Current Issues and Problems in the Chemical Vapor Deposition of Diamond

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Current issues and problems in the chemical vapor deposition (CVD) of diamond are those which relate to its characterization, its nucleation on foreign surfaces, the question of its formation in preference to the other phases of solid carbon (for example, graphite, chaoite, or lonsdaleite), why different morphologies and crystallographic orientations (textures) are seen in different experiments or with different parameters in the same experiment, and finally whether well-crystallized metastable phases can be obtained by CVD in other material systems or are only a peculiarity of carbon chemistry. Whether a given carbon coating is justly described as diamond has been such an issue, and coatings should clearly show evidence for diamond by x-ray diffraction and Raman spectroscopy before the claim of diamond is made. Experimental results have not been consistent in many cases, and much work remains to be done before an accurate assessment can be made of the technological impact of the development.

DIAMOND IS ONE OF THE MOST TECHNOLOGICALLY AND scientifically valuable crystalline solids found in nature, as it has a combination of properties effectively unrivaled by any other known material. Because of its unusual properties and commercial value, its synthetic production has long been a goal of numerous organizations and individuals, and, with the development of vapor-phase synthesis methods, the size of the research community concerned with diamond synthesis has expanded greatly. The history of efforts at its synthesis and an understanding of its properties is replete with all the essential elements of human drama. The work has entered a new phase with confirmation that well-crystallized diamond can be obtained as individual crystals as well as polycrystalline coatings and films through chemical vapor deposition (CVD). Pioneering work in this direction included the successful efforts of Eversole (*1*), Angus (*2*), as well as work in the Soviet Union by Derjaguin and others (*3*). Many of these earlier reports, however, were greeted with skepticism, prompted primarily by the well-known metastability of diamond relative to graphite (*4*), the relatively slow growth rates achieved at the time, and the eventual nucleation and growth of graphitic deposits.

A detailed history of diamond synthesis has been presented by Angus and Hayman (*5*). They also discussed at length diamond synthesis methods, molecular processes during nucleation and growth of diamond, diamond-like carbons and hydrocarbons. In this article, we complement that discussion by considering in detail the characterization of diamond, its nucleation and growth on nondiamond substrates, the competition for growth of other nondiamond carbons, and other critical issues and problems. Angus has noted that during the early period, many of those who stubbornly pursued the dream were considered foolish, and a colleague of his recently observed that now that the dream has become a clearly demonstrated reality, he is considered by many to be a prophet. The commentor went on to observe that for Angus's sake, he hoped the process was not cyclical (*6*).

Early in this decade, Japanese scientists (7) confirmed the earlier experiments that demonstrated that kinetically stable diamond growth was possible, provided certain conditions were established and maintained during the growth process. This work was rapidly reproduced in the United States (*8*), and today vapor-phase synthesis of diamond is an increasingly active area of research in all the major industrialized countries. Although the kinetically stable growth of noncrystalline or poorly crystallized forms of C, BN, BC, and other compositions have been known for some time, growth of well-crystallized metastable forms has been rare. The importance of this research may well lie not only in a new synthetic method for diamond but also in the possibility of exploiting the principles involved to synthesize other valuable and metastable, but highly crystalline, phases. A better understanding of the physical principles involved in CVD of diamond is necessary before an accurate assessment can be made of the possibilities for such application to other materials. To this end, critical examination of the major issues and problems currently attendant to the CVD of diamond is appropriate.

Preparation Methods

Many methods are now used for the stable growth of well-crystallized diamond, but these can be generally classified under four major headings; plasma-assisted CVD (*9*); thermally assisted (or "hot wire") CVD (*10*), reactive vapor deposition (for example, combustion methods) (*11*), and various combinations of these (*12*). The technique originally pioneered by Soviet and American researchers was the simple vapor deposition of solid C from hydrocarbon precursors onto preexisting diamond powders and surfaces. In this technique, the eventual nucleation and growth of graphite or other forms of nondiamond C was a limitation that necessitated either limiting the period of growth or alternating an etching cycle with a growth cycle so as to periodically remove any graphite or nondiamond C from the surfaces of the deposit. A major scientific as well as technological advance in the field occurred with the develop-

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ment of the various methods of supplying additional energy or external activation to the gas phase and surface species in the growth process. With these methods, diamond could be grown continuously without the eventual nucleation and growth of graphitic C. Of interest and importance to the various theoretical ideas are the commonalities between the various methods. Among these are: (i) high-energy densities are produced in the gas phase, sufficient to result in the considerable production of radical species, notably atomic H; (ii) the nature of the hydrocarbon used is relatively unimportant, in part because of the high total enthalpy of the gas phase; (iii) very similar substrate temperatures are used in most of the low-pressure experiments (~600° to 1000°C); (iv) deposits vary from nanocrystalline to single-crystal cubic diamond with little or no nondiamond C, depending upon proportions of C, H, or O in supply gases, but without reference to type of gas phase activation used. These common features strongly suggest that there is a common mechanism for the growth process, and thus the choice of method is dependent upon considerations of efficiency, convenience, cost, and applicability to the problem at hand.

Each of the major classifications can be further subdivided by such parameters as gas pressure, power consumption, capital cost, and maximum attainable growth rate. The highest growth rates, although not necessarily the highest efficiencies, have been obtained with the use of atmospheric-pressure plasma processes at high power density, where gas phase temperatures of ~5000° to 8000°C are readily obtained (*13*). Recently, growth rates of ~900 μm per hour were obtained with the use of two plasma torch nozzles and hydrocarbon introduction downstream of the discharge (*14*). The difficulty with making direct comparisons between the various methods is that such parameters as nucleation density, stability of operation, area and uniformity of deposition, and ultimate attainable thickness of a continuous coating are often not reported. In addition, many of these methods are still far from being fully optimized, and much current attention is on how to increase the area of uniform deposition, to reduce substrate temperatures without significant sacrifices in growth rate, and to deposit on nonplanar or convoluted surfaces. Substantial success on many of these questions will depend in large measure on progress on some of the underlying scientific problems, and in turn, progress on many of these problems requires better equipment and methods.

