these subsequent steps. Tsuda *et al.* compute a 129 kJ/mol (30.6 kcal/mol) initiation step (130 kJ/mol (31.0 kcal/

mol) if computed by the method used by Huang *et al.*) and 17 to 25 kJ/mol (4 to 6 kcal/mol) energy barriers for two of their subsequent steps. (ii) Certain multistep bond-breaking, atom-transfer, bond-forming processes proposed in the Frenklach and Spear mechanism were calculated to be energetically more favorable if they occurred as one simultaneous step rather than as sequential steps.

Although the mechanism is described in detail by Frenklach and Spear⁵⁰ for the addition of acetylene molecules, it is possible for other carbon-hydrogen species to enter into the reaction sequences. The mechanism is in general agreement with the macroscopic views of the Russian researchers and is consistent with experimental observations outlined in Section IV, such as the importance of atomic hydrogen and the independence of the diamond growth on the chemical nature of the input hydrocarbon species.

(2) Steric Aspects of Gas-Solid Growth Reactions

Relationships of the atomic structure of {111}, {100}, and {110} diamond surfaces with the growth behavior of these surfaces and the nature of the C₃H_x and C₂H_y species which arrive at the surface have been discussed by Spear and Frenklach⁸³ and Angus and Hayman.⁶ Attempts are made to rationally correlate experimental growth behavior with atomistic hypotheses on nucleation and growth mechanisms and to provide guidelines for designing experiments to test models that provide recipes for tailoring the type of deposited diamond required for a particular application, whether it is abrasive grit or single-crystal films. Although current information available for such correlations is sparse, it is instructive to illustrate the preliminary mechanistic conclusions that can be reached from steric considerations of the grow interface.

Faceted diamond crystallites are dominated by {111} and {100} surfaces. Very rarely are {110} surfaces observed. Dangling sp³ bonds exist on all three surfaces; one for each surface carbon on the {111} and {110} faces, and two for each carbon on the {100} face. Figure 9, used in Section V to illustrate an important role of hydrogen in the diamond growth process, shows a {111} surface with C-H bonds satisfying the dangling bonds of the surface carbons.

Figure 11 depicts the zigzag chainlike nature of the carbon atoms in a {100} diamond surface. The small figure of four unit cells shows these parallel surface carbon chains in the <110> direction. Every other carbon lies on the front surface, while the alternat-

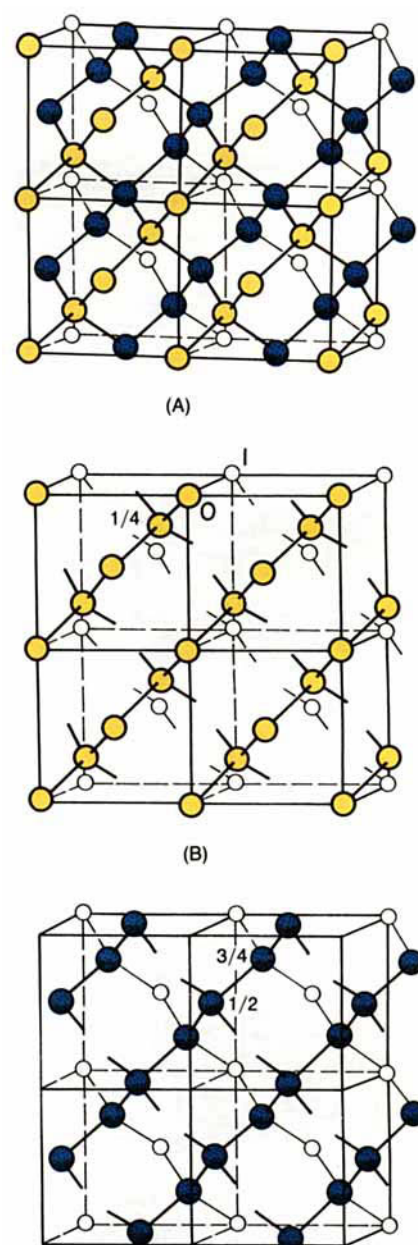


Fig. 11. (A) Four unit cells of diamond depicting the zigzag chainlike nature of the carbon atoms in the {100} and {110} planes of the structure. These parallel chains in the {100} planes extend in the <110> direction of the structure. (B) Every other zigzag carbon chain has carbon atoms on the surface of the unit cell (at the "0" position) separated by carbons which lie 1/4 toward the back surface. (C) the other chains, which also are in the <110> direction, have carbons at positions of 1/2 and 3/4 toward the back of the cell.

