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" Current issues and problems in the chemical vapor deposition of diamond "

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" Emerging technology of diamond thin films "

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" From diamond-like carbon to diamond coatings "

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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.

D IAMOND 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 non-diamond 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-

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 (sp³ hybridization) as well as trigonally bound C (sp² 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 ~1332 cm⁻¹ but also a broad maximum variously centered anywhere from ~1500 cm⁻¹ to ~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 ~1550 cm⁻¹ has been commonly attributed to the presence of graphitic or sp² hybridized C (32–34). This is not a universally accepted assignment, and Wild et al. (18) have argued that the ~1550-cm⁻¹ peak arises from a highly disordered C phase, possibly diamond-like C, consisting of both sp³ and sp² hybridized C that need not be graphitic in nature. Many nanocrystalline (that is, crystallite sizes of ~1 to 100 nm) diamond samples show additional features including a broad peak centered at ~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 ~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, ~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, m3m, 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 ~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 ~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

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 ~2000°C) and a 1% CH₄ in H₂ mixture. In addition to the diamond peak at 1332 cm⁻¹, a broad ill-defined maximum is seen at ~1550 cm⁻¹.
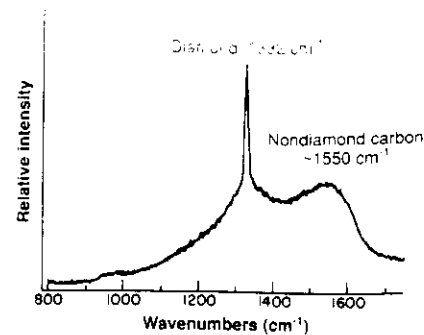
Fig. 2. Raman spectrum of a nanocrystalline diamond thin film. Sample prepared at a substrate temperature of 650°C using 1% CH₄ in H₂. Crystallite size estimated from broadening of (111) x-ray diffraction line (Scherrer formula) after correction for instrumental broadening of 19 nm. Note the appearance 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.
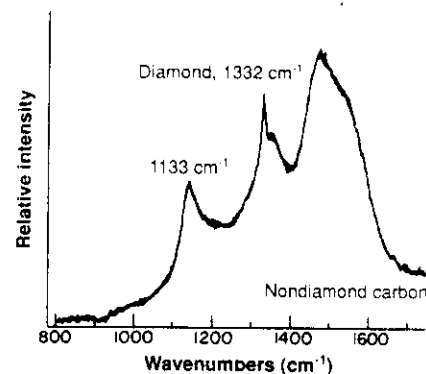
creates a potentially misleading situation. The most frequent problem is that the sampling depth of the incident light beam will vary with the size and transparency of any nondiamond inclusions; therefore, not only is the exact amount and nature of the NDC likely to be important, but also its distribution 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% CH₄ in H₂ vapor and was recovered by dissolving the molybdenum with nitric acid. The film (~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.

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).

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. 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.
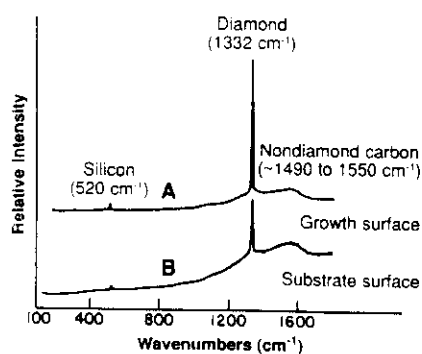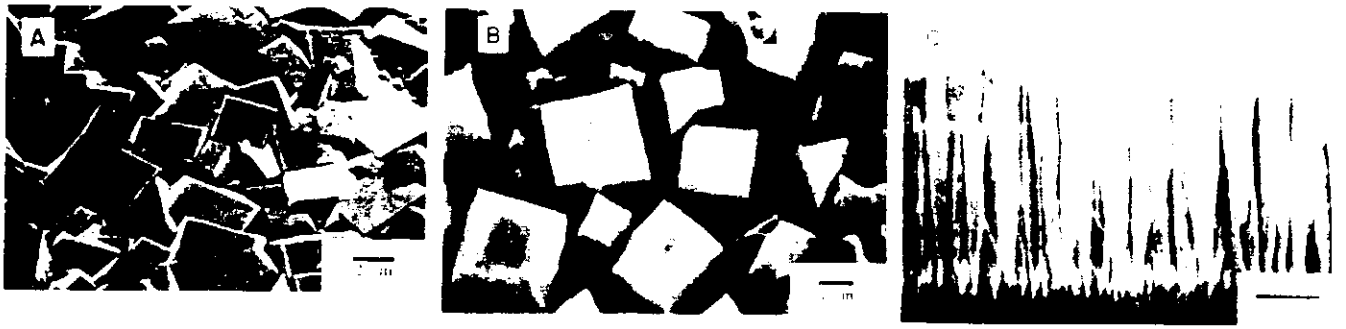
Fig. 4. Photomicrographs of CVD diamond thin film structure illustrating growth morphology in polycrystalline coatings. (**A**) Top surface of as grown CVD film showing dominant (100) morphology at high relative methane concentrations. (**B**) Surface of dominant (100) morphology after etching in oxygen-containing 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 ~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 ~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 ~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)]
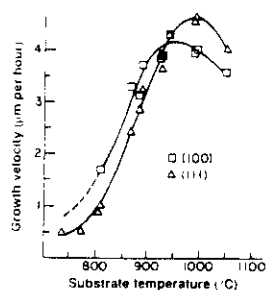
standially, that the growth was heteroepitaxial. However, lattice registry between c-BN and diamond, has not yet been demonstrated. Even if heteroepitaxy of diamond on c-BN is shown to occur, a significant technological problem remains: the vapor phase growth of c-BN has not been achieved, and the largest 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 O₂ 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 hydro-carbon 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· (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·, C_2H_4, and CH_4. A simple first-order model suggests that C_2H_2 (and possibly CH_3·) 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· 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· and C_2H_2 as additive species, but with CH_3· dominant (101). Indeed one of the roles suggested for atomic H has been the formation or maintenance of CH_3· 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·. 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 (111) 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 (111) 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 ((111) 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

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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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Emerging Technology of

Diamond

Thin

Films

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Hardness and resistance to wear are often distinct advantages for materials used in industry, and the archetypal substance displaying these properties is diamond.

But diamonds, at least in the size that many industrial uses demand, often are prohibitively costly—or totally unavailable. Now, however, advances in materials science are showing the way to put a coating of diamond on many other, less exotic materials, thereby imparting to them the beneficial properties—electronic and optical properties as well as hardness—that only diamond has.

The beauty and hardness of diamond—and its rarity, especially in sizes larger than a centimeter—have made it an object of fascination for nearly as long as recorded history. Natural industrial diamond is a by-product of the exploration for gemstones, and, since the early part of this century, its supply has been stagnant or uncertain, and far too low to match the growing demand for this material from the polishing, cutting, and drilling industries.

This shortage has fueled efforts to produce diamond synthetically. At first, the idea was to convert graphite directly into diamond at high temperature and pressure, conditions under which diamond is the thermodynamically stable form of carbon. During the 1940s, experimental attempts were based on the detailed knowledge of the carbon phase diagram developed by O. I. Leipunskii, R. Liljeblad, Robert Berman, Sir Francis E. Simon, and others. This extremely active and fruitful period of diamond research culminated in the successful synthesis of artificial diamonds from graphite by groups at Allemanna Svenska Elektriska A.B. (ASEA) in Sweden in 1953 and at General Electric in the U.S. in 1954. The more famous General Electric work was reported in 1955 in *Nature*. This manufacturing process involves both high temperature and high pressure, and usually—to permit crystal growth at reasonable rates, pressures, and temperatures—a metal such as iron, nickel, cobalt, manganese, chromium, or tantalum to serve as a solvent and catalyst.

This high-pressure, high-temperature method of making diamond yielded not only important industrial abrasives, but also a much more detailed knowledge of the carbon phase diagram, which, in turn, has advanced carbon research in general.

Another important early high-pressure method to synthesize diamond is the so-called shock wave technique. Diamond-containing material was prepared first by means of shock waves by Paul S. DeCarli of Stanford Research Institute and John C. Jamieson from the University of Chicago in 1961. This technique, industrialized by Du Pont, utilizes the high pressures in shock waves of explosions to directly convert crystalline graphite into diamond. The particles are subsequently separated from the starting material by sedimentation.
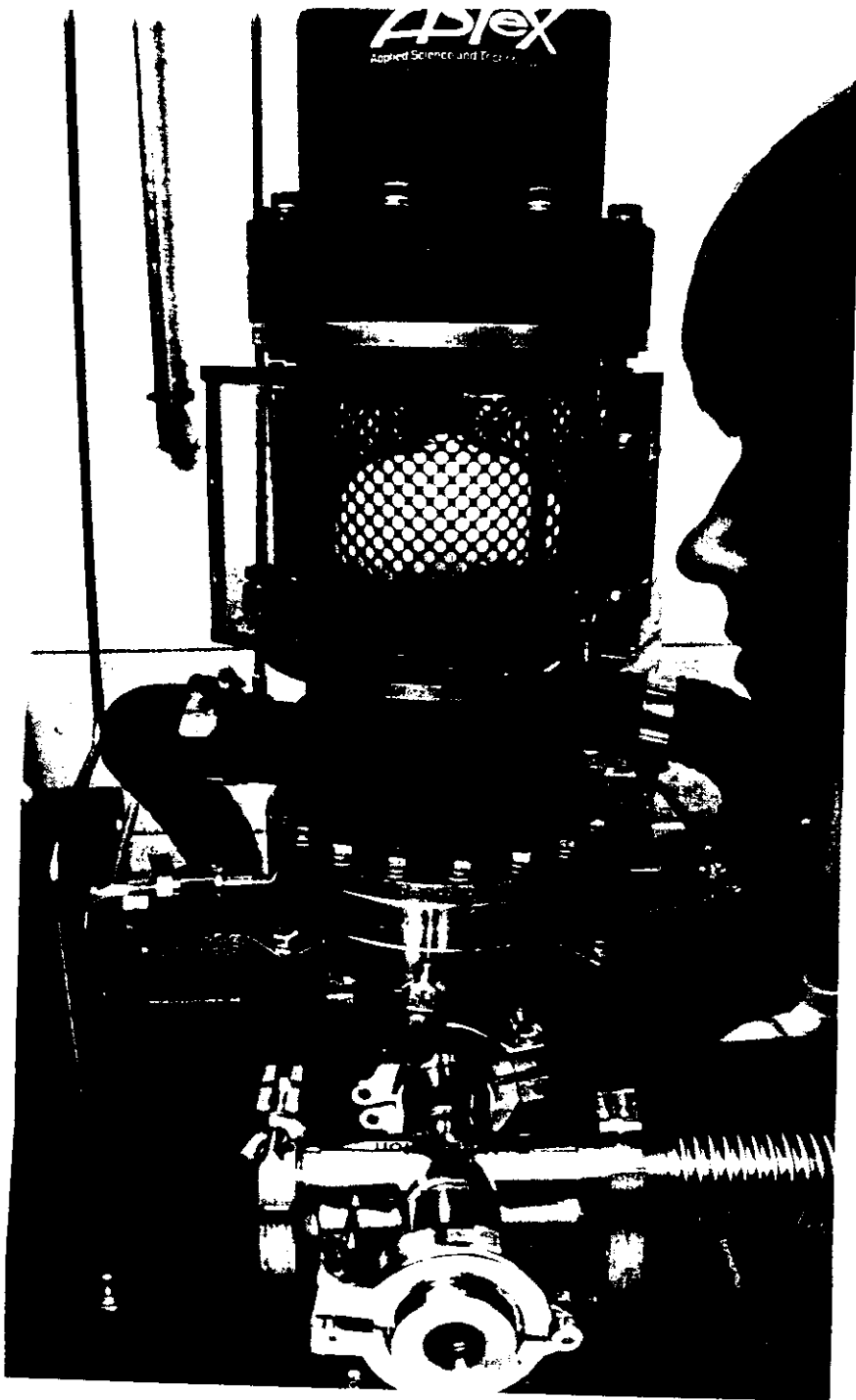
However, the company has never manufactured these diamonds in significant quantities. In 1985, Sumitomo Electric of Japan produced crystals of up to 2 carats (0.4 gram), as large as about 8 mm in their maximum dimension. De Beers of South Africa has made even larger single crystals—up to 17 mm. Because they contain small amounts of nitrogen, these synthetic gems often show an attractive deep yellow color.