Characterization of Diamond Coatings

Determination of when a C coating obtained by either CVD or physical vapor deposition (PVD) is diamond can be difficult. Of reports of essentially pure C coatings and films containing essentially no H (~1 atomic percent or less), many show clear evidence for the presence of diamond (*14, 15*). Many of these also show evidence for the presence of other C phases, including noncrystalline or highly disordered C phases. At some point it becomes necessary to differentiate between those deposits that are actually diamond and those that may contain diamond, but that consist primarily of various nondiamond C phases. Differentiation between diamond and what is better termed "diamond-like" C remains an issue in the materials community with significant uncertainty in many cases. Indeed much of the earlier skepticism concerning vapor-phase diamond growth was overcome only when crystals of sufficient size and perfection to clearly show the presence of facets and a cubic habit had been achieved. A clearly discernible crystalline morphology has been included as part of a working definition (*16*).

Two means have been most commonly used to differentiate between the different carbon coatings: x-ray diffraction and Raman spectroscopy. A diamond coating for the purpose of this discussion will be sufficiently well crystallized (that is, have crystallites ~10 nm or larger and present in sufficient quantity) to show an x-ray diffraction pattern characteristic for polycrystalline diamond. The x-ray diffraction lines may be weak, greatly broadened or show asymmetry resulting from strain, defects, or small crystallite size, but they should, in any case, be present. In addition, preferred crystallographic orientation (texturing) has been frequently reported in such films (*17–21*), and consequently the relative intensities of an as-deposited film may not correlate with a randomly oriented reference pattern. Although electron diffraction [particularly selected-area diffraction from transmission electron microscopy (TEM)] has been used to show the presence of diamond, its sensitivity is sufficiently great to introduce the possibility that the diamond seen represents only a small amount of the C present. In addition, significant errors and uncertainties can arise in electron diffraction as a result of the extremely small volume of material being sampled and the strong possibility of texture or preferred orientation in vapor phase–deposited thin films (*22*).

A diamond film or coating will show the characteristic Raman peak for diamond at 1332 cm^{-1} (*23*). Other peaks may be present, and the diamond peak may be broadened by defects or small crystallite size. In addition this peak may be shifted by as much as ±4 to 8 cm^{-1}, depending upon relative stresses in the coating, but again, it should be present. Those C coatings and layers that do not produce x-ray diffraction patterns consistent with the presence of diamond, or its characteristic Raman peak, but which do have many of the physical properties of diamond including hardness, chemical inertness, low absorption in the visible and infrared, and so forth, have become known as diamond-like C (*24*).

Difficulties can arise in the interpretation of the results from both the various diffraction techniques and Raman spectroscopy. Because of their high symmetry, cubic crystals, including diamond, present few diffracting planes to an incident beam, and in randomly oriented diamond, only one of these, the (111) diffraction line, is relatively strong (*25*). Hence accurate detection of each line is important in the characterization of the material. Because many of the deposits are highly oriented, the relative intensities can be significantly altered. Although techniques are available for overcoming the problem [for example, recovery of a small fraction of the deposit and the use of a Gandolfi camera (*26*)], they tend to be difficult to apply (particularly if the material is truly diamond), tedious, time consuming, and not available in many laboratories. Because of preferred orientation and anisotropic disorder in graphitic phases, either false positive or false negative interpretations can result. In transmission diffraction experiments, such as those commonly done on transmission electron microscopes, the problem of graphitic carbon "masquerading" as diamond is particularly common (*27*). In addition, the diffraction techniques suffer from being sensitive only to the crystalline phases and give little or no information on any noncrystalline C phases that might be present. Hence, determining whether the observed crystalline phase constitutes a minor or major component in the system can be extremely difficult. It is, in part, because of these difficulties Raman spectroscopy has been extensively used.

Raman spectroscopy offers the advantage of sensitivity not only to crystalline material, but also to the various possible noncrystalline phases. Well-crystallized diamond produces only a single first-order (single-phonon scattering) Raman peak at 1332 cm^{-1} (*23*). Well-ordered graphite, similarly, has only one symmetry-allowed Raman peak at ~1600 cm^{-1} (*28*). However, because of the high phonon density of states in graphite, at phonon wavevectors other than zero, the presence of disorder or small crystallite size easily gives rise to a "forbidden" Raman peak at 1355 cm^{-1} (*29*). Hence, most graphitic C phases will produce not one, but two Raman peaks, sometimes referred to as the "D" and "G" peaks [the D notation refers to disorder, not to diamond (*30*)]. In highly disordered graphitic carbons, which may contain tetrahedrally bound C (sp^3 hybridization) as well as trigonally bound C (sp^2 hybridization), the breadth, position and relative intensity of these two peaks can vary significantly; therefore, Raman spectroscopy has also been used extensively in the study of both hydrogenated and hydrogen free diamond-like C (*30, 31*). In many diamond coatings and films, one observes not only a sharp diamond peak at $\sim$1332 cm^{-1} but also a broad maximum variously centered anywhere from $\sim$1500 cm^{-1} to $\sim$1590 cm^{-1} (Fig. 1). The position and intensity of this broad peak depends on the deposition conditions used and the wavelength of the exciting photon. The peak at $\sim$1550 cm^{-1} has been commonly attributed to the presence of graphitic or sp^2 hybridized C (*32–34*). This is not a universally accepted assignment, and Wild *et al.* (*18*) have argued that the $\sim$1550-cm^{-1} peak arises from a highly disordered C phase, possibly diamond-like C, consisting of both sp^3 and sp^2 hybridized C that need not be graphitic in nature. Many nanocrystalline (that is, crystallite sizes of $\sim$1 to 100 nm) diamond samples show additional features including a broad peak centered at $\sim$1133 cm^{-1} (Fig. 2). Although definitive assignment of this peak is not yet possible, this peak may arise from the effects of small crystallite size or disorder in the tetrahedral C network similar to the explanation suggested for the similarly forbidden peak at $\sim$1355 cm^{-1} in nanocrystalline graphites (*17, 35*). The peak in the phonon density of states for diamond that might give rise to such a behavior occurs at the Brillouin zone boundary, and interestingly, this energy level, $\sim$1133 cm^{-1}, is almost exactly the average of the longitudinal and transverse optical phonon energy levels in diamond at the zone boundary (1127 cm^{-1} at symmetry point *X*) (*36*). Infrared absorption in type 1b diamond, which contains substitutional N, at approximately the same energy level, 1130 cm^{-1}, has also been observed (*37*), and, for the two to be related, the restriction that the diamond point group, *m*3*m*, is centrosymmetric has to be lifted (*38*). Because most diamond is known to be birefringent (*39*), including CVD diamond (*40*), the optical properties are known not to be those of "perfect" cubic diamond.