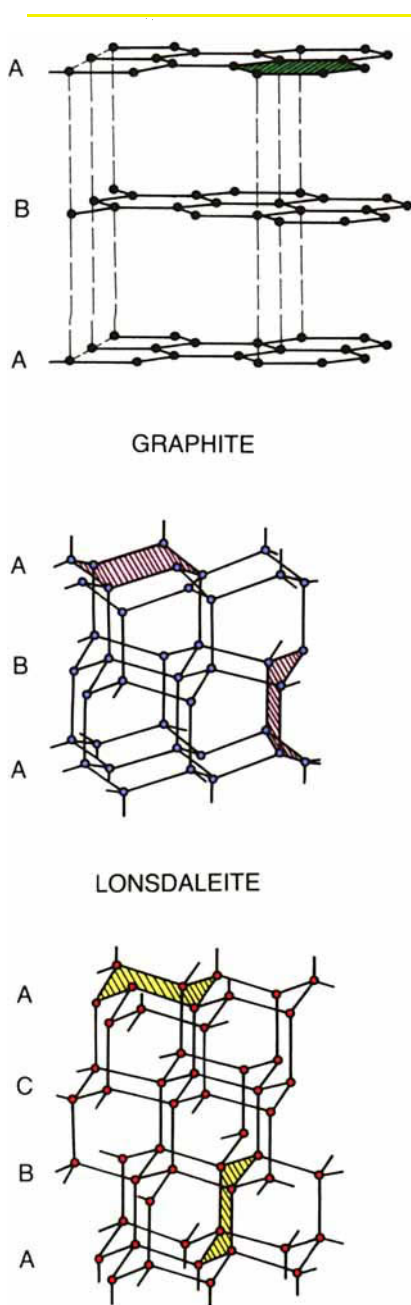


Fig. A1. Schematic drawings of the atomic arrangements in hexagonal graphite, hexagonal lonsdaleite, and cubic diamond. Note the shaded hexagonal rings of carbons in these three structures: planar (graphite), boat-form (lonsdaleite), and chair-form (diamond).

ing carbons are $\frac{1}{4}$ of the unit cell toward the back surface. The surface carbons in the chain are bonded to only two other carbon atoms, leaving two unsatisfied sp^3 bonds, unless a restructuring of the surface occurs or other atoms, such as hydrogen, form surface bonds.

The $\{110\}$ surface is composed of the same zigzag chains found in the $\{100\}$ planes, but they lie on their side in the $\{110\}$ face so that all carbon atoms composing a chain lie on the surface of this face. Each of these surface carbons is bonded to two other carbon carbons plus a third carbon which lies below the surface, leaving only one unsatisfied sp^3 bond.

Steric analyses of molecular species approaching each of the above three surfaces lead to the following preliminary conclusions concerning diamond growth at the gas–solid interface:

(1) For $\{111\}$ Surfaces:

(i) growth of a nucleated plane across the surface will occur rapidly with C_2H_{1-4} species (C_2H_1 , C_2H_2 , C_2H_3 , C_2H_4);

(ii) C_1H_{1-3} species can also contribute to the growth of these planes;

(iii) C–H bonds can satisfy all of the dangling sp^3 bonds of the surface carbons;

(iv) continuation of growth on a $\{111\}$ surface requires nucleation of a new $\{111\}$ plane upon the completion of each growing plane;

(v) stacking faults and twin planes can easily be introduced during the nucleation stage of each new $\{111\}$ plane (Once a plane is nucleated and growth is occurring, the formation of a planar defect is unlikely.); and

(vi) conditions leading to low rates of nucleation of new $\{111\}$ planes result in a morphology dominated by $\{111\}$ surfaces.

(2) For $\{100\}$ Surfaces:

(i) growth of these faces occurs most rapidly with C_1H_1 or C_1H_2 species (The attachment of C_xH_y species to this surface requires the formation of two sp^3 bonds (carbon bonds to surface carbons which are in two different chains).);

(ii) C_2H_y species are not preferred, but can add in combination with C_1H_{1-2} species;

(iii) C–H bonding cannot satisfy all of the dangling sp^3 bonds of the surface carbons because of steric hindrances (One C–H bond sterically hinders the formation of a C–H bond on the carbon in an adjacent chain.);

(iv) nucleation of new planes is not required for $\{100\}$ surfaces (Addition of carbon species to these planes produces new active growth sites.); and

(v) stacking faults and twin planes cannot be easily introduced during growth; and (vi) fast growth of $\{100\}$ surfaces results in the formation of $\{111\}$

surfaces.

(3) For $\{110\}$ Surfaces:

(i) growth of these faces occurs rapidly with either C_1H_{1-3} or C_2H_{1-4} species (Because the nature of the precursor is not important, these surfaces have fast growth rates and are rarely exhibited by diamond crystallites.);

(ii) C–H bonding can satisfy all of the dangling sp^3 bonds of the surface carbons—steric hindrances do not occur;

(iii) nucleation of new planes is not required for $\{110\}$ surfaces (Addition of carbon species to these planes produces new active growth sites.);

(iv) stacking faults and twin planes cannot be easily introduced during growth; and

(v) fast growth of $\{110\}$ surfaces results in the formation of $\{111\}$ surfaces.

More quantitative experimental information is needed to test these conclusions and to develop a better understanding of the growth processes, but the conclusions are consistent with experimental observations on diamond growth summarized in other parts of this review.

VII. Future Directions

The general properties and potential applications of diamond in advanced materials technology are outlined in Appendix B. These provide the driving force for the rapidly developing diamond coating science and technology which has been summarized in this review. Applications for these coatings include protection against wear and chemical attack, electrically insulating heat sinks, durable lenses for use in both the visible and IR regions, and high-temperature and high-power electronic devices. Development of coating techniques for growing clean diamond films at temperatures low enough to coat plastics would result in "crash-proof" optical and magnetic disks for information storage.

The major research and development problems which are slowing the commercialization of products incorporating diamond films are not trivial. The generic problem areas are as follows:

- (i) lowering substrate temperatures,
- (ii) controlling nucleation rates,
- (iii) increasing growth rates,
- (iv) better adhesion to a variety of substrate materials,
- (v) eliminating graphite codeposition,
- (vi) controlling defect densities,
- (vii) uniform thickness on irregular shapes,
- (viii) better electrical contacts, and
- (ix) heteroepitaxial growth of single-crystal films.

