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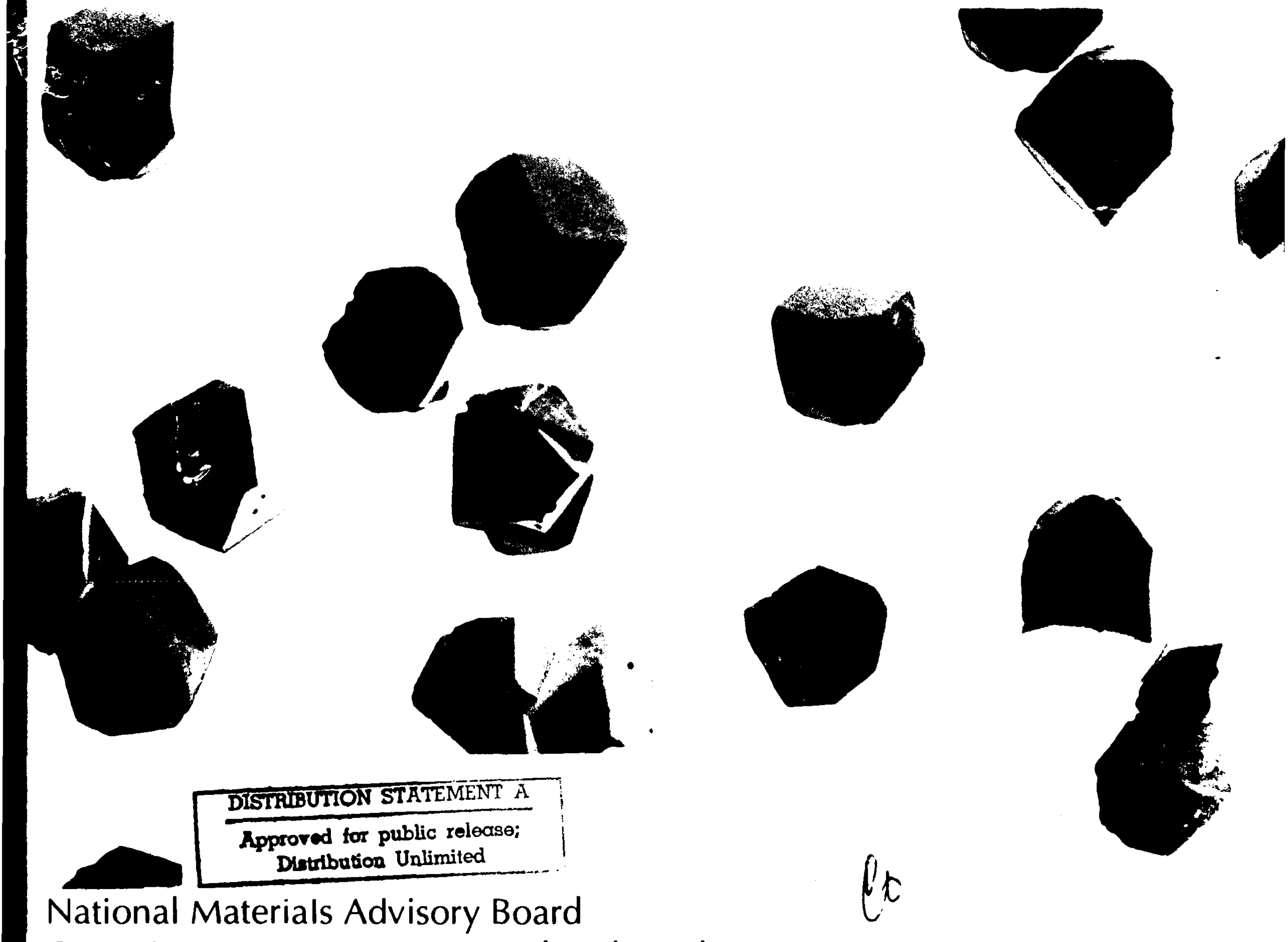
STATUS AND APPLICATIONS OF DIAMOND AND DIAMOND-LIKE MATERIALS: AN EMERGING TECHNOLOGY



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STATUS AND APPLICATIONS OF DIAMOND AND DIAMOND-LIKE MATERIALS: AN EMERGING TECHNOLOGY