There is a strong temptation to use the apparent relative intensity of these peaks [1332 and $\sim$1550 cm^{-1} (Fig. 1)] as a measure of the quality of the diamond deposit; the assumption is that the relative intensities reflect the relative volume fractions of diamond and nondiamond C (NDC) present. Whether this assumption is reasonable has been controversial, and at least three major objections can be raised, even in the case of careful experimental technique. The first is that the relative intensity of the $\sim$1550 cm^{-1} peak is sensitive to the wavelength of the exciting photon; this sensitivity suggests that the optical probing depth may vary with the crystal structure of the nondiamond material (*18*). If the apparent probing depth varies, as might be expected from the optical properties of the diamond-like carbons (*41*), the relative intensities of the two peaks may reflect the nature of the NDC and not only the volume fractions. This effect is particularly evident when Raman signatures for coatings prepared by different methods, or by the same method using different parameters, are compared. The second objection is that variations with thickness in crystallite size, morphology, and possibly the proportions of diamond and NDC in CVD diamond films might affect the relative intensities. Because the Raman scattering cross sections of diamond and the other forms of C are known to vary widely, it becomes arguable whether comparisons between different films of differing thicknesses, or crystals of differing sizes, are reliable. The intensity of the diamond Raman line is a function of beam polarization and crystallographic orientation (*23*), the effects of which are usually averaged out in polycrystalline films; however, the combination of a microfocus technique, crystallite sizes of the order of the beam size, and preferred orientation in the coating creates a potentially misleading situation. The most frequent problem is that the sampling depth of the incident light beam will vary with the size and transparency of any nondiamond inclusions; therefore, not only is the exact amount and nature of the NDC likely to be important, but also its distribution in the crystal or coating, and the domain or inclusion size of the NDC (*18, 42*). For example, Fig. 3 compares the Raman signatures of the growth and substrate surfaces of a free-standing diamond coating. This coating was prepared on molybdenum with the use of a tantalum hot-wire reactor and 1% CH$_4$ in H$_2$ vapor and was recovered by dissolving the molybdenum with nitric acid. The film ($\sim$18 μm thick) was placed onto a silicon wafer and examined with microfocus Raman spectroscopy with the focus adjusted to give the strongest possible signal at 520 cm^{-1} from the silicon underneath the sample in order to ensure that the entire thickness of the film was being probed. Clearly, the "quality" of this coating depends on whether the light is incident on the growth or the substrate surface of the diamond film.

Fig. 1. Raman spectrum of a polycrystalline CVD diamond thin film taken using an excitation wavelength of 514 nm. Diamond prepared using a hot-filament method (tantalum wire activation at a wire temperature of $\sim$2000°C) and a 1% CH$_4$ in H$_2$ mixture. In addition to the diamond peak at 1332 cm^{-1}, a broad ill-defined maximum is seen at $\sim$1550 cm^{-1}.

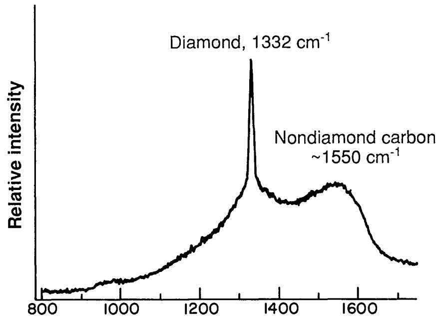
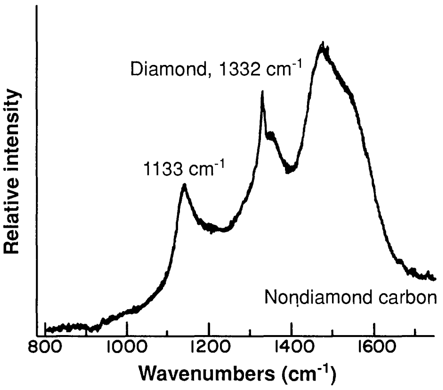


Fig. 2. Raman spectrum of a nanocrystalline diamond thin film. Sample prepared at a substrate temperature of 650°C using 1% CH$_4$ in H$_2$. Crystallite size estimated from broadening of (111) x-ray diffraction line (Scherrer formula) after correction for instrumental broadening of 19 nm. Note the appearance of a broad strong peak at 1133 cm^{-1}. Peak position does not move or change shape on change of excitation wavelength from 514 to 488 nm.



Development of Morphology in Diamond Growth

The most stable growth planes of diamond are the octahedral (111) faces, followed by the cube (100) faces and the (110) faces (*43*), on the basis of a simple Wulff criterion (*44*) for crystal habit. During growth of polycrystalline diamond films under conditions close to equilibrium, triangular (111) faces are the expected growth morphology because the ⟨111⟩ directions are the slowest growth directions and all other planes grow to extinction. As the deposition process moves away from equilibrium (100) cube faces appear and initially result in a mixture of growth faces and a generally more complex growth morphology. Further movement away from equilibrium can lead to a dominant (100) cube morphology in the later stages of growth evolution, unless the (110) faces become energetically favorable. At present there is little or no understanding of steady-state surface structures during growth, and these can be expected to depend on deposition conditions. Thus the growth morphology and its growth evolution reflect the growth-controlling variables such as temperature, supersaturation, impurities, defects, and so forth. If we understood all of these preparation-morphology relations, which we do not, then it would be possible to design diamond morphologies for specific applications or, conversely, understand the growth history of a film by examining its internal morphological evolution.