A recent *Popular Science* article²¹ quotes Thomas Anthony, a General

Electric Company scientist spearheading their low-pressure diamond research as saying that they have "found proprietary ways to get relatively uniform coatings on irregular objects," and that their coating process produces films "thicker than a millimeter." If they have indeed solved the film uniformity and growth-rate problems, then they have overcome two major hurdles for getting vapor-grown diamonds to the marketplace.

Correlations of hypothesized nucleation and growth mechanisms with diamond growth rates, crystallite morphologies, defect types and concentrations, and plasma chemistry would be of enormous benefit in eliminating the above problem areas as well as in providing efficient guidelines for advancing the technology needed to fully utilize the unique properties of diamond. If methods can be developed for producing sinterable diamond powder, bulk diamond ceramics can be considered for a host of new applications making use of unique combinations of its properties. Diamond could then become not only the ceramic coating of the future, but could also play a major role in bulk form as an advanced engineering material.

APPENDIX A

Phases and Crystal Structures of Carbon

Diamond and graphite are both pure carbon with well-known crystalline forms, but with quite different properties. Other crystalline forms of pure carbon which are not as common include lonsdaleite (sometimes called hexagonal diamond because its structure and properties are similar to those of diamond) and the carbynes (cross-linked linear carbon polytypes of which at least six forms have been reported).⁹⁴

Each of these phases of carbon is formed from carbon hybridized in an sp^3 , sp^2 , and/or sp state. The ideal structures of diamond and lonsdaleite are formed completely from tetrahedrally bonded sp^3 carbons. Graphite is formed completely from trigonally bonded sp^2 hybridized carbons. The carbynes are formed primarily from linearly bonded sp hybridized carbons, but the cross linking which is critical to their structure requires sp^2 and/or sp^3 carbons.

The atomic arrangements in graphite, lonsdaleite, and diamond are depicted in Fig. A1, which clearly indicates the similarities and differences expected in the properties of these materials. The graphitic sp^2 bonding is similar to that in benzene, and it creates strongly bonded two-dimensional planes, but weak bonding between the planes. On the other hand, the four equivalent sp^3 bonds in diamond and

lonsdaleite form strong, uniform three-dimensional frameworks.

The unit cells of cubic diamond and hexagonal lonsdaleite are shown in Fig. A2, and Table A1 shows their crystallographic data. These structures may at first appear quite different, but both are made completely of sp^3 -type tetrahedrally bonded carbon atoms. The structures are related to each other in a similar manner as sphalerite and wurzite.

The {111} planes of diamond are composed of puckered hexagonal rings of carbon atoms which have the chair form as indicated in Fig. A1. The {001} planes in lonsdaleite are identical to these diamond {111} planes. The difference in the two structures is in the stacking of these planes as is shown in Fig. A1 and is similar to the difference between cubic-close-packed and hexagonal-close-packed metal structures. Figure A3 shows the differences between the two structures in three ways. The differences in second-nearest-neighbor coordination as viewed down a C-C bond lying in the stacking direction is shown in Fig. A3(A). In diamond, the three carbons at one end of the bond are staggered with respect to the three carbons at the other end of the bond. In lonsdaleite, these same carbons eclipse each other. The slightly higher energy of these eclipsed lonsdaleite carbons causes its structure to be slightly less stable than the diamond structure.

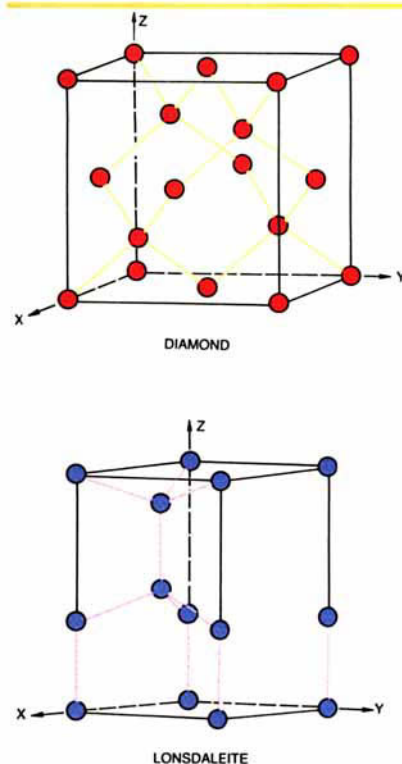


Fig. A2. Schematic diagrams of unit cells of diamond and lonsdaleite. Table A1 gives their crystal structure data.

Table A1. Crystal Structure Data for Diamond and Lonsdaleite

| Property | Diamond* | Lonsdaleite [†] |
|--|--|--|
| Symmetry | Cubic | Hexagonal |
| Space group | $Fd\bar{3}m$ | $P6_3/mmc$ |
| Atoms per unit cell | 8 | 4 |
| Positions of atoms | (000), $(\frac{1}{2} \frac{1}{2} 0)$, $(0 \frac{1}{2} \frac{1}{2})$, $(\frac{1}{2} 0 \frac{1}{2})$, $(\frac{1}{4} \frac{1}{4} \frac{1}{4})$, $(\frac{3}{4} \frac{3}{4} \frac{1}{4})$, $(\frac{1}{4} \frac{3}{4} \frac{3}{4})$, $(\frac{3}{4} \frac{1}{4} \frac{3}{4})$ | (000), $(00 \frac{3}{8})$, $(\frac{1}{3} \frac{2}{3} \frac{1}{3})$, $(\frac{1}{3} \frac{2}{3} \frac{2}{3})$ |
| Cell constant (298 K) (nm (Å)) | 0.356683(1)–0.356725(3) (3.56683(1)–3.56725(3)) | $a = 0.252$ (2.52) $c = 0.412$ (4.12) |
| Theoretical density (298 K) (g/cm ³) | 3.51525 | 3.52 |
| Carbon-carbon bond distance (nm (Å)) | 0.154450(5) (1.54450(5)) | 0.154 (1.54) |