The jewelry industry is already alert to these synthetic stones. In the winter 1986 issue of Gems & Gemology, James E. Shigley and others from the Gemological Institute of America discuss how to use ultraviolet fluorescence, optical and infrared absorption, color, size, and optical microscopy of the internal structure to distinguish Sumitomo diamonds from natural gems.

Sumitomo diamonds are not currently used for jewelry but, because of diamond's high thermal conductivity, find a market as heat sinks in the electronics industry. The synthetic stones, machined and laser-cut to about $3 \times 3 \times 1$ mm in size, are commercially available for less than $150 per piece.

Although high-pressure techniques provide sufficient amounts of diamond grit for abrasive operations and larger single crystals for heat sinks and a few other applications, they have their limitations. A press for commercial high-pressure diamond synthesis is a large, expensive device, and further scaleup is difficult. Impurity-free synthesis is possible, but expensive, and even the gem-quality stones produced by Sumitomo contain metal inclusions that diminish the electrical properties of the material. Finally, and most important for many technological applications, these crystals are too small for many uses.

These limitations could be overcome by large-area diamond coatings chemically bonded to inexpensive nondiamond surfaces to provide the unexcelled hardness and wear resistance of diamond at lower costs. Such coatings also would open up a much wider

Today, plants in many countries produce about 30 to 40 tons per year of synthetic diamond grit for abrasive use by one of these high-pressure methods. The product is often black, the result of the inclusion of graphite or metals and metal carbides from the solvent-catalyst. The high-pressure synthesis of diamond particles has proved to be economical and provides industry with a product of consistent quality in terms of chemistry, morphology, and other properties important for abrasive applications.

But not all synthetic diamonds are black grit and not all are used as abrasives. High-pressure, high-temperature technology also can produce large stones of gem quality. The first gem-quality synthetic diamonds were announced in 1970 by General Electric.

Single-crystal synthetic diamonds make excellent heat sinks for semiconductors

Power
supply

Semiconductor
laser
diode

Laser
light

Copper
heat
sink

Thermal conductivity, watts per cm °C

Natural
diamond (type 2a)

Silver

Copper

Temperature, °C

Large single-crystal synthetic diamonds (top right), mass produced by Sumitomo Electric Industries in Japan, are used as heat sinks for electronics components such as semiconductors. The rough, yellow stones about 8 mm in

diameter, are produced by high-temperature, high-pressure methods. Their yellow color is caused by trace amounts of nitrogen. When cut to size and polished or coated with a metal such as copper (to ensure good surface contact), they become the diamond heat sinks shown below them. In electronics applications, a heat-producing component, such as a semiconductor laser diode, is mounted directly on the diamond block, which, in turn, is mounted on a larger, but less efficient, copper heat sink, as shown in the diagram. Natural diamonds are also used as heat sinks, particularly nitrogen-free natural diamonds (called type 2a). At room temperature the thermal conductivity of a type 2a diamond is four times that of silver or copper, two other commonly used heat sink materials, although this advantage is less at higher temperatures. Sumitomo claims similar thermal conductivity of 20 watts per cm °C for their synthetic single-crystal diamond at room temperature.

range of applications that could take advantage of many of the other favorable properties of diamond. This potential prompted research that eventually led to a diamond thin film technology based on low-pressure deposition of diamond from the vapor phase onto a supporting material.

Diamond properties and applications

Although graphite, soot, and carbon black all have the same chemical composition as diamond—all are forms of carbon—x-ray diffraction shows they have very different crystal structures. Graphite consists of layers of condensed, six-membered aromatic rings of sp^2-hybridized carbon atoms. It absorbs visible light and appears grayish-black. In the plane parallel to the aromatic network, graphite is a good electrical conductor. The lengths of the aromatic bonds in the ring system are 1.415 Å. The spacing between the layers, however, is 3.354 Å because these atoms are held together by weaker van der Waals bonds. The layers

can slide over each other, making graphite a soft material, suitable as a lubricant. Soot and carbon black are microcrystalline forms of graphite.

Diamond has a different, yet clearly related, structure. Its crystallographic network consists exclusively of covalently bonded, aliphatic sp^3-hybridized carbon atoms arranged tetrahedrally with a uniform distance of 1.545 Å between atoms. The tetrahedrons are connected to one another at their tips to form the crystal lattice. Single-crystal, impurity-free diamond is transparent in wavelength from 220 to 2500 nm (extreme ultraviolet through the visible spectrum to the near infrared) and for wavelengths larger than 6000 nm (mid-infrared and beyond).

Diamond's structure accounts for many of its extreme properties of hardness, wear resistance, and low-friction coefficient that would make it useful as a coating on drills and cutting tools. Other potential applications that are being actively pursued in research laboratories in the U.S. and abroad include

Diamond's cubic lattice distinguishes it from other forms of carbon

Diamond   Graphite   Lonsdaleite
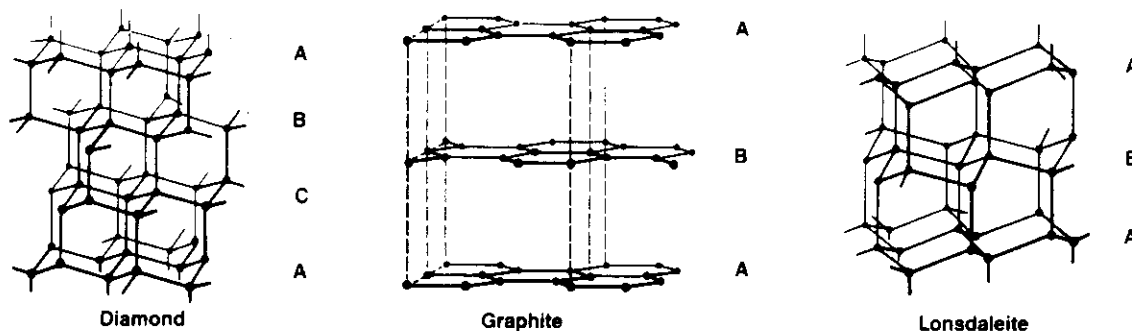
Diamond has a cubic lattice built up from sp^3-hybridized, tetrahedrally arranged carbon atoms. In diamond, the lattice layers follow the sequence ABCABC . . . so that every third layer is identical. The graphite lattice consists of layers of condensed, aromatic, sp^2-hybridized rings. The sequence of layers is ABAB . . . so that every other lattice plane is identical. Lonsdaleite is a hexagonal modification of the diamond lattice in which the layers follow an ABAB . . . scheme but the lattice consists of sp^3-hybridized carbon atoms. It has been found in meteorites and also synthesized by General Electric. Its properties are much the same as those of diamond, since they share the same symmetrical, covalent, sp^3 bonding character.

abrasion-resistant coatings for bearings, watch glasses, sunglasses, and even softer gemstones like zirconia. Diamond is also resistant to most chemicals. Only hot, carbide-forming metals or strongly oxidizing agents like molten sodium nitrate attack it. Thus, diamond has potential to be the premier containment material for chemical or nuclear reactors. Its chemical resistance also makes it attractive as a coating for more mundane articles, such as sweat resistant watch cases.

Diamonds are generally classified into four groups, based on their optical and electrical properties and the impurities they contain. Two of these, types 2a and 2b, are characterized by extremely low amounts of nitrogen incorporated in place of carbon into the diamond crystal lattice. Because they contain so little nitrogen, these diamonds are excellent thermal conductors. In fact, at room temperature they exhibit the highest thermal conductivity of any solid, more than four times that of copper or silver. Because these diamonds are also electrically insulating, they make ideal heat sinks for electronic devices. Sumitomo Electric claims similar thermal properties for its synthetic stones, which contain similarly low levels of substituted nitrogen.

Diamond coatings have the added advantage that they could be used to make substantially larger heat sinks for electronic devices. Instead of cooling individual electronic components, as is done now, com-

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Optical and electrical properties of diamonds divide them into types

Diamonds are classified according to their optical and electrical properties and their impurities into four types of single-crystal material and two types of polycrystalline natural diamond:

Type 1a. By far the most abundant type of natural diamonds, about 98% of the total, these diamonds contain up to 0.1% nitrogen in small aggregates or platelets, causing them to strongly absorb ultraviolet light. They are optically transparent at wavelengths >320 nm. The nitrogen also induces infrared absorption and limits thermal conductivity to 9 watts per cm K (at room temperature). Electrical resistivity is $> 10^{16}\Omega$ cm.

Type 1b. Typical for high-pressure synthesized diamonds but accounting for only 1% of natural diamonds, these stones contain up to 0.2% paramagnetic nitrogen incorporated in the lattice. Optical, thermal, and electrical properties are similar to type 1a diamonds.

Type 2a. This very rare type is practically free of nitrogen and transparent to ultraviolet above 225 nm. Thermal conductivity at room temperature is 26 watts per cm K. Electrical resistivity is in general similar to type 1a diamonds.

Type 2b. Extremely rare in nature and virtually nitrogen-free, these diamonds contain boron in small quantities, producing a bluish color, an electrical resistivity of only 10 to 1000 Ω cm, and p-type semiconductivity.

Carbonados and ballas. These naturally occurring, but exceedingly rare, polycrystalline diamonds together make up less than 0.2% of all natural diamonds. Carbonados, which contain graphite and other impurities, are much tougher than single-crystal diamonds and therefore are often used in drill crowns. Synthetic carbonado, a sintered diamond compact made from diamond grit, is an important material for cutting tools. Ballas are round, dense, randomly oriented polycrystalline diamonds. They do not cleave, are very impact resistant, and are used in tools. Polycrystalline diamond films are similar to carbonados and ballas in their properties.