In several studies, the top surface morphology of diamond films, typically 2 to 20 μm thick and viewed with a scanning electron microscope, has been related to the various deposition parameters including substrate temperature, gas composition, and gas pressure (*20, 21, 45*). Although growth morphology is generally similar for the different deposition techniques, there have been some notable differences. Additional studies have included TEM of diamond film defects and second phase, NDC material and x-ray and electron diffraction for preferentially oriented growth patterns.

For deposition from hydrocarbon-H_2 gas mixtures there is generally a narrow range of conditions where essentially single-phase diamond films are deposited at the highest rates (*46*). If the temperature is too low ($<800°C$), a significant amount of amorphous carbon is co-deposited, whereas if the temperature is too high ($>1100°C$), nondiamond components, including microcrystalline graphite, are found (*47*). In both cases, the morphology is fine grained with no distinguishable faceting. Within the optimum temperature range, the film is highly faceted (typical facet sizes are 0.3 to 3 μm), but there is no consistent variation in form with temperature. With increasing temperature, changes of predominant faces from both (100) to (111) (*48, 49*) and (111) to (100) (*50, 51*) have been reported. With increasing methane concentration (from 0.2 to 2% CH_4 in H_2), (111) facets shift to predominantly (100) facets (*20, 48*). Over this same methane concentration range, Zhu *et al.* (*52*) have shown that the density of stacking faults and twins, which lie on the {111} planes in the diamond films, and dislocations increase and that their dimensions become smaller. Other electron microscopy studies (*33, 53, 54*) have observed these same types of defects, as well as multiply twinned five-fold symmetry features that are related to rare pentagonal crystals. Although (110) planes are the third most energetically favored, based on the simple Wulff criterion (*44*), in several cases (*17, 21, 33*) preferentially oriented films with the ⟨110⟩ direction perpendicular to the substrate surface have been prepared.

At lower methane concentrations the C supersaturation is lower (that is, the system is close to equilibrium) and the morphology is predominantly (111), as would be expected, and the defect concentration is also lower. These results imply that although the homoepitaxial growth on (111) diamond surfaces may be best at these optimum growth conditions, (100) homoepitaxy might be best sought at some nonoptimum deposition conditions where (100) cube faces are preferred. Recently Fujimori *et al.* (*55*) have shown that 6% CH_4 yielded the smoothest (100) homoepitaxial films with the lowest defect density. Their choice of conditions was based in part on the results of Sato *et al.* (*45*), who have shown that at 3 and 4% CH_4 highly oriented ⟨100⟩ needles of diamond, about 0.5 to 3.0 μm in diameter and about 30 μm long can be prepared. As seen in Fig. 4A, the as-deposited film has a smooth top surface consisting of (100) faces. When the nondiamond material surrounding these columns is preferentially etched by an air plasma, a pyramidal top surface is revealed (Fig. 4B). A cross section shows that the film is fine grained in the part representing the early stages of growth, but through preferential selection during the growth process, nearly parallel, needle-shaped single-crystal columns developed (Fig. 4C). The narrow Raman 1332 cm^{-1} peak (FWHM = 1.8 to 1.9 cm^{-1}), comparable to that for good-quality single crystals of natural diamond, suggests that these columns contain a low defect density, in that an interruption of translational symmetry has been shown to broaden Raman scattering in crystals (*56*).

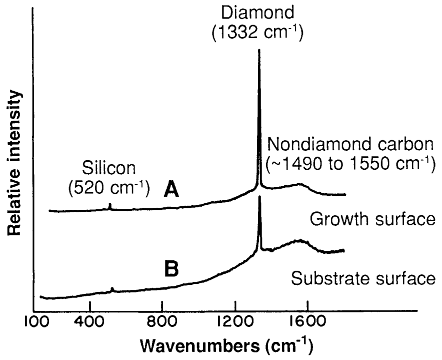


Fig. 3. Raman spectra of a free-standing CVD diamond thin film taken on growth and original substrate surfaces. The apparent quality of the film depends upon whether the laser beam is incident to the growth (**A**) or substrate (**B**) surface. Film prepared using tantalum wire activation of CH_4 in H_2 mixture on a Mo substrate and removed by dissolution of the Mo in acid. The film was supported on a Si wafer and Raman scattering from the underlying Si at 520 cm^{-1} is clearly seen in both spectra the presence of this peak demonstrates that the entire thickness of the film is sampled in both cases.

Caution is urged in interpreting the above growth relations as well as those implied by earlier work, however. It appears that the relative growth rates of the three most energetically favored crystal planes are similar and that small changes in preparation conditions can change the relative rates and the final growth morphology. One of the few pieces of reliable data on relative growth rates is for diamond on Cu (*50*) (Fig. 5). These data clearly show that even small shifts in the temperature dependence of growth rate for the (111) and (100) planes can have a large effect on the final morphology. Also, Geis (*57*) recently reported that the deposition rate of homoepitaxial diamond on the three primary faces changes greatly with the addition of a B dopant. Other additions, such as O_2 have been found to be effective in expanding the range of diamond formation and, therefore, the growth morphology. These results indicate that there may be more than one set of optimum deposition conditions and that one must be careful to define specifically what is being optimized. In the low-temperature regime deposition rate is much lower (*58*) (and nonoptimum); however, the thin-film quality, as determined by Raman spectroscopy appears to be improved as compared to the high-temperature optimum film described above. In that the experimental conditions in many of the studies that have been compared are similar but not the same, especially at low substrate temperatures (where, for example, calibration errors, impurities, differences in gas phase excitation and so forth can have large effects, variations in morphology and quality should be expected and are hard to predict. One of the challenges ahead is to understand the effects of process variables on morphology and then to use this knowledge in preparing films ranging from low defect homoepitaxial films to controlled morphology polycrystalline films.