*Data from Field.⁷¹ [†]Data from Hanneman *et al.*¹¹¹

The puckered hexagonal rings are present in the chair form throughout the diamond structure, but not throughout the lonsdaleite structure. As can be seen in Figs. A3(B) and (C), the hexagonal rings which lie in the stacking direction of lonsdaleite are in the boat form. The first carbons which begin nucleating a new layer in lonsdaleite and in diamond are shown in Fig. A3(B), and the basic structural unit of these two structures (which is also the nucleation kernel) is shown in

Fig. A3(C). Twin planes (stacking faults similar to those found in silicon carbide) could nucleate and form on diamond {111} planes.

APPENDIX B Properties and Applications of Diamond

(1) General Properties and Applications

Table B1 lists some of the properties of diamond which can lead to advanced applications in areas ranging from cutting and grinding to high-power, high-speed electrooptic devices. Although certain properties of diamond such as its room-temperature hardness and thermal conductivity are the best of any known material, its unique combination of properties is what has caught the attention of many industries.

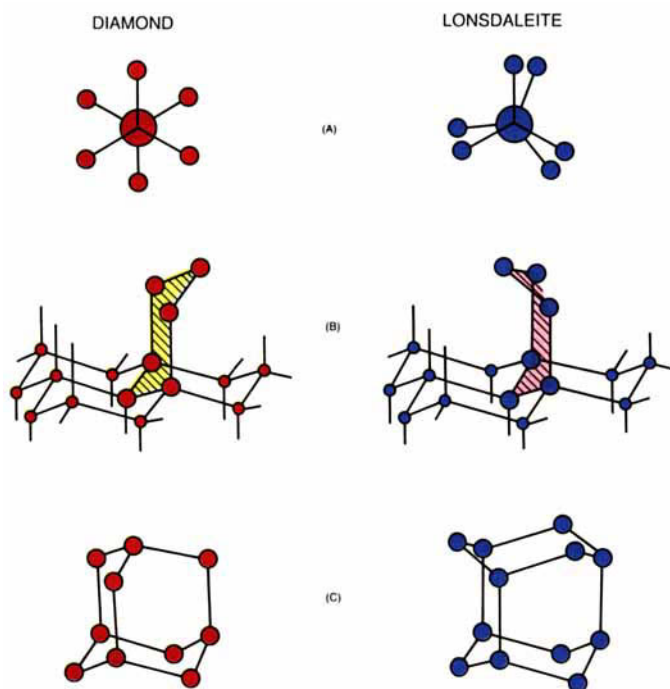


Fig. A3. Comparisons of structural aspects of diamond and lonsdaleite. (A) View down C-C bond in stacking direction of planes shown in Fig. A1; diamond shows a staggered configuration of the C-C second-nearest-neighbor bonds (chair-form configuration of puckered hexagonal rings), and lonsdaleite shows an eclipsed configuration (boat-form configuration of hexagonal puckered rings). (B) Initial carbon configuration as a new plane is nucleating. (C) Basic structural unit for each of the structures. These are also the nucleation kernels for new planes.

Sumitomo Electric and Sony are retailing the first product involving a diamond coating: their APM-66ES speakers contain diamond-clad tweeters.

The following paragraphs outline more details of the chemical, thermal, mechanical, electronic, and optical properties of diamond. However, many of the applications mentioned in these discussions critically depend on combinations of these properties. Badzian *et al.*⁴ provide an extensive listing of many possible applications of diamond.

(2) Chemical Properties

Diamonds are resistant to all acids, even at high temperatures. However, they can be etched by fluxes of caustic alkalis, various oxysalts, and metals. Etch figures were formed with NaClO_4 and KClO_4 , both very strong

oxidants, on {111} faces at 380°C and 181 h.⁸⁴ Sodium nitrate is known to attack diamond at 430°C. The dissolution of diamond (and carbon in general) in metals has been examined in detail because of the use of metal solvents/catalysts in high-pressure/high-temperature diamond growth.^{71(e)}

O_2 , CO , CO_2 , H_2 , H_2O , and Cl_2 at high-temperature have been used to etch diamonds. In oxygen, appreciable oxidation will begin at about 600°C. Diamonds will burn in an oxygen jet at 720°C and in air at 850°C. Under low vacuum, residual oxygen causes a dense black film of graphite to form on a diamond surface, but it can be easily removed by boiling in HClO_4 . Aqua regia will also remove the black surface film.⁸⁴ These films, which can form above 600°C, are not true graphitization of the diamond; i.e., they are not a result of a solid-state transformation of diamond to graphite, but are almost certainly a result of a mineralization process through a CO-CO_2 transport mechanism. If diamond is heated in a clean, inert environment, the onset of graphitization begins at about 1500°C, and the rate increases rapidly until 2100°C, where a 0.1 carat octahedra is totally converted to graphite in less than 3 min.^{71(h)} The {001} planes of graphite form parallel to the {111} planes of diamond.⁸⁴

Heating diamond to 1500°C produces only very slight surface graphitization due to small quantities of oxygen which remain in the heated system even under a vacuum of 10^{-2} to 10^{-3} Pa (10^{-7} to 10^{-8} atm). Slightly higher pressures result in a thicker film, but if the residual oxygen pressure becomes too high, the surface film is removed by oxidation.⁸⁴

Efremov *et al.*⁸⁵ developed an ion-beam-assisted etching technology for use in fabricating diamond-thin-film devices. Nitrogen dioxide is physically adsorbed on the diamond surface where it is bombarded with an ion beam and is activated so that oxidation of the diamond occurs. This process produces etching rates of 200 nm/min (2000 Å/min) as compared with reactive-ion etching with oxygen which has a rate of 20 nm/min (200 Å/min).