Vapor deposition produces diamond at low pressure

Pressure, kbar
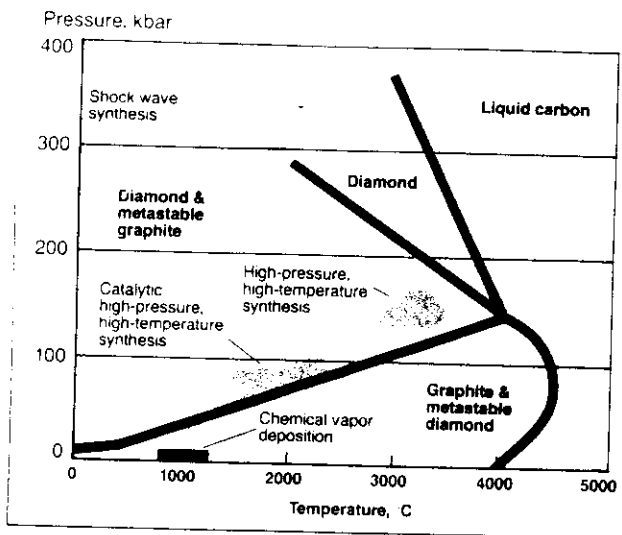
plete integrated circuits could be cooled by a diamond layer. Large diamond-coated heat sinks would be very much cheaper than similarly sized single-crystal diamond heat sinks and might solve the problem of dissipating generated heat, which already severely limits the operation of very-large-scale integrated circuits. The ability to make heat-dissipating diamond coatings would also add flexibility to the design of future ultralarge-scale integrated circuits.

Diamonds with a low nitrogen content are transparent down to 220 nm. If they have nitrogen impurities, they absorb at wavelengths lower than 320 nm. Low-nitrogen diamonds, therefore, are of interest for optical applications. Slabs of natural or larger sized synthetic stones are already used as small, highly transparent windows in harsh environments such as free-electron lasers, where diamond's ability to dissipate heat rapidly and resist thermal fracture is important. Diamond film coatings can add strength to lenses or be used to make large, ultrathin, free-standing windows. Because of its high refractive index, a diamond film could be applied as a filter or antireflection coating. Applications also can be envisioned in optical telecommunications, optical computing, and integrated optics.

Because diamond is compatible with biological tissue, it also can be used to coat prosthetic materials and biosensors. Sumitomo Electric describes the successful implantation of a diamond-coated hip joint in a rabbit in one of its numerous patent applications. This company is a key player in a strong field of Japanese companies whose diamond research activities have collectively generated more than 200 patent applications worldwide on the preparation and use of diamond coatings in the past five years.

The acoustic properties of diamond are also outstanding. Its high sound propagation velocity, high stiffness, and low weight provide the ultimate combi-

nation of properties for tweeter diaphragms in loudspeakers.

Natural 2b diamond crystals are generally blue, very pure (although they contain small amounts of boron in the diamond lattice), and very rare. The famous Hope diamond is an outstanding example of this class of diamonds. Boron is responsible for the blue color as well as the p-type semiconducting properties of 2b diamonds. Although most other types of diamonds show high resistivity, 10^{16} ohm-cm, the resistivity of 2b diamonds is only on the order of 10 to 1000 ohm-cm.

Boron-doped synthetic diamond layers would be a very useful material for electronics. So would phosphorus-doped synthetic diamond; with n-type semiconducting properties, it would expand the range of properties found in natural diamond. Both electrons and positively charged carriers are highly and almost equally mobile in diamond. These properties— along with high-temperature stability, low dielectric constant, and high electrical field breakdown voltage— make doped diamond an interesting material for high-frequency, high-power semiconducting devices.

The history of low-pressure diamond synthesis

Although diamond is the stable form of carbon at high pressure and the well-known General Electric process is a high-pressure one, this is not the only way that diamonds can be synthesized. If the activation energy between stable and metastable states is high enough, it serves as a barrier to interconversion, and metastable material can be formed under kinetically controlled conditions. In fact, numerous reactions in organic chemistry work this way, so it is not surprising that chemists began exploring metastable diamond synthesis at low pressures 40 years ago.

The early 1950s were not only an extremely productive period for research on high-pressure methods of diamond synthesis, but significant advances were also made then in metastable diamond synthesis at low pressures. Methods to deposit diamond from a reactive vapor phase were explored at different places, and it is difficult to determine who really was the first to successfully grow diamond. Starting as early as 1949, William G. Eversole of Union Carbide experimented with synthesis of diamond from carbon-containing gases. The first diamonds may well have been made by the Eversole group in 1953, although written reports of this work did not appear until 1956.

Eversole's work formed the basis for two patent applications, filed in 1958 and granted in 1963, on "synthesis of diamond" from carbon monoxide or from "a gas decomposable to a methyl radical."

In 1956, Boris V. Derjaguin and Dimitri V. Fedoseev at the Institute of Physical Chemistry of the Academy of Science of the U.S.S.R. in Moscow filed a U.S.S.R. author's certificate (the equivalent of a patent application) for a method of growing diamond crystals from the gas phase by thermal decomposition of carbon-containing gases. Their patent was granted in 1980.

In 1953, Heinz Schmellenmeier at Potsdam Teachers College, East Germany, reported the formation of very hard carbon films from acetylene in an electrical

discharge. He was not trying to make diamond films, but was instead studying the reactions of tungsten and carbon. Nevertheless, x-ray data of his coatings, published in 1956, reveal that they contained crystalline diamond, rather than graphite.

Both Eversole and the Derjaguin group used diamond particles as a substrate. Diamond and graphite were codeposited on seed crystals, then the graphite was removed by etching. To do this, Eversole transferred the substrate and deposit into a separate autoclave and removed the graphite with hydrogen at a temperature of more than 1000 °C and pressures of more than 50 atms. Derjaguin and Fedoseev removed the graphite by oxidizing it in air at atmospheric pressures. In both processes, the deposition step had to be interrupted to remove accumulated graphite. These deposition/etching cycles were repeated frequently to obtain a measurable weight gain in the particles.

In 1966 John J. Lander and James Morrison of Bell Telephone Laboratories pointed out that at temperatures below 1300 °C, the conversion of diamond to graphite is impeded by a hydrogen atmosphere. They reasoned that the growth of single-crystal diamond layers on a single-crystal diamond substrate should be possible as long as the carbon was added at a rate low enough to prevent stable graphite nuclei from forming.

John C. Angus and his coworkers at Case Western Reserve University combined these results with those of Eversole to both produce a diamond film and use atomic hydrogen to preferentially etch graphite from the film during the cleaning cycle. They demonstrated, as well, deposition of boron-doped semiconducting diamond and increased diamond yield by using a mixture of methane and hydrogen as the starting material in the deposition process.

In 1978, Earl C. Vickery of Diamond Squared Industries patented a process for growth of diamond layers on a diamond substrate that combined the deposition and cleaning cycles in a single-step process using a

mixture of 95% hydrogen and less than 5% of a hydrocarbon in the presence of catalysts like platinum or palladium.

Because it reacts faster w.th graphite than with diamond, atomic hydrogen effectively removes any graphite from the growing film and leads to net growth of diamond. The Derjaguin group in Moscow suggested three different approaches to achieving a "super equilibrium" with atomic hydrogen—catalysis, heated filament, and electric-discharge plasma—in their book "Growth of Diamond and Graphite from the Gas Phase" published in 1977. Boris V. Spitzyn, L. L. Bouliov and Derjaguin also demonstrated single-phase diamond growth on both diamond and, for the first time, nondiamond substrates. Their diffraction data and scanning electron micrographs of large-faceted diamond crystals and continuous films, appearing in 1976 in a Russian-language journal and in the *Journal of Crystal Growth* in 1981, were unmistakable evidence that they had produced diamond films. Deposition of diamond on nondiamond materials was a big step forward.

By the beginning of the 1980s, the continuous efforts of different groups had yielded a variety of methods and patents to produce synthetic diamond at low pressure. The input of another group of scientists was necessary, however, to trigger a diamond thin film technology. Nobuo Setaka, Seiichiro Matsumoto, Yoichiro Sato, Matsukazu Kamo, and other scientists at the National Institute for Research in Inorganic Materials (NIRIM) in Tsukuba, Japan, began working in 1974 to deposit diamond from the vapor phase. Their publications in 1982 and 1983, inspired by the 1981 Soviet paper, pushed diamond thin films toward practical applications. Using a heated filament approach, in which atomic hydrogen forms at a hot tungsten wire, they deposited diamond films from methane-hydrogen mixtures. Evidence for diamond formation was obtained not only by electron microscopy and x-ray diffraction, but also by Raman spectroscopy showing the very typical sharp peak at 1332 cm^{-1} that characterizes diamond.

These researchers have continued to experiment with both radio-frequency and microwave-supported plasmas as sources for atomic hydrogen. Their methods made the formation of crystalline diamond coatings remarkably easy and reproducible. Today they are collaborators with many of the strong industrial diamond groups in Japan and their names are on many Japanese papers and patents of the past seven years.

The work of these Japanese and Soviet scientists triggered our research group at Pennsylvania State University to reconsider data from plasma polymerizations done here by Bruce E. Knox in the early 1970s. In 1976, he described coatings deposited from hydrocarbon microwave plasmas that showed typical diamond electron diffraction patterns. Rustum Roy, Andrzej R. Badzian, Karl E. Spear, and Russell F. Messier from Penn State's Materials Research Laboratory repeated the experiments of the Japanese and Soviet scientists. This work led to a revival of diamond thin film research in the U.S. that is manifested
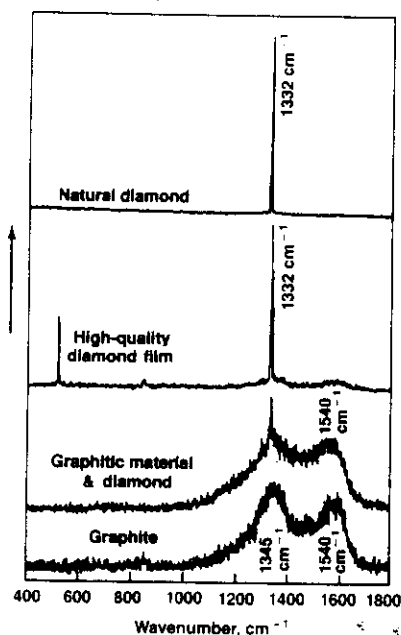
By 1996, semiconductors may take 60% of worldwide diamond thin film market

$ Millions

■ 1988 market for diamond thin films

☐ Expected increase in diamond thin film market by 1996
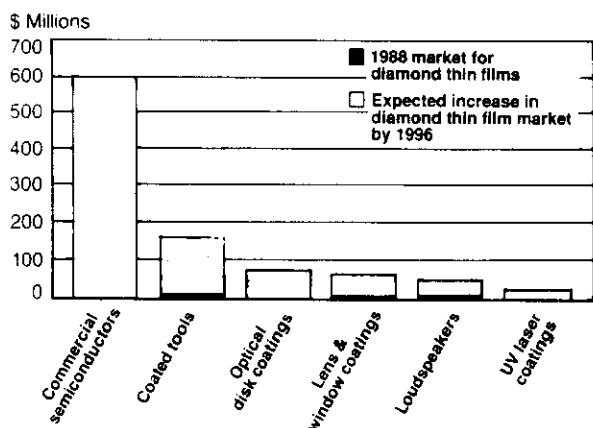
Note: Global market in 1996 projected at $985 million for these uses only
Source: International Resource Development Inc.