Nucleation of Diamond on Nondiamond Surfaces

One of the many issues that have yet to be resolved is how diamond is nucleated on the surface of a nondiamond substrate. Although there have been reports that diamond can be nucleated homogeneously in the gas phase (*5, 59, 60*), in almost all of the experiments to date, diamond was produced instead by nucleation on a solid surface, including on graphite (*61*). In many cases, some kind of surface pretreatment was used to enhance nucleation density

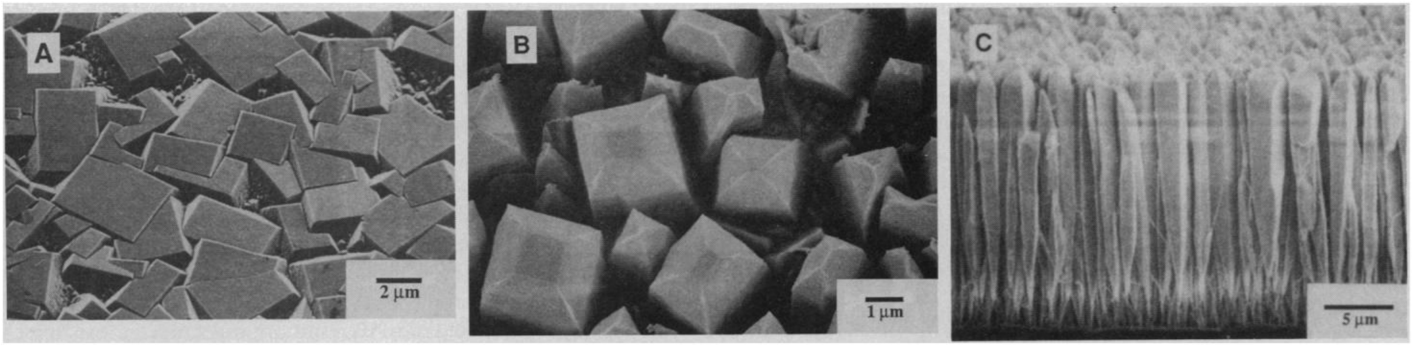


Fig. 4. Photomicrographs of CVD diamond thin film structure illustrating growth morphology in polycrystalline coatings. (**A**) Top surface of as grown CVD film showing dominant (100) morphology at high relative methane concentrations. (**B**) Surface of dominant (100) morphology after etching in oxygen-containing plasma. (**C**) Cross section of the film seen in (B) showing both the columnar morphology and the increasing size and perfection of the grains with continued growth. [Used through courtesy of Y. Sato (*69*)]

to produce a continuous coating or film at an early stage of growth. In the original work by Setaka and co-workers, this pretreatment consisted of polishing the substrate surface with diamond powder before deposition (*62*). Other researchers have preferred ultrasonification of the surface in diamond powder suspensions before deposition (*63*). Alternatively a coating of diamondlike C on the substrate has been reported to enhance nucleation density and, similarly, produce a continuous thin film of diamond (*64*).

Polishing with diamond powder is known to produce high nucleation density ($\sim 10^8$ sites/cm^2) on substrate surfaces as varied as Si, Mo, and cemented WC (tungsten carbide). Two fundamentally different suggestions have been made to account for this observation. The first is that diamond, diamond-like carbon, or other carbonaceous residues from the polishing or abrading powder left adherent to, or embedded in, the polished surface supply the nucleation sites for subsequent diamond growth (*65*). The second is that because of the type and amount of damage done to the substrate surface, highly disordered surface material or microscopic crater-edge sites in the polished surface create, in effect, high-energy sites that are preferred nucleation sites for diamond (*66*). Diamond can be nucleated on foreign surfaces, notably elements that form refractory carbides (Si, Mo, Ta, W), without such polishing treatments. However without a diamond prepolish, nucleation density is normally low and a significant induction period may be required before the first evidence of diamond formation can be obtained (*67*). The largest number of experiments to date have used single-crystal Si wafers as substrates, and the mechanism of heterogeneous nucleation of diamond on Si remains under investigation. Badzian (*68*) suggested that nucleation on Si is preceded by the formation of silicon carbide (SiC), and that nucleation occurs on the surface of the carbide. This suggestion is supported by experimental data from both high-resolution TEM (*54*) (HRTEM) and spectroscopic ellipsometry (*69*) which show that in the microwave plasma CVD of diamond, the Si surface is indeed transformed to SiC under the conditions of diamond growth, and that lattice registry does occur between the SiC and diamond in at least some experiments. However, a SiC interlayer was not found in all of the samples examined with HRTEM (*54*), and the spectroscopic ellipsometric work shows that the carbide interlayer grows to its equilibrium thickness within $\sim$2 to 5 min of plasma exposure. In some of the earlier work, it was shown that in the absence of a pretreatment, an induction period of $\sim$10 hours was necessary before the first evidence of diamond crystallization could be obtained (*67*). Clearly if SiC formation is both a necessary and sufficient condition for the nucleation of diamond, then some rationalization for the large difference in time between carbide formation and the initiation of diamond growth is needed. In addition, other TEM studies of single diamond particles have suggested that the actual diamond nucleation site is devoid of an interfacial layer, whereas at other points remote from the initial site of nucleation, an interfacial layer is observed (*70*). Kawarada *et al.* (*70*) suggested that diamond is first nucleated at a site that ". . . satisfies a heterogeneous nucleation condition" and that interlayer formation occurs at substrate sites exposed to the plasma. Subsequent growth of the particle occurs over this interlayer until interference with neighboring particles form a continuous coating. Hence, although SiC interlayer formation may be an important contributing factor, it is not in itself a sufficient rationalization of all of the data.