(3) Thermal Properties

Table B11 lists a number of the thermal properties, including thermodynamic properties, of diamond and the graphite to diamond transition.^{71(d)} The maximum thermal conductivity occurs at about 80 K. At room temperature, the conductivity of diamond is about 4 times greater than the value for β -silicon carbide, 15 times greater than that for silicon, and 5 times greater than that for copper.

Small amounts of boron impurity,

such as used for semiconductor doping, have little effect on the thermal conductivity of diamond. However, nitrogen impurities markedly effect its conductivity.⁶⁶ The tendency of nitrogen to cluster in diamond may cause this effect. The natural type IIa diamond contains very little nitrogen impurity whereas type Ia contains up to about 0.1 at.% nitrogen. The thermal conductivity of type IIa is about 3 times that of type Ia.⁶⁴

Ono *et al.*⁸⁷ made thermal conductivity measurements at 100° and 130°C on 7- to 30- μm -thick vapor-deposited diamond films. They used reference films of oxygen-free copper and pure silver and obtained average values of 4.5 and 4.8 W/(cm · K), respectively. The maximum value for a vapor-deposited diamond film was 10.0 W/(cm · K) at these temperatures. They found a strong correlation between the diamond conductivity values and the methane content in the input gas for film deposition. The Raman spectra of the films, which provide a measure of the non-diamond carbon codeposited with the crystalline material, also showed a similar strong correlation with methane concentration. The films exhibiting the highest thermal conductivity and the cleanest Raman spectra (least amount of non-diamond carbon) were grown with methane concentrations of 0.1 mol% in hydrogen. The conductivity dropped from 10 to 4 W/(cm · K) as the methane concentration in the deposition gas increased from 0.1 to 0.5 mol%. The values dropped below 1 W/(cm · K) for methane contents of 2 mol% and higher. The amount of non-diamond carbon in the films, as measured qualitatively by the Raman spectra, increased with increasing methane concentration in the reactant gas.

The coefficient of thermal expansion of diamond is quite small. It is $0.8 \times 10^{-6} \text{ K}^{-1}$ at room temperature, and then increases to $4.8 \times 10^{-6} \text{ K}^{-1}$ at about 1200 K. Gruneisen's law is obeyed between 420 and 1200 K.⁷¹

(4) Mechanical Properties

Specific values for the mechanical properties of diamond, as given by Field,⁷¹ are listed in Table BIII. Diamond is perfect for many abrasives and wear-resistant applications, except for its high-temperature chemical interactions with ferrous alloys.^{71(b)} Cubic boron nitride is a good substitute for diamond in these cases.⁸⁸ Diamond is often used with well-defined cutting edges, as in turning or milling; as bonded grit in grinding, sawing, drilling, and dressing; and as loose abrasive grit in lapping and polishing. At near room temperature, diamond is the hardest known material, has a low coefficient of friction, and has the

Table BI. Properties and Applications of Diamond Coatings*

| Properties | Applications |
|---|------------------------------------|
| Hardest known material | Coatings for cutting tools |
| Low coefficient of friction | Abrasive coatings |
| High thermal conductivity (highest known at room temperature) | Coatings for bearings |
| Low thermal expansion | Heat sinks for electronic devices |
| Heat resistive | High-power microwave devices |
| Acid resistive | Radio-frequency electronic devices |
| Radiation resistive (to X-ray, ultraviolet, γ -ray) | High-speed electronic devices |
| Electrical insulator | Sensors for severe environments |
| High band gap semiconductor (either <i>p</i> - or <i>n</i> -doped) | Window and lens materials |
| Low dielectric constant | Electrooptic devices |
| High hole mobility | |
| Visible and infrared transparent | |
| Large refractive index | |

*Expanded version of table given by Nishimura *et al.*⁶²

largest thermal conductivity of any material. These properties and its low coefficient of thermal expansion greatly reduce the problems of heating during cutting and grinding and, therefore, possible problems with thermal shock.

Cleavage occurs primarily along the {111} planes of diamond although the energy differences for several planes are quite small.^{71(a)} For example, the cleavage energies in J/mm² are 10.6 for {111}, 11.7 for {332}, 12.2 for {221}, and 12.6 for {331} planes. Cleavage cracks can travel at velocities of thousands of meters per second. Theoretical strengths of diamond and various other materials are compared by Field.^{71(a)} The best value for the tensile strength of diamond is 300 kg/mm².