## A variety of analytical techniques confirm that vapor deposition produces diamond

Intensity, arbitrary units

Natural diamond

High-quality
diamond film

Graphitic material
& diamond

Graphite

400   600   800   1000 1200 1400 1600 1800
Wavenumber, cm⁻¹

Typical Raman spectrum of a high-quality diamond film deposited on single-crystal silicon (second from top) is compared with spectra from natural diamond, graphite, and films containing both diamond and graphitic material. The sharp peak at 1332 cm⁻¹ is distinctive for diamond. The second peak at 520 cm⁻¹ comes from the silicon substrate. Film deposited at nonoptimum conditions (third from the top) has a much smaller diamond peak and shows, in addition, the two broad peaks at 1345 cm⁻¹ and 1540 cm⁻¹ that characterize graphite.

Deposition conditions and substrate preparation determine whether vapor deposition techniques will produce diamond particles (left) or polycrystalline film (right), which can be distinguished by scanning electron microscopy. The fivefold symmetry and twinned structure, typical of graphite-free diamond, are apparent in the free-standing particles. The rough upper surface of diamond films is also easily seen.
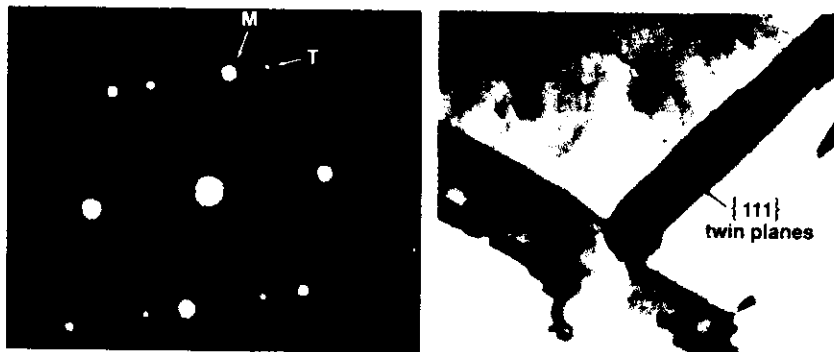
Electron diffraction pattern (left) and transmission electron micrograph (right) are both of a diamond film deposited from 0.5% methane in hydrogen at 950 °C. The diffraction pattern is taken from a 0.8-μm diameter area of a microtwinned crystal and shows diffraction spots produced by the matrix (M) and by twinning (T). The transmission electron micrograph also shows twinning on {111} planes typical for diamond. Most crystals in graphite-free films are twinned.

in a number of ways: by the participation of more than 30 companies in the diamond and related materials industrial consortium organized by our laboratory, by many conferences with sessions on diamond coatings, and by a large number of research groups seeking federal funding for work on diamond thin films.

Diamond and diamondlike films

In 1971, Sol Aisenberg and Ronald Chabot of Whittaker Corp, Waltham, Mass., bombarded a growing film with low-energy ions and produced clear and hard carbon coatings. They called this material "diamondlike" carbon. This term has frequently been used since then for films that have some properties that resemble diamond. Some of these films would be termed diamond today. In 1976, Edward G. Spencer and others at Bell Laboratories published a paper on ion-beam deposition of diamondlike films at room temperature. They established that most of the material deposited was polycrystalline with crystallite sizes of 50 to 100 Å but with some crystals as large as 5 μm in diameter.

The deposition process from carbon-containing gases can yield a wide range of materials, depending on reaction conditions. With varying amounts of impurities, especially hydrogen, and with varying crystallite sizes and connective "phases" bonding the individual crystallites, these materials can range from amorphous carbon to diamondlike to genuine diamond.

Diamondlike carbon films are generally amorphous, though they can have very small crystals (less than 2 to 20 nm in diameter) and can contain from almost zero to more than 50% hydrogen. When the carbon gram-atom number densities are high (greater than 0.2 gram-atoms per cc), these films can possess properties very close to diamond. They can have a very high

carbon density, which is caused by ion bombardment during deposition, and they can grow at temperatures as low as room temperature. Their hardness approaches the values of diamond, and their amorphous character results in smooth coatings. These properties, along with low deposition temperature, make them useful for protective coatings and in some optical applications. Diamondlike deposits are already in use as diffusion barriers to protect silica glass optical telecommunication fibers.

Although diamondlike carbon forms an interesting and useful group of materials that already have some technical applications, it is not genuine diamond and so is outside the scope of this article. Its optical band gap, electrical properties, and thermal conductivity are all quite different from genuine diamond. By genuine diamond films we mean essentially single-phase films with grain sizes greater than about 1 μm. Such films are leading the way in the emerging diamond thin film technology.

It is easy to tell a lump of coal from a sparkling diamond. But a diamond or diamondlike coating deposited on diamond particles or on a silicon wafer does not at all resemble a precious jewel, and sophisticated methods are needed to determine the purity and other properties of diamond films. In General Electric's 1955 announcement of synthetic diamonds in *Nature*, the researchers listed x-ray diffraction, chemical analysis, hardness tests, and repeatability as ways to verify diamond formation. In 1968, Angus and his colleagues burned some of their deposits to determine the carbon and hydrogen content. They used wet-etching techniques to separate diamond from graphite, measured the densities of the diamond-containing particles, and also used diffraction techniques to identify the products of their experiments. Conclusive proof that diamond was formed was time-consuming and difficult at that time.

Currently the techniques used most often to characterize such coatings are x-ray or electron diffraction, scanning electron microscopy, and Raman spectroscopy. Raman scattering is especially sensitive to any second phase (nondiamond, but diamondlike) and gives the best measure of the relative degree of perfection of the diamond film. Diffraction methods alone are not enough for conclusive characterization. This fact is impressively illustrated in two publications by Katsuki Kitahama and coworkers of Osaka University in Japan. In a 1986 paper, these researchers described the laser-induced deposition of diamond film on a silicon wafer at deposition temperatures of 40 to 800 °C. This exciting result was confirmed by electron diffraction. What seemed to be an important breakthrough—the deposition of genuine diamond at close to room temperature—had to be corrected in late 1988, however, when Raman spectroscopy revealed the authors had been misled by the similarity of electron diffraction patterns for diamond and graphitic phases.

To avoid such problems, we have proposed a working definition of diamond films: Génuine diamond coatings should have a crystalline morphology discernable by scanning or transmission electron mi-

croscopy, a single-phase crystalline structure identified by x-ray or electron diffraction, and a Raman spectrum with the distinct, single, narrow line at 1332 cm^{-1} typical of diamond.

In principle, diamond films could be synthesized in the average kitchen with the help of a silica glass bell jar and a microwave oven. The jar needs to be pumped down to about 50 millibar pressure. At this pressure, it is quite easy to sustain an electrical discharge by means of microwave radiation in a mixture of about 1% methane in hydrogen. Within such a discharge, methane decomposes and hydrogen dissociates into atoms. A substrate, such as a silicon wafer, placed close to the glowing plasma will heat up to about 950 °C and polycrystalline diamond will start forming on its surface. Just such a simple setup was demonstrated at the Materials Research Society's 1987 fall meeting in Boston by Thomas R. Anthony of General Electric.

Other methods to prepare diamond films differ chiefly in the way they produce the atomic hydrogen that is needed to prevent graphite deposition. Probably the simplest way to form diamonds at low pressure is the heated-filament method, originally developed by Matsumoto at NIRIM. The gas composition in this method is the same as in Anthony's demonstration. This mixture enters a reactor that is evacuated to about 50 mbar. The gases pass over a wire or mesh made of a metal such as tungsten or tantalum heated to about 2200 °C. Thermodynamic calculations show that under these conditions, more than 5% of the hydrogen is dissociated into atoms. Methane is decomposed, too, and a diamond film forms on the substrate, which is mounted at a distance of 5 to 15 mm from the hot filament. The substrate is kept at 700

Heated-filament method uses a hot wire to decompose source carbon
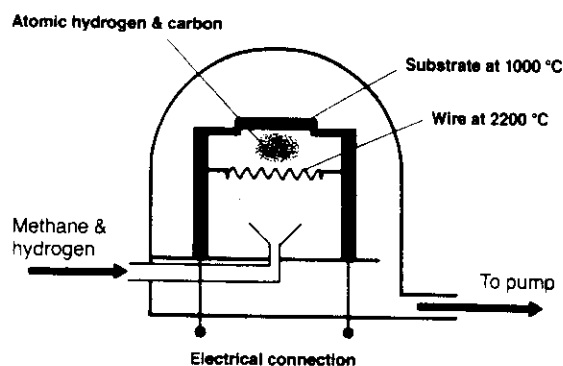
In the heated-filament method of preparing diamond films, a mixture of about 1% methane in hydrogen enters the reactor and flows past a heated wire that decomposes the gases into atoms. The diamond film forms on a heated substrate, mounted 5 to 15 mm above the hot wire. The entire reaction takes place within a silica bell jar that is evacuated to 50 millibar. Oxygen-containing species can be added to the reactant gases to increase deposition rates.

to 1000 °C either by radiation from the filament or by a separate substrate heater.

NIRIM's straightforward and inexpensive setup has been used in many places. Problems are associated with the long-term stability of the hot wire and with contamination of the growing film caused by metal evaporating from the hot wire or mesh. Deposition rates with the heated filament method vary from 0.5 to 20 μm per hour. By adding oxygen-containing starting materials, such as carbon monoxide, water, or molecular oxygen, rates can be increased to as high as 40 μm per hour. We find 1 μm per hour to be a typical rate for high-quality films. Coated areas as large as 20 × 20 cm have been deposited, and for many applications where an ultraclean film is not mandatory, this fabrication method is a good choice.

A variation of this method uses a bias voltage applied between the filament and the substrate. Electrons emitted by the filament wire accelerate toward the substrate at the same time that heavier ions in the gas phase are repelled by the positively charged substrate surface.

It is easy to imagine a process in which the bias voltage is high enough to form a glow discharge between the substrate and the filament. Such a system is the basic concept for the direct-current plasma method of making diamonds. Normally, larger substrate plates are used in this approach. At pressures of about 50 mbar, this method can coat areas of more than 50 mm diameter. The method suffers, however, from a very low growth rate (less than 0.1 μm per hour), which makes it impractical for many industrial purposes. Kazuhiro Suzuki of Japan's Kyoei Plastic Co.

and his colleagues at Aoyama Gakuin University recently overcame this drawback by applying direct-current voltages of more than 1 kV and high discharge currents. They can sustain a plasma at 200 mbar. They increased the deposition rate to 10 to 20 μm per hour but had to reduce the deposition area to only 10 mm in diameter.