To complicate matters further, the nature of the polishing agent used, as well as its particle size, is important in determining the efficacy of the pretreatment (*65*). In a particularly provocative set of experiments, both diamond and cubic boron nitride (c-BN; Borazon, General Electric, Worthington, Ohio) were used to polish a Si wafer. When the diamond polish was used first, followed by polishing with sub-micron c-BN, the nucleation density of diamond was reduced to well below that obtained with the diamond polish only. Separate experiments showed that diamond can nucleate on cubic BN, including the powder used in the polishing, to the extent that the c-BN particles quickly become uniformly covered with diamond. If indeed residual detritus from polishing is the reason for the efficacy of diamond prepolish, then some rationalization for the difference in efficacy of diamond and c-BN as polishing agents is needed, at least on Si. Of course, these mechanisms are not mutually exclusive and both may contribute to nucleation; the dominant mechanism may be determined by the specific parameters used in a given experiment.

Understanding and controlling the heteroepitaxial growth of diamond have been and continue to be major research goals, and although some progress has been made (*71*) the characterization problems noted above continue to haunt the effort and considerable uncertainties remain (*72*). One of the difficulties attendant to this effort is the small number of materials with suitable crystal structures and lattice constants. Among the few isostructural materials with sufficiently similar lattice constants (less than $\sim$5% mismatch) are some transition metals and metal alloys (notably Ni, Cu and austenitic Fe) and c-BN. Much effort has been expended in efforts to achieve diamond growth on many of the transition metals, let alone heteroepitaxial growth, without success. The reasons for the difficulty are not understood, however, they may be related to a high solubility or mobility for C on or in some metals (for example, Ni and Fe). Diamond has been successfully grown on Cu, in which C is relatively insoluble (*73*) but not yet by epitaxy. As discussed above, nucleation on cubic BN is easily achieved, and the uniform coverage of BN particles by diamond in these experiments suggests, circum-

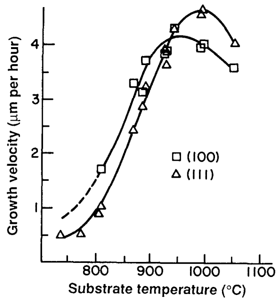


Fig. 5. Growth rate curves for the (111) and (100) habit planes of CVD diamond. Triangles represent (111) habit planes and squares (100). Measurements taken from photomicrographs of diamond single crystals grown on copper substrates. [Used through courtesy of B. Spitsyn (*74*)]

stantially, that the growth was heteroepitaxial. However, lattice registry between c-BN and diamond, has not yet been demonstrated. Even if heteroepitaxy of diamond on c-BN is shown to occur, a significant technological problem remains: the vapor phase growth of c-BN has not been achieved, and the largest synthetic c-BN crystals grown by high-pressure techniques are only ~1 mm in size. One possible solution is growth of a thin, passivating layer of c-BN epitaxially on other lattice-matched substrates, for example, Ni, with the use of techniques for the single-crystal growth of compound semiconductors.

Diamond Versus Graphite

Why should well-crystallized diamond, instead of graphite or some other graphitic carbon, be obtained in any of these experiments? The technological importance of the issue lies in the need to improve crystal quality, growth rate, and reduce the temperatures needed at the growth surface. Many of the applications (principally electronic and optoelectronic) envisioned for this technology rest on the growth of defect-free, single-crystal material. Much of the skepticism faced by the early workers in the field stems from the well-recognized thermodynamic instability of diamond relative to graphite, and numerous ideas and mechanisms have been suggested to account for metastable diamond formation. Many of these ideas assign a role to atomic H and particulary its presence in the gas phase at partial pressures and temperatures where it is not a stable species, that is, at "superequilibrium" partial pressures. Two different approaches have been taken: early Soviet work (*50, 74*) emphasized the relative kinetics of graphite and diamond deposition; more recent work has been on the role of surfaces and atomic H in the stabilization of diamond surfaces (*17, 75*). The original suggestion made by Soviet researchers was that, in effect, the "grow and etch" cycles used in the earlier work had been combined in a single process through the presence of atomic H (*76*). The relative gasification rates of diamond and graphite are known to be different by orders of magnitude. Graphitic C reacts at high rates with atomic H (77) and this effect is commonly referred to as an "enhanced" etching of graphite relative to diamond. From this point of view, diamond growth is possible because the nucleation and growth of graphitic material is suppressed; hence, the growth of diamond is kinetically stable relative to the growth of graphite. The relatively high rate of graphite gasification by atomic H has been incorporated into a thermochemical model for the CVD diamond process with the result that a region of parameter space (temperature, pressure, and gas composition), consistent with many of the published experiments, is predicted in which the growth of diamond is stable relative to graphite or other graphitic C phases (*78*). In the specific case where diamond growth on foreign surfaces occurs as a result of a preexistent nucleating surface (for example, diamond detritus from a diamond prepolish or a specific carbide structure surface), then this model of the effect of H appears to be consistent with most of the experimental data. This quantitative model (*78*) fails to predict stable diamond growth at atmospheric pressure or low temperatures (≤600°C); however, refinement of the calculation to include, for example, the effects of O_2 or oxygenated compounds as possible gas phase species may account for the results of these experiments.