Above 1800°C, dislocations become

Table BII. Thermal Properties of Diamond*

| Property | Value |
|--|------------------------|
| Thermal conductivity (W/(cm · K)) | |
| Typical values at 293 K | |
| Type Ia | 6–10 |
| Type IIa | 20–21 |
| Thermal expansion (linear) ($\times 10^{-6} \text{ K}^{-1}$) | |
| 193 K | 0.4(0.1) |
| 293 K | 0.8(0.1) |
| 400–1200 K | 1.5–4.8 |
| Debye temperature, Θ , at $T > 600 \text{ K}$ (K) | 1880 |
| Molar volume, V_{298}° (cm ³ /mol) | 3.417 |
| Bulk modulus, B (Pa) | 4.4×10^{11} |
| $C_p - C_v$ at $T > 1100 \text{ K}$ (J/(mol · K)) | $4.2 \times 10^{-4} T$ |
| C_p at 1800 K | 24.7 |
| C_p at 3000 K | 26.3 |
| Transition reaction: Graphite \rightleftharpoons diamond | |
| ΔH_{298}° (J/mol) | 1872 ± 75 |
| ΔS_{298}° (J/(mol · K)) | -3.22^{\dagger} |
| ΔC_p above 1100 K (J/(mol · K)) | 0^{\dagger} |
| Equilibrium pressure at 2000 K (Pa) | 64×10^8 |
| Volume change at 2000 K transition (cm ³ /mol) | 1.4 |

*Data from Berman.^{71(a)} [†]Data from DeVries.⁸⁸ [‡]Thus, ΔH_T° and ΔS_T° for the transition are constant above 1100 K.

Table BIII. Mechanical Properties of Diamond*

| Property | Value |
|---|---|
| Hardness | Indentation hardness typically taken as 10 000 kg/mm ² |
| Friction | Coefficient of friction in air is ~0.1; approaches unity under vacuum |
| Elastic moduli ($\times 10^{11}$ N/m ²) | |
| C_{11} | 10.8 |
| C_{12} | 1.25 |
| C_{44} | 5.77 |
| Pressure coefficient, dC/dP | |
| C_{11} | 6.0(0.7) |
| C_{12} | 3.1(0.7) |
| C_{44} | 3.0(0.3) |
| Temperature coefficient, $(1/C)(dC/dT)$ ($\times 10^{-5}$) | |
| C_{11} | -1.4(0.2) |
| C_{12} | -5.7(1.5) |
| C_{44} | -1.25(0.1) |
| Young's modulus, E (N/m ²) [†] | 10.5×10^{11} |
| Poisson's ratio, $\nu_{21} = C_{12}/(C_{11} + C_{12})^{\ddagger}$ | 0.104 |
| Bulk modulus, $K = \frac{1}{3}(C_{11} + 2C_{12})$ ($\times 10^{11}$ N/m ²) | 4.42 |

*Data were taken from Field.^{71(a)} More details on the mechanical properties of diamond are given in this reference. [†]The anisotropy is 1.21 ($= 2C_{44}/(C_{11} - C_{12})$) for diamond. The condition for isotropy is 1.00, so Young's modulus does not vary greatly with orientation. [‡]The value of ν varies between 0.1 and 0.29, with an average ν of ~0.2.

relatively mobile, and it is possible to produce appreciable plastic deformation. At room temperature, diamond behaves as an elastic brittle solid. However, there is still a question whether plastic deformation can occur around an indenter at room temperature.^{71(g)}

The coefficient of friction (μ) of diamond on diamond is about 0.1 in air, and about 1 under vacuum. If the surfaces are cleaned under vacuum by heating or bombardment, the high value of unity is approached. Continual sliding on a dirty surface under vacuum will result in continual increases in μ until a value of unity is approached. The high friction leads to marked disintegration of the diamond surface.^{71(g)}

Friction depends on the crystallographic surface of the diamond. The {111} surface shows an isotropic μ of 0.05 in all directions in air, whereas the {100} cube face gives values of 0.05 along the <011> direction, and 0.1 to 0.15 along the <010> direction. The direction of polishing the surface before the test can also effect the coefficient of friction value. The addition of a lubricant has little effect on the value. Other than for clean surfaces under vacuum, the coefficient of friction rarely exceeds a maximum of 0.2.

(5) Electronic and Optical Properties

Table BIV shows a comparison of properties of semiconducting diamond, β -silicon carbide, and silicon. The atoms in these systems all exhibit sp^3 bonding with cubic unit cells. Silicon has the diamond structure, and β -silicon carbide is the diamond structure with

alternating silicon and carbon atoms.

Two figures of merit for semiconductor developments which have resulted in practical considerations of diamond for use as a semiconductor.⁸⁶ The Johnson figure of merit, which compares the product (power) \times (frequency squared) \times (impedance), is suitable for semiconductor applications in power amplifiers at frequencies greater than the UHF spectrum. Relevant semiconductor properties are breakdown field and saturated velocity. The values given in Table BIV show that the Johnson figure of merit for diamond is about 8000 times larger than that for silicon and about 8 times larger than that for β -silicon carbide.

The Keyes figure of merit, also shown in Table BIV, is relevant for high-density integrated circuits. Important semiconductor properties are dielectric constant, thermal conductivity, and saturated velocity. Diamond has a Keyes figure of merit about 30 times larger than that for silicon and about 6 times larger than that for β -silicon carbide.

Linear arrays of diamond diodes have advantages over their silicon counterparts for the detection of radiation in the far-ultraviolet and X-ray regions because diamond does not respond to electromagnetic signals in the visible and infrared (IR) regions of the spectrum. Therefore, the background current of the diamond diode arrays is much lower.⁸⁶

The radiation hardness of semiconducting diamond has not yet been verified, except that its neutron hardness is unmatched.⁸⁶ However, because the carbon atoms in diamond exhibit much stronger bond energies than any other semiconducting material in use, diamond is expected to be much more immune to radiation damage than any other semiconductor.

Berman^{71(d)} has discussed the use of diamond for heat sinks, using an example of bonding a natural type IIa diamond to a semiconductor microwave generator. At temperatures at which such microwave generators operate, the thermal conductivity of type IIa diamond (~ 20 W/(cm \cdot K) at 298 K) is 4 to 5 times larger than that for copper. The efficiency of the cooling of such a device can be doubled if the generator is bonded to such a diamond. For a given working temperature, the microwave power can be more than doubled. The thermal resistance of the device itself and the bonding layers prevent any greater improvements. The direct deposition of a well-adhering diamond coating to such a device could help to eliminate the bonding resistance.