All the direct-current plasma chemical vapor deposition methods for making diamond mount the substrate on the anode of the deposition system. Mounting on the cathode seems to result in deposition of graphitic material rather than diamond, probably because impinging ions deteriorate the growing film.

The normal glow discharge can be varied by operating at higher pressures of 100 mbar to 1 bar and using a direct-current arc discharge between the electrodes. In this approach, the substrate is mounted on a separate water-cooled holder, rather than on one of the electrodes. The plasma arc expands into the reactor chamber with the help of a hydrogen/methane/argon gas mixture flowing at several liters per minute. Such a thermal plasma looks like the flame of a welding torch.
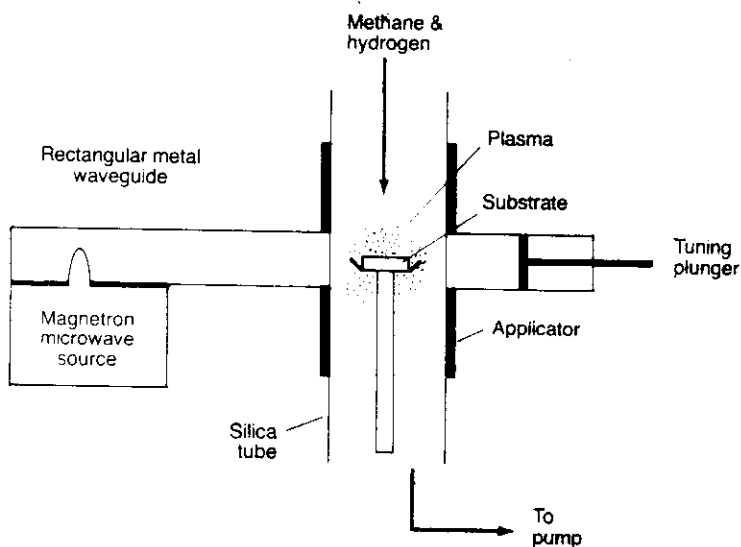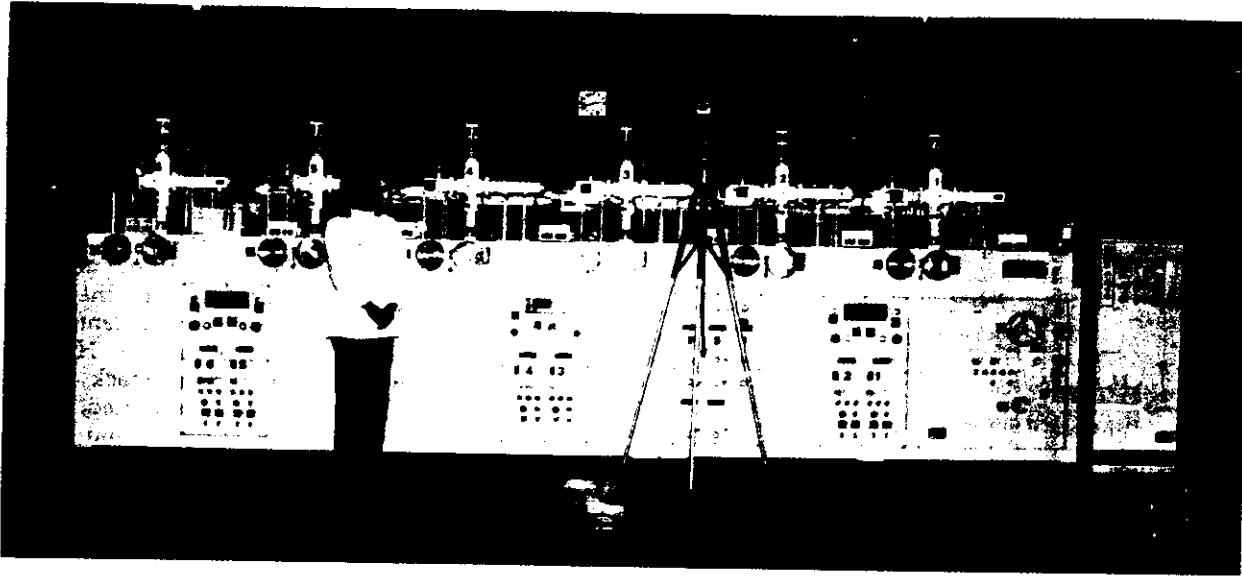
The unique feature of this type of discharge is the high temperature of the isothermal plasma. Heavy particles (ions and radicals) as well as free electrons are heated to about 5000 °C. In this environment, almost all of the hydrogen molecules dissociate and a sufficient supply of the active carbon species necessary for diamond formation is created. Optical emission spectra of plasma jets indicate that CH radicals may play a vital role in diamond growth but details of the reactions steps are still unknown.

Direct-current plasma jet focuses coating on small area of substrate
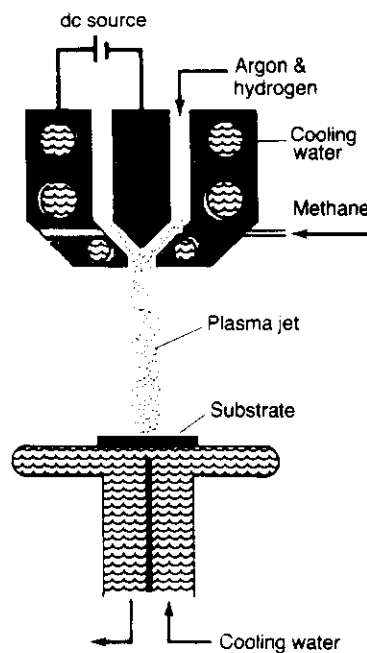
Glowing plasma (far left) of the direct-current arc discharge or "plasma jet" method deposits a diamond film over a relatively small (5 × 5 mm) area, but the plasma can be scanned over the substrate to coat a larger area and produce a uniform coating. The technique uses a high-temperature plasma (shown in red in the diagram) in which nearly all molecules are completely dissociated. Because the temperature of the plasma jet can reach several thousand degrees Celsius, the substrate has to be cooled to keep it at 1000 °C or lower. Growth rates of more than 500 μm per hour have been achieved by this method. The method, first used at Fujitsu Laboratories in Japan, looks very promising, especially for preparing large quantities of bulk polycrystalline diamond. The plasma shown here is an experimental jet located at Eindhoven University of Technology, the Netherlands.

Diagram labels: dc source; Argon & hydrogen; Cooling water; Methane; Plasma jet; Substrate; Cooling water

Japanese microwave plasma deposition unit runs six reactors at once

The prototype semicommercial microwave plasma deposition system developed by Idemitsu Petrochemical, shown above, is a scaled-up version in which six microwave tubular reactors run in parallel. Rectangular metal waveguides direct the microwave energy from a magnetron source to the applicators, as shown in the diagram. A tuning plunger ensures maximum coupling of the microwave energy with the methane and hydrogen gas mixture, which flows through the applicator and is confined by a cylindrical fused silica tube. Where the microwave power and the gas coincide, a plasma forms that creates the conditions for diamond growth on a substrate that is placed either in the middle (as shown) or at the edge of the plasma. The original plasma system of this type was developed by the diamond technology group at Japan's National Institute for Research in Inorganic Materials.

Similar reaction conditions can be obtained using an inductively coupled, radio-frequency-induced thermal plasma at atmospheric pressure. Very high growth rates of 300 to 500 μm per hour have recently been reported for both methods by Nagaaki Koshino, Kazuaki Kurihara, and their coworkers at Fujitsu Laboratories and also by Matsumoto at NIRIM. Matsumoto finds thermal radio-frequency plasmas are difficult to handle and tend to be unstable. The thermal plasma-jet method is easier to use but contamination from the plasma nozzle can deteriorate the quality of the film.

Despite poor energy efficiency, small deposition area, and difficult process control with both the arc plasma jet and the thermal radio-frequency plasma methods of chemical vapor deposition of diamond, the high local growth rates achieved represent a milestone in diamond thin film technology. In little more than a decade, the deposition rate has been increased more than three orders of magnitude, surpassing the 100 μm-per-hour mark considered necessary for chemical vapor deposition to be commercially competitive with high-pressure diamond synthesis even for the production of abrasive grit. Fujitsu and Asahi Diamond are actively developing the direct-current arc plasma approach in Japan.

Microwave plasma chemical vapor deposition also

Bell jar microwave reactor produces ball-shaped plasma
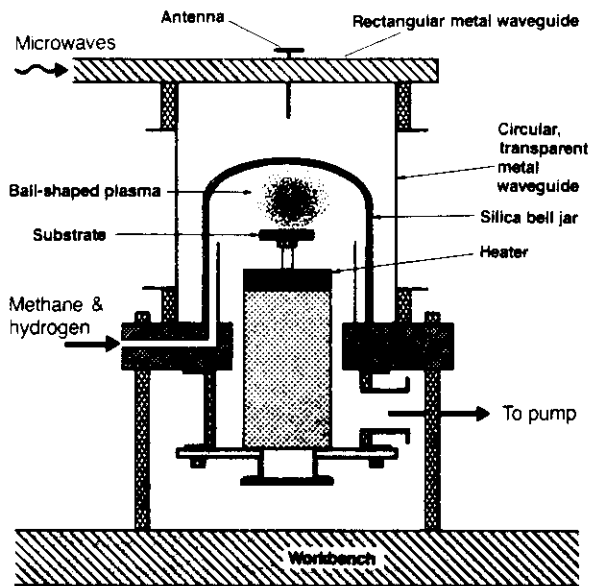
A bell jar reactor for microwave plasma deposition of diamonds, developed jointly by our group and Applied Science & Technology, is shown schematically here and in the photograph on page 25. Microwave radiation is guided to the top of the reactor by rectangular metal waveguides and picked up by an antenna that sticks into the circular, symmetric waveguide, which contains a silica glass bell jar that is evacuated to about 50 millibar. The substrate can be mounted either on a substrate holder heated by a plasma discharge generated in the bell jar or on a separate heater. Methane and hydrogen entering the system are guided to the plasma region, where the microwaves decompose them to form a ball-shaped plasma that does not touch the walls of the bell jar. At a substrate temperature of 950 °C, a diamond film can be deposited onto substrates up to 8 cm in diameter.

originated with the diamond technology group at NIRIM. The carbon-containing gases and the hydrogen molecules are dissociated by microwave radiation at a frequency of 2.45 GHz, the same frequency found in a home microwave oven. In the commonly used system, the gases are fed into a silica tube connected to a vacuum pump and surrounded by a microwave applicator. Idemitsu Petrochemical of Japan has developed a prototype production system in which six microwave tubular reactors (with tubes having an inner diameter of about 50 mm) run in parallel.

A different apparatus, a bell jar reactor, has been jointly developed by our group and Applied Science & Technology, a startup company based in Cambridge, Mass. This system allows the operator to visibly inspect the deposition process through a perforated cylindrical waveguide. The highly uniform microwave glow discharge used to decompose the carbon source gas and to make atomic hydrogen has the shape of a

ball. At pressures higher than 20 mbar, this ball stays away from the silica bell jar, thus avoiding etching the glass walls and contaminating the growing film. The system is capable of growing high-quality films on a substrate up to 75 mm diameter. Denki Kogyo in Japan and Wavemat in the U.S. have independently developed similar systems using different methods to tune and transfer the microwaves from rectangular waveguides to a circular reactor.