The second approach emphasizes the role of surfaces in the CVD process, and in some formulations, again assigns a special role to atomic H (*79–81*). These approaches argue that the bulk instability of diamond relative to graphite is effectively irrelevant as (i) it is small [~0.5 kcal/mol at 298 K (*82*)] and, (ii) growth occurs at surfaces, not in the bulk. Atomic H, instead of acting as a means of etching graphite, is thought to stabilize the surface of diamond (*17*) and to prevent reconstruction of the diamond surface (*80, 83*); growth of diamond occurs not necessarily because of any specific kinetic competition between graphitic material and diamond but because, under the conditions of growth, the diamond surface is thermodynamically stable relative to the surfaces of graphite. In support of this point of view, thermochemical estimates of the enthalpies of formation for the principal surfaces of diamond and graphite, with and without hydrogenation, indicate that any of the hydrogenated surfaces of diamond have lower enthalpies of formation (at 298 K) than any of the hydrogenated surfaces of graphite (*17*). Without the stabilizing influence of surface hydrogenation, reconstruction and graphitization of previously grown diamond would be expected. The enhanced etching of graphite is viewed as a reflection, in part, of the relative instability of graphitic surfaces to gasification. Another suggestion again emphasizes surface stabilization as a rationalization for diamond formation, but appeals instead to the role of the interface between the substrate and the growth layer (*84*). There are numerous examples where solid phases are deposited in metastable crystalline forms because of a strong epitaxial relation between the substrate or bulk and the surface of the material. The continued growth of diamond, once nucleated, is thus thought to reflect, at least in part, the influence of the bulk structure for inhibiting reconstruction and graphitization of the surface. This suggestion is a tempting rationalization of some of the pioneering experiments where growth on diamond seed crystals was reported and where little or no atomic H was likely to be present (*85*).

All of these formulations suffer from being inconsistent with at least some experimental results. Although the kinetic arguments appear to rationalize the preferential growth of diamond to graphite, in their simplest formulation they do not explain well why crystallized diamond should grow preferentially to other relatively unreactive forms of carbon, for example, the diamond-like carbons or lonsdaleite, particularly at low temperatures. In addition, gasification of graphite by atomic H can vary over as wide a range as three to four orders of magnitude; indeed some unreactive forms can be produced by low-temperature exposure to atomic H (*86*). Similarly, the stabilization of diamond surfaces by atomic H appears to rationalize much of the data satisfactorily except that there are now experiments at low substrate temperatures (*17, 87*) and in combustion flames at low pressure and oxygen to acetylene ratios greater than unity (*88*) where no form of solid carbon is thermodynamically stable and some appeal to kinetics must be made to account for the deposition. Surface stabilization by the substrate also becomes problematic as, although the short-range growth of diamond on diamond might well be explained this way, the eventual nucleation and growth of graphite would be expected. This was, indeed, the result obtained in the pioneering simple CVD experiments, however, to date there is no evidence that the externally assisted methods are limited in the amount or quality of the diamond that can be grown. Consequently most researchers appeal to some combination of the above arguments in their attempt to understand the process (*89*).

The reaction mechanism for the growth of diamond from hydrocarbon vapors is also of intense interest, but, like much reaction chemistry, a great deal remains unknown. Many of the suggestions focus on one or two principal species or a specific reaction sequence. The list of potentially important species is extensive and includes ions, such as CH_3^+, (*90*) or positively charged surfaces (*91*); numerous hydrocarbon radicals ranging from $CH_3\cdot$ (*92*) to free atomic carbon (*93*); and stable molecules, such as C_2H_2 (*94, 95*). The simplest reaction system known to produce the stable growth of well-crystallized diamond is one of the earliest: the hot-wire or hot-filament reactor in which a refractory metal, commonly Ta or W, is electrically heated to temperatures of ~2000°C. A suitably prepared substrate placed within a few millimeters of the wire and heated to between ~600°C and 1000°C will become coated with diamond at growth rates of 0.1 to ~2 μm per hour, most typically at ~0.5 to 1.0 μm per hour. Various gases can be used, but a simple system with methane in H_2 at ~0.1 to 2% by volume has been modeled thermochemically and by measurements of the gas phase (*96, 97*) during reaction. The principal species predicted and detected included C_2H_2, $CH_3\cdot$, C_2H_4, and CH_4. A simple first-order model suggests that C_2H_2 (and possibly $CH_3\cdot$) is the principal additive species (*127*); this result is consistent with the mechanism suggested by Frenklach and Spear (*94*). However, this model does not include the possible effects of Soret (or thermally induced) diffusion (*98*), believed important in the modeling of many CVD processes (*99*), and near surface gas phase reactions. In a recent study, when mixtures of C^{13} and C^{12} hydrocarbons were introduced to a hot-filament reactor, the proportions of C^{13} and C^{12} in the deposited diamond were more consistent with a methane-based growth mechanism ($CH_3\cdot$ was the specific additive species suggested) than with an acetylene-based mechanism (*100*). More recent data from the same laboratory, could be best rationalized by a mechanism involving both $CH_3\cdot$ and C_2H_2 as additive species, but with $CH_3\cdot$ dominant (*101*). Indeed one of the roles suggested for atomic H has been the formation or maintenance of $CH_3\cdot$ close to the growth surface so as to eliminate the need for diffusional transport over long distances (*102*). Atomic H could not be detected in these experiments, but its presence can clearly be inferred from the presence of $CH_3\cdot$. In separate experiments, the relative amounts of atomic H, measured with resonance enhanced multi-photon ionization (*103*) decreased with increasing CH_4 content in the feed gas (*104*). This is as might be expected in that the primary channel for the gas phase recombination of atomic H is probably through reactions with carbonaceous species (*105*). In a recent experiment in which deuterium was substituted for H, it was shown that the rate determining step for diamond nucleation was likely the breaking of C–H bonds (*106*). Measurements made by emission spectroscopy show that highly reactive species such as CH, C_2, and electronically excited atomic H are present in the microwave plasmas used for the synthesis of diamond (*107*). Such species may be quenched to the more stable species seen in the hot-wire techniques as they diffuse through the static surface boundary layer believed to develop at commonly used pressures (*108*). However, given the large number of possible and detected species, it appears unlikely that a single reaction channel or reactive species is the key in all of the different experiments. Rather the mechanism of diamond formation may involve a complex set of surface or near surface reactions, in which case much more research will be needed.