Fujimori *et al.*⁸⁹ synthesized boron-doped diamond films on both silicon

and diamond substrates using microwave-plasma-assisted CVD methods and characterized the conductivity of these films. For boron doping, they used diborane in B_2H_6/CH_4 ratios of 0.001 to 0.02, and obtained respective resistivities of 1 to 10^{-3} Ω -cm. The boron concentration in the film was on the order of 10^{20} atoms/cm³. The activation energy for conduction in a film produced from a reactant gas with a diborane/methane ratio of 0.001 was 0.013 eV.

Prins⁹⁰ fabricated the first bipolar transistor using natural *p*-type diamond and ion implantation to form *n*-type regions. This device did not exhibit current gain, but demonstrated device potential. Geis *et al.*⁹¹ later reported point contact transistors formed on synthetic *p*-type diamond. These devices exhibited power gain even at 510°C, which was the highest temperature reported for any transistor. Geis and co-workers summarized possible applications of diamond devices.⁹² Gildenblatt *et al.*⁹³ studied the electrical characteristics of Schottky diodes fabricated from microwave-plasma-assisted CVD polycrystalline diamond films.

Diamond is excellent as a window or lens material, or as a protective coating for these materials because of its transparency to both visible and IR radiation, its resistance to abrasion, its resistance to chemical attack, its resistance to radiation damage, and its ability to efficiently conduct heat. A natural diamond window was chosen for transmissivity over a large IR spectrum on Venus probes.⁸⁶ Transmission losses in diamond are typically as much as 4 orders of magnitude lower than in competing materials in the IR spectrum.

APPENDIX C Development of Vapor Growth Methods

Early attempts to vapor deposit diamond on diamond seed crystals by thermal pyrolysis methods resulted in low crystalline diamond growth rates of angstroms per hour, and the codeposition of non-diamond amorphous and graphitic carbons.^{3,7,9-11} Both scientific and commercial interest was minimal. However, discoveries by Deryagin and co-workers in the 1970s markedly increased deposition rates and reduced the codeposition of non-diamond carbon. These discoveries illustrated the importance of (i) using excess hydrogen in the deposition gas and (ii) activating the gas before deposition to produce superequilibrium concentrations of atomic hydrogen. (The important role of atomic hydrogen in the diamond growth process is discussed in Sections IV and VI.) As the rest of the world began to ab-

Table BIV. Comparison of Semiconducting Properties

| Properties* | Diamond | β -Silicon carbide | Silicon |
|--|-------------------|--------------------------|----------------|
| Lattice constant (nm (Å)) | 0.3567 (3.567) | 0.4358 (4.358) | 0.5430 (5.430) |
| Thermal expansion ($\times 10^{-6}/^\circ\text{C}$) | 1.1 | 4.7 | 2.6 |
| Density (g/cm ³) | 3.515 | 3.216 | 2.328 |
| Melting point ($^\circ\text{C}$) | 4000 [†] | 2540 [†] | 1420 |
| Band gap (eV) | 5.45 | 3.0 | 1.1 |
| Saturated electron velocity ($\times 10^7$ cm/s) | 2.7 | 2.5 | 1.0 |
| Carrier mobility (cm ² /(V · s)) | | | |
| Electron | 2200 | 400 | 1500 |
| Hole | 1600 | 50 | 600 |
| Breakdown ($\times 10^5$ V/cm) | 100 | 40 | 3 |
| Dielectric constant | 5.5 | 9.7 | 11.8 |
| Resistivity ($\Omega \cdot \text{cm}$) [§] | 10^{13} | 150 | 10^3 |
| Thermal conductivity (W/(cm · K)) | 20 | 5 | 1.5 |
| Absorption edge (μm) | 0.2 | 0.4 | 1.4 |
| Refractive index | 2.42 | 2.65 | 3.5 |
| Hardness (kg/mm ²) | 10 000 | 3500 | 1000 |
| Johnson figure of merit [¶] ($\times 10^{23}$ (W · Ω)/s ²) | 73 856 | 10 240 | 9.0 |
| Keyes figure of merit** ($\times 10^2$ W/(cm · s · $^\circ\text{C}$)) | 444 | 90.3 | 13.8 |

*Typical room-temperature values for these properties were obtained primarily from Field,⁷¹ Nishimura *et al.*,⁹² and Yoder.⁸⁶ [†]Triple point of carbon, but conversion of diamond to graphite under vacuum becomes rapid at about 2000°C. [‡]Two reported values given in the JANAF Tables¹¹⁰ for the peritectic decomposition of β -SiC to Si(l) and graphite are 2540° and 2830°C. Decomposition under vacuum to graphite and vapor will occur at lower temperatures. [§]Values vary widely with impurity and defect levels. [¶]Johnson figure of merit is primarily for comparing power amplifiers at frequencies above the UHF spectrum. Relevant factors are breakdown field and saturated velocity. **Keyes figure of merit is primarily for comparing high-density integrated circuits. Relevant factors are dielectric constant, thermal conductivity, and saturated velocity.

sorb these results, interest in the low-pressure growth of diamond began a rapid acceleration, and new modifications on vapor growth methods began to be developed.