The advantage of microwave plasma deposition over other diamond fabrication methods is its stability. This system can easily run for days without any problems. Its deposition area is quite large and the process does not involve any hot electrodes or filaments, which can lead to metal contamination of the film. However, present deposition rates are still a drawback. Rates of up to 20 μm per hour have been reported, but for high-quality films with faceted crystals and without graphite contamination, the rate is only about 1 μm per hour and uniform coatings are currently limited to diameters of less than 50 mm.

Amorphous materials, such as silica glass for optical fibers, have been deposited at rates of 2 to 3 mm per hour on areas of more than 1000 sq cm using microwave plasma deposition techniques. Considerably more work is still needed to approach these values for crystalline diamond films. On the other hand, conventional chemical vapor deposited coatings of materials such as titanium carbide or aluminum oxide for cemented carbide cutting tools and other wear-resistant parts are now produced commercially at slower deposition rates—about 1 μm per hour or less. Such commercial reactors coat thousands of pieces in a single batch process, which makes the process economically feasible.

None of the plasma-assisted or heated-filament-assisted diamond deposition methods has yet been scaled up to such an extent. Similar sample throughputs will be needed to make diamond-coated products economically competitive. Also needed will be successful scaling of the process to larger coating areas and process development that minimizes energy costs.

All of the preparation techniques that have been explored so far to make diamond have a few steps in common:

• When the carbon source is a hydrocarbon, they use a mixture that is less than 10% by volume of the carbon carrier diluted in hydrogen.

• Some of the hydrogen is activated to form hydrogen radicals.

• For high-quality films, the substrate temperature has to be between 850 and 1050 °C.

The substrate materials used so far include metals such as titanium, molybdenum, nickel, copper, tungsten, and tantalum; ceramic and other hard materials like silicon carbide, silicon nitride, silicon aluminum oxynitride, boron nitride, alumina, and tungsten carbide; single crystals of diamond, sapphire, silicon, or nickel; and graphite and silica glass.

Many hydrocarbons, alcohols, amines, and ethers have been converted into diamond films. Recent experiments even use mixtures of carbon monoxide and

Cutting tools coated with polycrystalline diamond film resist abrasion
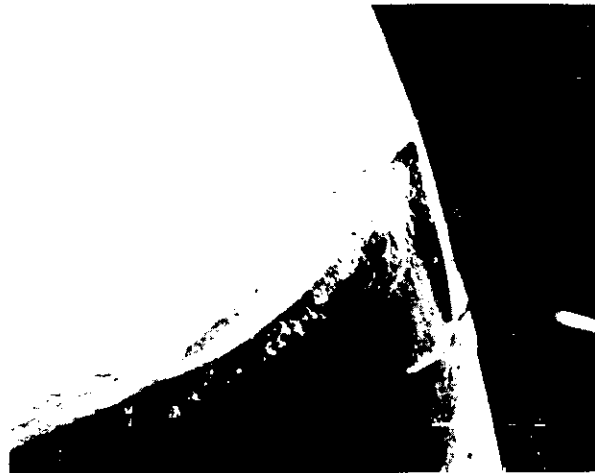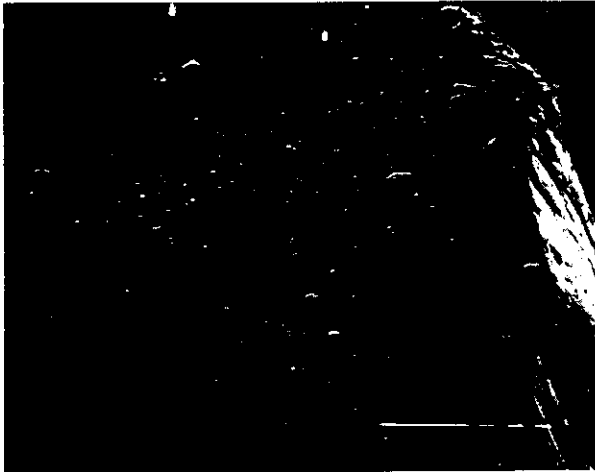
Increased wear resistance of cutting tools coated with polycrystalline diamond film is shown dramatically in these electron micrographs. Two cutting tool inserts made of silicon aluminum oxynitride, one with a 3-μm-thick diamond film coating (left) and one without (right), were each used under similar conditions to cut an aluminum alloy containing 7% silicon. The uncoated insert clearly shows wear at the cutting edge; the coated part is almost unaffected by the test. The polycrystalline diamond film was deposited from 1% methane in hydrogen at 980 °C. The large bar in the micrographs corresponds to 100 μm.

hydrogen. Researchers at Idemitsu Petrochemical in Japan find that a film deposited from 40% carbon monoxide in hydrogen still exhibits a reasonable Raman spectrum for diamond.

Although single-crystal diamonds can be grown on single-crystal diamond substrates, most films are deposited as a polycrystalline material. The size of the crystallites ranges from 25 μm to 25 nm, depending on deposition temperature, gas composition, and sub-strate pretreatment. Diamond crystals nucleate much faster when the substrate surface has been scratched with diamond polishing paste or boron nitride powder.

None of the currently available processes can be considered the best. Which method to choose depends on the specific requirements of the application for purity, size, or simplicity of operation. Integration of the best features of each process into a single fabrication process, if possible, will need additional research.

Diamond-coated tweeters have less high-frequency sound distortion

High-fidelity loudspeakers for high-frequency sound (tweeters), jointly developed by Sumitomo Electric Co. and Japanese Victor Corp. (JVC), have a diaphragm coated with a diamond thin film, (shown below the assembled loudspeaker). Both polycrystalline and diamondlike films are used to coat dia-

phragms in tweeters, on different substrates. Their frequency-response characteristics are compared in the diagram at right. The dip below the 100-decibel level and the sharp spike above it both represent sound distortions. Frequency distortions that occur in the 15- to 20-kHz range for uncoated titanium can be shifted to the 20- to 50-kHz range by using diamondlike carbon coating and to even higher frequencies by using a diamond thin film on an alumina substrate. Human ears are sensitive to sound up to about 20 to 25 kHz, but sound distortions at higher frequencies may affect a harmonic component of sound that determines its tone. Both diamond-coated and diamondlike carbon-coated tweeters are currently marketed by JVC.
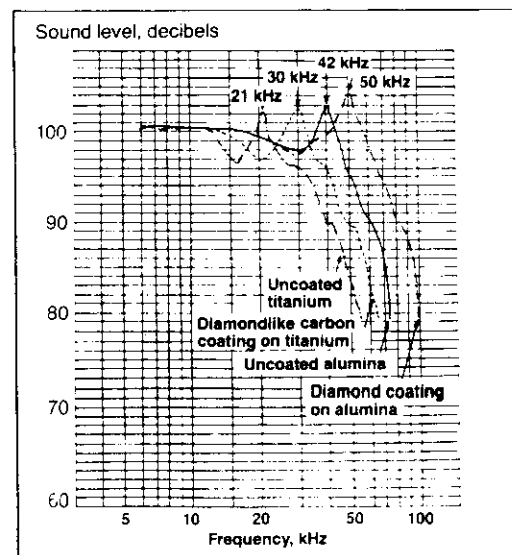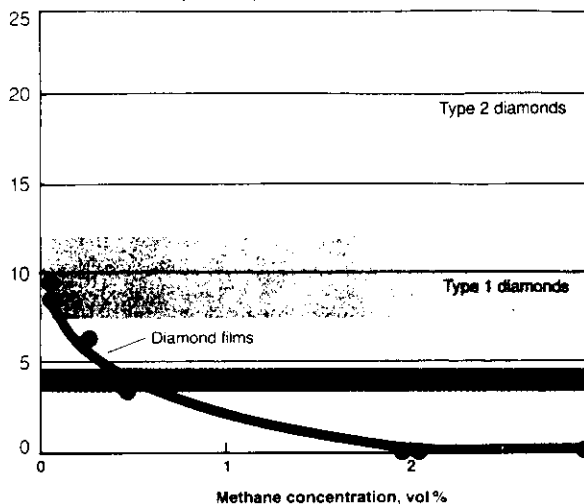
Diamond thin films at work

Low-pressure methods of making diamond particles and coatings have created many expectations for exciting applications. It is important to examine how realistic some of these applications may be and how long it may take before specific diamond-coated products reach the marketplace.

Naturally, products that do not require pure and perfect crystals are closer to market introduction than those that require perfect, ultraclean, single-crystal deposits. On cutting tools, for example, a hard polycrystalline coating that adheres to the tool surface is all that is needed. Tool inserts made from cobalt-cemented carbides or, especially, silicon nitride or silicon aluminum oxynitride are excellent substrates for diamond deposition. The ceramic parts of such tools are quadratic or triangular in shape, are about 4 mm thick, and typically have a cutting edge about 6 mm long, dimensions for which diamond coating techniques are available. The thickness of the coating needed varies from 2 to 10 μm, depending on the application. These substrates can withstand the high temperatures currently needed to form diamond. Coating adhesion, however, though sometimes reasonable, is inconsistent. Mitsubishi Metals is test marketing such inserts in Japan, and other Japanese tool manufacturers, such as Mitsubishi Metals, Sumitomo Electric, Toshiba Tungaloy, and Asahi Diamond, as well as their U.S. and European competitors, are not far behind them.

It is not yet possible to coat high-speed steel drill bits and cutting tools with diamond because the deposition temperature is too high. A reduction by 300 to 400 °C is essential to prevent the steel from losing its structural hardness in the coating process. If the temperature can be lowered this much—and recent reports on the addition of oxygen in the deposition step are encouraging—then the problem of chemical reac-

Vapor-deposited diamond heat sinks near commercialization

Polycrystalline diamond heat sink prepared by the plasma jet method at Fujitsu Laboratories in Japan has thermal conductivity similar to type 1 natural diamond (in the range of 10 watts per cm °C). Heat sinks manufactured from these chips are expected to be commercially competitive with existing diamond heat sinks, such as those synthesized as single crystals at high pressure and marketed by Sumitomo Electric.

Low-methane gases make diamond films with best thermal conductivity

Thermal conductivity, watts per cm K

The thermal properties of diamond thin films depend heavily on the methane concentration of the gas used to deposit the films. As shown in these data from Akira Ono and coworkers at the National Research Institute of Metrology, Tsukuba, Japan, and Seiko Instruments, Japan, only diamonds that are formed at methane concentrations of 0.1% by volume have thermal conductivity comparable to natural type 1 diamond.

tions between iron in the substrate and carbon in the coating will have to be solved.

High-quality loudspeakers that include diamond-coated tweeters and midrangers are already marketed by Japanese and U.S. companies such as Japan Victor Corp., Kenwood, Onkyo, and Altec Lansing. These expensive audio systems are intended primarily for professional applications, where high-quality sound reproduction is essential.