STATUS AND APPLICATIONS OF DIAMOND AND DIAMOND-LIKE MATERIALS: AN EMERGING TECHNOLOGY

Report of the Committee on Superhard Materials

NATIONAL MATERIALS ADVISORY BOARD
Commission on Engineering and Technical Systems
National Research Council

NMAB-445
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1990

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This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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Cover: *Small single crystal diamonds produced by APCI filament assisted CVD process (Courtesy of Air Products and Chemicals, Inc.)*

Frontispiece: *Continuous polycrystalline diamond coating produced by APCI filament assisted CVD process (Courtesy of Air Products and Chemicals, Inc.)*

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ABSTRACT

Recent discoveries that make possible the growth of crystalline diamond by chemical vapor deposition offer the potential for a wide variety of new applications. This report takes a broad look at the state of the technology following from these discoveries in relation to other allied materials, such as high-pressure diamond and cubic boron nitride. Most of the potential defense, space, and commercial applications are related to diamond's hardness, but some utilize other aspects such as optical or electronic properties. The growth processes are reviewed, and techniques for characterizing the resulting materials' properties are discussed. Crystalline diamond is emphasized, but other diamond-like materials (silicon carbide, amorphous carbon containing hydrogen) are also examined. Scientific, technical, and economic problem areas that could impede the rapid exploitation of these materials are identified. Recommendations are presented covering broad areas of research and development.

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Valuable briefings were presented to the committee by Professor Robert Davis, North Carolina State University, who discussed epitaxy, doping, and characterization of nanocrystalline β SiC thin films, and Dr. John W. Coburn, IBM, who spoke on mechanistic aspects of diamond film deposition. The committee acknowledges their assistance with thanks.

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SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

Recent success in deposition of diamond and diamond-like coatings on a variety of substrates at practical growth rates is one of the most important technological developments in the past decade. It places within the reach of science and industry an opportunity to exploit the many desirable extreme properties of these materials (e.g., modulus, hardness, thermal conductivity, high breakdown voltage). Indeed, the ultimate economic impact of this technology may well outstrip that of high-temperature superconductors. Consequently, it is imperative that the United States take a leading role in the commercialization of diamond technology.

The committee focused on materials that can be grown at practical growth rates by various vapor-phase techniques. These include principally diamond, diamond-like hydrocarbons (DLHC), and diamond-like carbons (DLC).

- **Diamond**--This refers to crystalline diamond grown at relatively low pressure by various chemical vapor-deposition (CVD) processes in the presence of hydrogen and hydrocarbons such as methane. Substrate temperatures generally are required to be above 600°C. Surface morphology is usually faceted.

- **Diamond-like hydrocarbons (DLHC)**--These are metastable, amorphous materials prepared by various techniques (e.g., ion beam deposition) involving thermal decomposition of hydrocarbons and having atomic number densities greater than approximately 0.19 g-atom/cm^3. Hydrogen content ranges from 17 atomic percent to 60 atomic percent. Properties vary widely, depending on hydrogen content; surface finish is usually optically smooth, and substrate temperature requirement is low (<150°C).

- **Diamond-like carbons (DLC)**--There is evidence to suggest that hydrogen-free DLC films exist. These might be considered "microcrystalline" diamond, but much work remains to further describe their structure and properties.

- **Other materials**--In addition to the foregoing, the study includes a discussion of high-pressure diamond to provide background for the low-pressure processes and to indicate technological opportunities for the more conventional approach to diamond manufacturing. Also, a brief description of related materials involving boron, carbon, nitrogen, and silicon is given, with particular emphasis on SiC and BN.

The ability to deposit diamond and diamond-like films on a variety of substrates (including diamond-like materials on paper and plastics) vastly expands the potential application areas for these materials over that possible with high-pressure, high-temperature technology.

Although current applications in actual production are limited to high-modulus tweeter speaker cones (for improved high-frequency performance) and instrument windows, other uses are being actively pursued. The committee felt that there are applications that have not been realized but which exhibit potential for high payoff, assuming adequate funding.

In electronics, there is potential payoff in the following applications:

- High-temperature electronics for space with improved heat dissipation capability via the T^4 dependence for the radiation of energy.

- Cold cathodes (current densities greater than 1000 A/cm^2) that take advantage of expected low work function.