In a book published in Russian, Deryagin and co-workers¹² outlined the following three methods of obtaining hydrogen-atom superequilibrium in a diamond vapor growth system: (i) catalytic, such as heated Pt for dissociating H_2 ; (ii) an electric discharge; and (iii) a heated tungsten filament located just in front of the substrate. Because this book was not readily available outside the Soviet Union and Eastern Europe and because of the general "lack of belief" by the scientific community, these techniques were not quickly pursued in other laboratories.

In 1981, in the *Journal of Crystal Growth*, Spitsyn, Bouilov, and Deryagin¹³ wrote a paper in English on the growth of crystalline diamond that showed photographs of deposits that exhibited many faceted crystals with dimensions up to about 30 μm . They also showed an electron diffraction pattern characteristic of crystalline cubic diamond and listed a number of physical property measurements on grown films which were characteristic of diamond. Growth rates were on the order of micrometers per hour. One sentence in this paper mentions an "electric dis-

charge" in the system, but no further details were given. However, the importance of having atomic hydrogen present during growth was emphasized as a means of suppressing the crystallization of graphite.

Immediately following the Spitsyn paper, Mania *et al.*⁹⁵ published a paper on the synthesis of diamond utilizing an ac discharge in a low-pressure flowing-gas system. Varnin *et al.*⁹⁶ later reported more details of the Russian dc electric discharge system mentioned earlier.^{12,13} A hollow-cathode plasma-assisted CVD method which combines thermal and plasma dissociation of a methane–hydrogen mixture for diamond growth was developed by Singh *et al.*⁹⁷ They doubled the growth rates that they had been obtaining from their heated filament system.⁹⁸

Following the paper in English by Spitsyn,¹³ many papers were published in Japan, primarily from the National Institute for Research on Inorganic Materials (NIRIM), on techniques for growing diamond from activated gases composed of hydrocarbons and excess hydrogen. In 1982, Matsumoto *et al.*^{79,81} used the technique mentioned by Deryagin *et al.*¹² of activating the precursor deposition gases with a filament heated to approximately 2000°C about 1 cm from the 1000°C growth surface. This hot-filament method (HFCVD) has since been studied and used with great success by many researchers around the world.

Matsumoto⁹⁹ reported on diamond growth in a radio-frequency (rf) glow discharge system (rf-PACVD). This method has also been combined with a heated filament¹⁰⁰ to improve on the diamond growth rates. However, Matsumoto reported that the combined method "does not produce a clear crystal habit of diamond." Sawabe and Inuzuka¹⁰¹ later developed an electron-assisted method (EACVD) for growing diamond with growth rates of 3 to 5 $\mu\text{m}/\text{h}$, as opposed to many of the earlier rates of about 1 $\mu\text{m}/\text{h}$ and less.

The successful use of a microwave-plasma-assisted method (MPACVD) to activate the gas for growing crystalline diamond was reported by Kamo and co-workers.¹⁰² Kawarada *et al.*¹⁰³ developed a magneto–microwave system so that large areas could be coated. On a historical note, in 1976, Knox¹⁰⁴ reported the use of a microwave plasma to activate hydrocarbon–hydrogen mixtures in an attempt to produce hard coatings for IR window materials. He obtained electron diffraction patterns indicating diamond had been produced, but this work was not pursued because of skepticism and the termination of the research contract.

The above methods typically utilize total pressures of about 10^4 Pa (0.1 atm) or less, pressures at which "cold plasmas" operate. Therefore, it was a major breakthrough when Matsumoto and his colleagues¹⁰⁵ grew diamond particles and films on molybdenum substrates using an rf induction thermal plasma with a 10^5 -Pa (1-atm) argon–hydrogen–methane mixture. Their growth rates were on the order of 60 $\mu\text{m}/\text{h}$ (1 $\mu\text{m}/\text{min}$), much higher than the typical growth rates of a few micrometers per hour and less. The molybdenum substrate was placed on a water-cooled holder, and held at 700° to 1200°C. The rf frequency used was 4 MHz, and the total plate power was 60 kW. The total gas flow rate was about 72 L/min through the approximately 50-mm diameter tube, with the hydrogen flow rate making up 12 L/min, and the methane flow rate was maintained between 0.1 and 1.2 L/min. The hot plasma makes it difficult to maintain the low substrate temperature and to obtain uniform coating thicknesses across the substrate.

Other novel methods developed include diamond growth at rates up to 80 $\mu\text{m}/\text{h}$ by the application of plasma jets at high temperatures and flow rates.¹⁰⁶ Diamond crystals and films have also been grown using 10^5 -Pa (1-atm) oxygen–acetylene flames.^{57–59}

The homogeneous crystallization of diamond from a vapor utilizing laser preheating or other gas activation methods was reported in the Soviet Union in Refs. 14, 15, 107, and in references cited in these papers, but no further reports on the development of these techniques have been found. The nucleation of diamond powder from methane in an rf plasma was reported by Mitura,¹⁰⁸ but the evidence that diamond was actually produced is not very strong.

The growth of single-crystal films of diamond is critical to many electronic and optical applications, but is a feat that has not been achieved except for homoepitaxial growth on diamond substrates. Spitsyn *et al.*¹³ reported the growth of single-crystal films on {110} diamond surfaces. Matsumoto *et al.*⁸⁰ showed a beautiful SEM photograph of an approximately 10- μm thick single-crystal diamond film grown on a {111} diamond surface. Fujimora *et al.*⁸⁹ have repeated that growth on {111} diamond surfaces in preparing doped single-crystal samples for electrical measurements. Fujimora¹⁰⁹ later reported that the epitaxial growth of diamond on {100} diamond surfaces gave better quality films than those grown on {111} diamond surfaces.

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