Another product that seems to be close to commercialization is a heat sink for electronic circuits based on vapor-deposited polycrystalline diamond. Fujitsu Laboratories in Japan has developed its plasma jet deposition method so that it can be used to produce polycrystalline material up to 4 X 6 X 1 mm.

Diamond-coated heat sinks require films with excellent thermal properties. In a study of the thermal properties of polycrystalline diamond, Akiro Ono and coworkers at the Japanese National Research Laboratory of Metrology and at Seiko Instruments correlated the thermal conductivity of microwave plasma-deposited films with the methane concentration in the reactive gas. They find that only graphite-free films prepared with low methane concentration (0.1% by volume of the reactive gas) have the thermal conductivity of natural diamond. Values so far reach about 10 watts per cm K, comparable to those of natural type 1 diamond, but still considerably lower than the thermal conductivity of natural type 2 diamonds, which can be as high as 21 watts per cm K. David T. Morelli

and his colleagues at General Motors' research laboratories attribute this difference to the influence of grain boundaries in polycrystalline vapor-deposited diamond. Even this conductivity level, however, is about twice that of metals like copper or silver, and polycrystalline diamond heat sinks made by the plasma jet method are nearing commercialization at Fujitsu Laboratories.

The most demanding application for vapor-grown diamonds will certainly be diamond semiconducting devices. Diamond point-contact transistors that operate at temperatures higher than 600 °C have been made using synthetic diamond crystals by Michael W. Geis and his coworkers at Lincoln Laboratories of Massachusetts Institute of Technology. These transistors demonstrate that diamond semiconductor devices can handle the temperatures occurring in high-power applications. In fact, they withstand temperatures five times higher than silicon devices can, making them candidates for use in harsh environments, such as in motors or jet engines.

Penn State's Gennady Gildenblatt and coworkers also have demonstrated that devices such as a Schottky diode can be fabricated using vapor-deposited polycrystalline material. Ultimately, however, low-defect-density single-crystal films may be needed to make diamond high-power transistors and microwave devices. The purity of such films will need to be extremely high, and processes will have to be developed that eliminate completely both hydrogen and heavy metal contaminants that would deteriorate the electronic properties of such films.

Most current diamond electronic devices use natural or high-pressure synthetic diamonds. Considerable progress has been made during the past three years, however, to open up this field to low-pressure diamonds. MIT's Lincoln Laboratories is a center for these activities. Researchers there have developed an integrated circuit etching technology that will be needed for the manufacture of prototype transistors. So far, excimer laser diamond etching has produced topological structures as small as 0.3 μm, a size that is suitable for very-large-scale integrated circuits. Growth of boron-doped diamond using the microwave plasma and the heated-filament technique has been reported by several research groups, including the MIT researchers, and the availability of this material will definitely give diamond electronics an additional push.

Some of the advantageous properties of diamond films have already found commercial applications but a number of critical problems still remain to be solved. For cutting tools, bearings, and other applications that take advantage of diamond's mechanical properties, the reproducible fabrication of highly adherent coat-

ings is still not achieved. Optical applications, such as coatings for lenses, watch glasses, and sunglasses, suffer from the high scattering caused by the rough, faceted surfaces and internal grain boundaries of polycrystalline material. And for electronic applications, preparation of n-type, phosphorus-doped diamond deposits and the fabrication of single-crystal material on nondiamond substrates are critical problems that are by no means solved. For some applications, hard, diamondlike carbon coatings are sufficient; for others, genuine diamond is necessary. Despite these problems, however, the promise of the emerging diamond technology for a wide range of industries makes further development well worthwhile. □

Peter K. Bachmann (left) is a member of the research staff at Philips Research Laboratories in Aachen, West Germany, part of Philips N.V. of the Netherlands. He received a Ph.D. degree in chemistry from the Technical University of Darmstadt, West Germany, in 1980, the same year he joined the Philips staff. He is a member of the Optical Society of America and the Bunsen Society for Physical Chemistry in West Germany. Bachmann has worked for more than six years on the design and preparation of silica glass optical fibers for telecommunication using low-pressure microwave plasma-induced chemical vapor deposition, one of the few plasma deposition techniques that has matured into a large-scale industrial process. He spent a sabbatical year in 1987–88 with the diamond thin films group at the Materials Research Laboratory of Pennsylvania State University working on microwave plasma deposition of diamond thin films and other aspects of the nucleation and growth of diamond.

Russell Messier, associate professor of engineering science and mechanics at Penn State, is a member of the staff of the Materials Research Laboratory and director of Penn State's diamond and related materials consortium. He holds a bachelor's degree in electrical engineering from Northeastern University and a doctorate in solid state science from Penn State. His studies have ranged from conventional thin film research to development of x-ray phosphors to theories on the optical behavior of daguerreotypes. For the past 10 years, he has been studying the relationship between basic sputtering processes, thin film morphology, and resulting film properties. He is a member of several professional societies and is a trustee of the American Vacuum Society.

CHEMICAL & ENGINEERING

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News of the Week

Cover: Closeup view of microwave plasma used to produce diamond thin films at Penn State's Materials Research Laboratory. Photo by Bruce Frisch

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Special Report

FROM DIAMOND-LIKE CARBON TO DIAMOND COATINGS*

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Carbon films deposited by pyrolytic and plasma-activated deposition from hydrocarbon-containing gases encompass a virtual infinity of compositions (hydrogen concentrations) and structures (from amorphous to single crystal and with variable amounts of sp^1, sp^2 and sp^3 bonding). Coatings which have a high degree of sp^3 bonding generally have properties, especially hardness, close to those of single-crystal diamond and are often referred to as diamond-like carbon. Recently, large grain size diamond crystals and continuous diamond coatings have been prepared by plasma chemical vapor deposition methods. Although such materials are different from the diamond-like carbon class of materials, there is clearly a continuum of materials which is expected to lead to vagueness and confusion in nomenclature. In this paper, such issues are dealt with and a working definition of "diamond" coatings is offered.

1. INTRODUCTION

The widespread realization of diamond coatings by vapor phase synthesis has occurred in the U.S.A. and Europe only over the last 2 years. However, it is now becoming clear that such an achievement is over a decade old in the Soviet Union and half a decade old in Japan. In addition, during this period, considerable effort has been placed upon another type of material commonly called diamond-like carbon (DLC). The common denominator in stabilizing sp^3 carbon atoms in DLC has been ion bombardment of the growing film. These latter materials represent a broad range in structure (primarily amorphous with variable ratio of sp^2 to sp^3 bonding) and composition (variable hydrogen concentration). However, what might be considered "pure" diamond coatings are stabilized by controlling

chemistry in the gas or plasma and at the growing film surface. Futhermore, by changing the nucleation density by carefully choosing and modifying the substrate, the resulting diamond growth morphology can be controlled. However, our results and the results of others also show that impurities can be incorporated into the crystalline diamond films. The details and implications of these results for hard coatings will be discussed. We shall also discuss the importance of each of these two diamond stabilization processes — bombardment and chemistry — and use them in classifying previous results and predicting the achievement of a whole continuum of carbon coatings with varying structure and impurities, both major and minor.

2. HISTORY OF DIAMOND GROWTH

Although the quest for diamond growth from a low pressure vapor started at least as far back as 1911[1], it was not until 1955 that this effort intensified. During that year the General Electric process[2] for making industrial diamonds at high pressures and high temperatures was announced, and Bridgeman[3] soon followed with an article in Scientific American, speculating that diamond powders and films should be equally achievable at low pressures during vapor deposition.

The first attempts by Eversole[4] of Union Carbide were extremely slow and impractical and the evidence for diamond film growth was meager. This process was studied in detail in the 1960s and 1970s by Angus and coworkers[5-7] at Case Western Reserve University. Eversole's findings were fully confirmed but the low growth rates (about 0.001 μm h^{-1}) were not substantially increased. The various techniques developed relied on a two-step process of first producing a layer with a small percentage (less than 1%) of diamond bonds and second removing the much larger percentage of graphitically bonded material by a selective hydrogen reduction process at a high temperature and pressure. The process was repeated many times to produce a single film (on diamond powder) with enough material for analysis. The number of literature references are few and it would be fair to say that there was a considerable amount of suspicion (not well founded) on the validity and significance of these results.

Derjaguin, Fedoseev, Spitsyn and co-workers at the Institute of Physical Chemistry in Moscow also heeded the work of Eversole, in conjunction with some earlier predictions of growing diamonds by Lejnunskij[8] and Frank-Kameneckij[9]. During the course of their studies starting in the mid-1950s, they investigated the kinetics of the pyrolysis of various hydrocarbon–hydrogen gas mixtures, including methane–hydrogen, and the mechanisms of nucleation and growth of diamond on diamond seed crystals. This early work is summarized in a review article in Scientific American by Derjaguin and Fedoseev[10] in 1975.

During their research the Russian workers began to realize the importance of atomic hydrogen as a selective etchant, for removing graphite but not diamond, and its utility to dissolve continuously any graphite that forms during deposition. It became clear that, to accelerate diamond growth, it was necessary to introduce even higher concentrations of atomic hydrogen than the equilibrium concentration related to the thermal dissociation of hydrocarbon–hydrogen gases. This important break in thinking apparently occurred between 1975 and 1977 when Derjaguin and

Fedoseev[11] published a book entitled *Growth of Diamond and Graphite from the Gas Phase*. In Chapter 4 ("Epitaxial films of diamond and whiskers"), they outline three different methods for producing a superequilibrium of atomic hydrogen: catalytic; electric discharge; heated tungsten filament (HF).

It was not until 1981 that these results were published in English[12]. They used a chemical vapor transport process in a closed tube to which an unspecified "electric discharge" was used to generate the necessary atomic hydrogen. In that paper, scanning electron microscopy (SEM) micrographs of large crystals (up to 30 μm) and highly faceted thick continuous films were seen alongside the confirming electron diffraction data. This was followed immediately by an a.c. plasma discharge technique in a flowing gas system used by Mania et al.[13], and the HF chemical vapor deposition (HF CVD) approach was taken by Matsumoto and coworkers[14-16] at the National Institute for Research in Inorganic Materials (NIRIM) in Ibaraki, Japan. In all these cases, SEM micrographs of diamond particles and faceted coatings were present together with other evidence. The catalytic approach had been taken previously by Vickery[17].

Matsumoto et al.[15] showed in detail that the concentration of methane in the methane–hydrogen gas mixture must be about 1% to get optimum diamond growth. Most subsequent work confirms this curious result: use copious amounts of hydrogen to produce diamond with very little, if any, hydrogen. The NIRIM group has since published a series of papers continuing with the HF CVD method[18] and expanding to microwave-plasma-assisted CVD[19,20] and r.f. plasma-assisted CVD[20,21].

Other activated CVD approaches to diamond growth that have been reported include electron-assisted (EA) CVD[22,23] and UV-assisted CVD[24]. Within the last year a number of new papers and abstracts have appeared and no attempt will be made to review these here. However, a few papers of importance include EA CVD[22,23] with a growth rate of 3–5 μm h^{-1}, HF CVD[25] with organic compounds, such as acetone, with growth rates of 8–10 μm h^{-1}, doping of semiconducting diamond[26] and use of hydrogen ion beams to grow diamond at room temperature[27].