Although twinning of the crystals across the (111) planes is quite common, leading to icosahedral crystal habits even in well-crystallized deposits, the hexagonal sp^3 polymorph, lonsdaleite (*109*), has not been reported with the use of any of the methods known to produce well-crystallized diamond. These methods produce a wide variety of C structures, including noncrystalline carbons, depending upon the conditions used, and it seems remarkable that some parameter space leading to well-crystallized lonsdaleite (or a mixture of lonsdaleite and diamond) has yet to be reported. This is even more curious in that the analogous hexagonal and cubic polymorphs of SiC are readily obtained by vapor-phase deposition. If the vapor-phase deposition of diamond is by some specific reaction mechanism, for example, as in the acetylene hypothesis (*94, 95*), then the absence of lonsdaleite in these deposits might result from the nature of the deposition process itself, and any proposed reaction sequence would have to be consistent with the formation of diamond, but not lonsdaleite. Alternatively, it has frequently been observed that the diamond structure consists essentially of six-membered carbon rings in a "chair" conformation, by analogy to cyclohexane, and has the C-atom stacking sequence ABCABCABC . . . along the $\langle 111 \rangle$ direction. This direction corresponds to the *c*-axis direction in lonsdaleite, which has, by contrast, the stacking sequence ABABAB . . . and can be thought of as a twinned modification of the diamond structure with the twin planes at every other C lattice plane along the $\langle 111 \rangle$ direction. This structure requires that the C atoms lie in a polycyclic "boat" conformation in any low index or principal plane parallel to the *c*-axis ($\langle 111 \rangle$ direction in diamond), by analogy to cyclohexane. The "boat" conformation is known to be less stable than the "chair" in cyclohexane, by about ~6.9 kcal/mol (*110*), because of the nonbonding steric repulsion between two of the axial H atoms (the "flagpole" hydrogens), and the perfect eclipsing of sp^3 bonds along two of C–C bonds needed to form the six-membered ring (*111*). In the case of lonsdaleite, nonbonding steric repulsions are not present in the bulk; however, the eclipsing of sp^3 orbitals on neighboring C atoms would, if anything, be more destabilizing than in cyclohexane, where larger bond angles can be tolerated. Consequently lonsdaleite might be expected to be less stable than either diamond or graphite, and the failure to observe its formation might be argued as logical and independent of mechanism, provided the deposition process occurs under conditions close to equilibrium.

Conclusion

Obviously many more experiments and much more data will be needed to resolve most of these issues. As progress continues during the next few years and some issues approach resolution, a fundamental question of importance to both science and technology can be addressed. This is whether CVD of diamond is simply a peculiarity of C chemistry and unlikely to lead to the successful synthesis of other metastable phases. Alternatively there may be general principles involved, which if learned and mastered, could lead to the successful synthesis of numerous metastable, but well-crystallized phases. Most important and most analogous to diamond is c-BN. To date numerous efforts to produce well-crystallized single phase c-BN by a similar method have been frustrating, although some success has been reported from Japan (*112*). In addition to the synthesis of other phases, the answer to this question may determine which of many possible composite structures and superlattices might be obtained. Depending on how this issue is resolved, new crystal chemistries may be developed, not previously synthesized or observed in nature, with new sets of properties heretofore not believed possible. Although the level of research activity in the field has grown rapidly during the past half decade, much more work will be needed before the question can be answered with confidence and the potential impact of CVD of diamond on the materials science field accurately assessed. Based on both past performance and current levels of investment and activity, it is reasonable to expect that many critical experiments and future progress will come from

Japan. Hence a continued healthy and collaborative relation with Japanese researchers will continue to be of importance to progress in the field both within the United States and worldwide.

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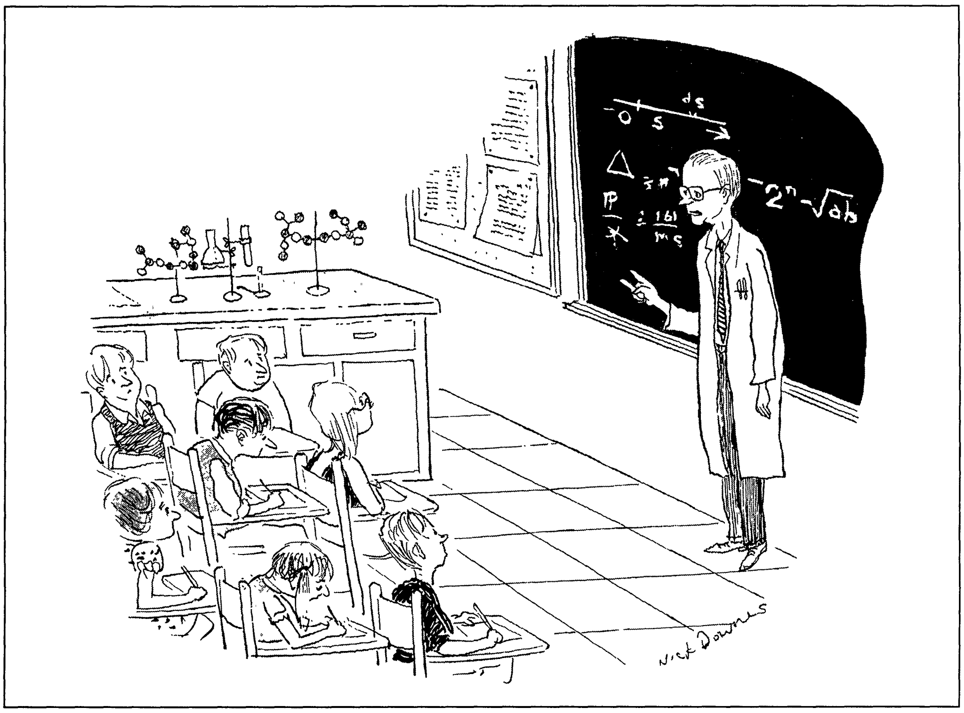

" Conversely, time slows down when you're* not *having fun."