3. DIAMOND-LIKE CARBON

It would be simple if the story ended here, but there is a whole other set of literature which must be considered, albeit reconsidered. The term diamond-like carbon was coined by Aisenberg and Chabot in 1971[28]; it covers a wide range of materials including both amorphous and microcrystalline atomic structures and containing anywhere from 0 to more than 30 at.% H. Unfortunately, there has been essentially no distinction made among these materials using structural and compositional criteria.

Angus et al.[29] have recently reviewed DLC coatings and classified them primarily according to their method of preparation. One group of methods used solid carbon as a source of carbon vapor atoms and molecules. In all instances, high energy particle bombardment (greater than 40 eV, and in some cases up to several megaelectron volts) was present during growth because of either energetic carbon

primary ions or inert gas secondary ions (e.g. argon). The second group of methods uses hydrocarbon gases as a source of carbon atoms and some kind of electrical discharge is applied to produce ionized and excited state gas phase species. In these cases the bombardment occurs because of floating potential differences betweeen the substrate and the plasma.

When only the reports of microcrystalline diamond with essentially no hydrogen (1 at.% or less) are considered, there have been several papers with conclusive evidence that diamond was achieved. For instance, Spencer et al.[30] presented detailed diffraction data while Sokolowski et al.[31] showed both transmission electron microscopy (TEM) micrographs and electron diffraction of a very-fine-grained diamond structure. Golyanov and Demidov[32] filed a U.S. Patent on October 24, 1972, claiming a "Method for producing an artificial diamond film" using an opposing target sputtering technique. Mori and Namba[33] published similar results in 1983 and Namba and Mori[34] in 1985 and referred to the films, at least in the titles, as diamond-like and diamond respectively.

4. CHARACTERIZATION AND NOMENCLATURE OF DIAMOND COATINGS

The characterization of microcrystalline materials (a crystallite size of less than 100 Å) is not easy and to convince oneself that a second amorphous phase containing some sp^2 or sp^1 bonding is absent is difficult. Thus, many of these previous reports have erred on the side of caution and referred to the films as diamond-like carbon despite their diamond crystalline nature. However, now that almost everyone is trying to make diamond rather than DLC, we can probably be assured that the terminology will begin to err on the side of the word "diamond". The main point is that better-defined terminology and characterization techniques will be essential for distinguishing between the whole infinity of structures (amorphous → microcrystalline→ large-grained polycrystalline → single crystal) and compositions (hydrogen and other impurities in interstitial sites and at grain boundaries) that have been, and will be, made.

We can only hope that the lessons learned in the amorphous and microcrystalline silicon fields do not go unnoticed. In this case after 10 years and probably 5000 papers there is still considerable uncertainty regarding such basic concepts as the detailed electronic conduction mechanisms or light-induced defects, and yet no sp^2 bonding is involved in this analogous system of materials. An early plea is thus made for a complete characterization of diamond-related materials as we rush to exploit their desirable properties and forget that we are not dealing with a singular fixed low free-energy state material but rather one that can reside in an infinity of free-energy states. Also this variable free-energy state can be related to not only local but also long-range bonding defect structures such as voids and grain boundaries. It will be shown below that one of the few facts at present known in any detail about large-grained polycrystalline diamond coatings is their morphology. In fact, it is probably these beautiful SEM micrographs, more than any other factor, which has finally captured the attention of researchers throughout the world.

Thus, as a working definition of diamond coatings, we shall consider vapor-deposited diamond particles and continuous diamond coatings which have a

crystalline morphology discernible by electron microscopy, a single-phase crystal-line structure identified by X-ray and/or electron diffraction and a Raman spectrum typical of crystalline diamond. Furthermore, the presence of impurities (e.g. hydrogen or silicon) is allowed within this definition so long as they are incorporated in the diamond lattice either substitutionally or interstitially. It is interesting to note that natural diamond may also contain considerable amounts of impurities of "dopants", e.g. nitrogen, hydrogen or boron. As the crystallite size falls below about 0.2 µm the definitive characterization becomes more difficult and the distinction between diamond and DLC coatings is tenuous. At this point, we shall partially avoid the question of whether or not amorphous carbon films with complete sp^3 bonding can be referred to as "amorphous diamond". To be precise, this term should not be used since diamond specifically refers to a crystalline structure. For lack of a concise term to describe this material, we suspect that amorphous diamond will be used. The first question, however, that must be answered is whether completely sp^3 bonded amorphous carbon is even possible.

5. MORPHOLOGY CLASSIFICATION

In the area of amorphous and microcrystalline thin films, where adatom mobility is generally low, random aggregation leads to clustering and clustering leads to random competition for cone growth[35]. This possible fractal model is currently being developed to describe quantitatively[36] the cauliflower-like top surfaces and columnar cross-sectional morphologies which are related to the internal void networks which define the columns.

In a similar fashion it is expected that a quantitative description of the grain boundary structure of large-grained diamond films will be a critical link for quantitative preparation–property relations for many properties. For instance, thermomechanical properties, including thermal expansion, adhesion, toughness and hardness, will not be predicted by simply considering the intrinsic properties of diamond but will require an intimate knowledge of the exact grading of the film's crystal structure with film thickness, the impurities and adhesion at the internal grain boundaries, and the exact way in which grain boundaries are interconnected (e.g. knowledge of nucleation density, renucleation rate and rules of growth evolution). Also, properties such as thermal conductivity, electronic conductivity, dopant diffusion, optical scattering, coefficient of friction, dielectric breakdown, acid and radiation resistance, and oxidation behavior are all expected to have some connection with the detailed nature of the grain boundary network.

Very little is known about morphology evolution models for large-grained polycrystalline films. In the structure zone model classification scheme[37] of morphology, such films would be classified as zone 2, but this model does not describe evolution. The only quantitative model developed to date for considering the non-random rules of crystals competing for growth when they come into intimate contact, is a 20 year old model developed by van der Drift[38]. This model, although useful in guiding our thinking, does not consider such factors as twinning, poisoning of certain crystal faces, renucleation and relative growth rates of different crystal planes. Only recently has this model been modified[39] to consider particle

drift (mobility) between adjacent crystal planes due to factors such as directional ion bombardment. Thus new models will have to be developed.

It is important to have first a conceptual model that contains realistic details of morphology evolution. To date, our preparation and characterization efforts have yielded films spanning the range from microcrystalline (Fig. 1) to large-grained continuous films (Fig. 2) to semicontinuous films with some large polyhedral grains indicating a high degree of twinning (Fig. 3). These various morphologies represent quite accurately the range of morphologies seen in the literature, as reviewed above. In Fig. 1 the corroborating evidence for diamonds was transmission electron diffraction, while the thicker films in Figs. 2 and 3 were characterized by X-ray diffraction and Raman spectroscopy. The literature, furthermore, shows that the diamond crystallite size increases with increasing film thickness and that renucleation and twinning can alter this growth evolution. Also, factors such as surface preparation are known to control initial nucleation density (see Fig. 4).

In Fig. 5 is a representation of all these factors. It shows that a real surface is not smooth. The fact that no scale was placed on this figure was purposeful since roughness can occur at all length scales. Exactly at which levels of roughness nucleation occurs remains to be understood and is probably due to a complex
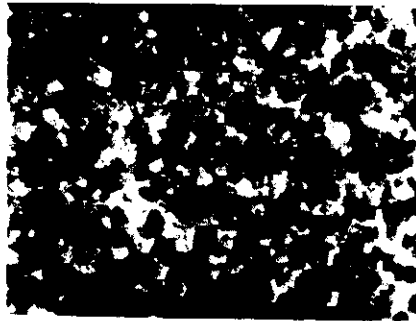

Fig. 1. TEM micrograph of a thin (100 nm) diamond film on a silicon substrate.
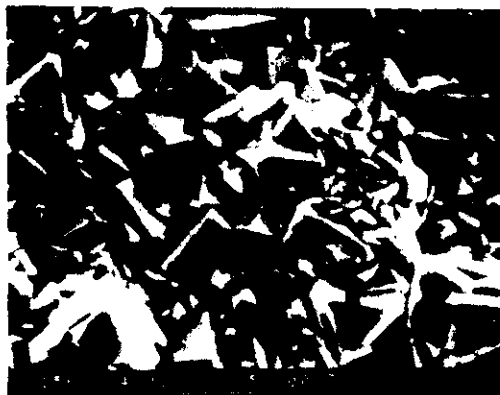

Fig. 2. SEM micrograph of a large-grained polycrystalline film of diamond on silicon. The nucleation density is smaller than in Fig. 1.

interface chemistry and structure (indicated by the broken lines). Regardless of the nucleation density, crystals nucleate and initially grow unaffected by surrounding crystallite until they come in contact. Thus by simply controlling nucleation density

Fig. 3. SEM micrograph of diamond on silicon in which smaller diamond crystal clusters (about 1 μm) partially cover the substrate and are dwarfed by a large twinned polydedral crystal. The nucleation density is smaller than in Fig. 2.
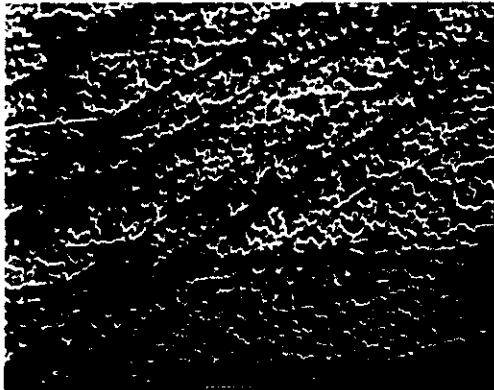

Fig. 4. Lower magnification SEM micrograph of a similar area to that in Fig. 3. The individual scratch marks on the substrate can be seen, the nucleation and crystallization thus resembling, in a general fashion, ice formation on a window in winter.
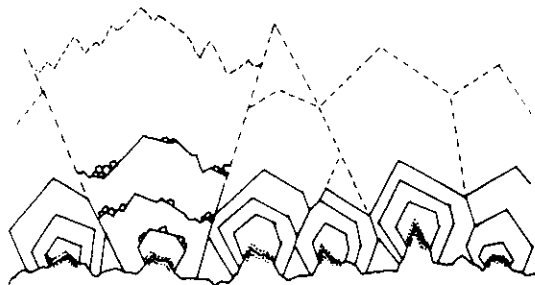

Fig. 5. Schematic representation of the evolutionary selection of diamond crystal growth.

the range of crystallite-size morphologies can be controlled. In one portion of Fig. 5 the effects of renucleation (or twinning) are schematically represented and are shown to create finer-grained and more complex morphologies.

Although additional factors and details will ultimately have to be added, this model should have some utility as we design new experiments and categorize morphology evolution more closely. For instance, as we come to understand the growth of diamond on different crystallographic faces, the final film morphologies will begin to give information on the relative growth rates of different faces and, at least, the slow growth rate planes. Thus, carefully designed experiments should link kinetic and mechanistic model studies of film growth with morphology evolution.

ACKNOWLEDGMENTS

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