- Thermal conductors and heat sinks, particularly for electronic packages.

- High-power, high-efficiency radar electronics, with a potential for a hundredfold increase in power capability over silicon transistors.

- Solar-blind detectors, which take advantage of the large energy gap (greater than 6.4 eV) of BN.

In optics, potential payoffs could occur in the following:

- Anti-abrasion, anti-erosion coatings for infrared lenses and windows. Some success has already been achieved, for example, in applying diamond-like coatings to ZnS and ZnSe windows using a Ge-C intermediate layer.

- Anti-abrasion coatings on optical fibers for fiber-optic-guided (FOG) missiles.

- Compact ultraviolet lasers (for diamond, this requires a stress-induced conversion to a direct-gap material, possibly by a strained superlattice approach).

- Large single-crystal optical elements for use in infrared devices (e.g., windows and lenses).

Other potential applications could include the following:

- Abrasion-resistant coatings for computer disks and read-write heads.

- Machine tool guides to produce precise, very reproducible parts.

- X-ray lithographic masks.

- Anti-friction (low-friction) coatings for prosthetics.

- Corrosion protection and passivating films.

As more and more potential applications of diamond and diamond-like films became apparent, it was clear that the impact of this emerging technology on the defense, space, and commercial sectors could rival that of high-temperature superconductors but with more immediate applications. For this to happen, however, certain technical and economic problem areas must be identified and decisive addressed. Also, some approaches and policies that have been carried out correctly in the past should be encouraged and promoted. Few applications have as yet reached the marketplace; the enthusiasm of workers in the field is based substantially on the feelings that applications—often completely unforeseen—follow when a product with unique properties is developed.

CONCLUSIONS AND RECOMMENDATIONS

This emerging technology must be exploited. The following conclusions and recommendations address those areas that the committee feel will expedite this exploitation.

Conclusion 1

While General Electric and DeBeer have the bulk of the high-pressure diamond market, Japan apparently leads in vapor-deposited diamond research and development. However, the ability to transfer a technological development from the laboratory stage into useful applications can be the most difficult part in the growth of a new technology. Fortunately, in the case of diamond and diamond-like films, it appears that transfer has been facilitated by the excellent university, industry, and government interactions that have developed in this country. As a result, many companies, large and small, are now growing films in the United States after receiving training from government- and industry-sponsored programs.

Recommendation

Funding for university, industry, and government programs that will turn this emerging technology into a national pivotal technology with important useful applications must be continued and expanded in the future. The programs should be interdisciplinary, with theoreticians working with chemists, optical scientists, electrical engineers, and materials scientists to establish relationships among growth processes, structure, and properties. They should be carefully coordinated with and should draw upon the results of the individual basic research programs discussed in Conclusion and Recommendation 2. In order to ensure the greatest impact, emphasis should be placed on the optimization and use of combinations of properties (e.g., hardness and infrared transparency for window coatings) for well-defined applications.

Conclusion 2

The new films can exhibit many of the extreme properties that make diamond attractive but the effect of variables such as hydrogen content, other impurities (dopants), crystallinity, and sp^3/sp^2 ratio on mechanical, electrical, and optical properties is not well understood. An appreciation of the influence of additional elements in the diamond lattice on, for example, tribology could be of considerable industrial significance. Thus, the ability to produce films with predictable material properties to satisfy specific application requirements is currently lacking.

Recommendation

A coordinated interagency effort is recommended to address fundamental problems that have arisen in attempts to exploit diamond and diamond-like technology applications. Among the most pressing problems that should be addressed are:

- Nucleation and growth processes, with specific emphasis on increasing growth rates of both diamond and diamond-like films and on growing larger high-quality single crystals of diamond for electronic and optical applications. An integral part of this study should be substrate development and adhesion to substrates. Current work involves deposition from vapor;

other possibilities should be explored. Much needs to be done to enable deposition over large areas and at lower temperatures.

- Growth of cubic BN films and crystals, with specific emphasis on their use for ultraviolet detectors (BN can be doped both p and n type) and solar-blind detectors.

- Modulated structures incorporating layers of BN and diamond, for example, to develop materials that are harder and/or tougher than diamond.

- Cold cathode development for high-power electron sources (greater than 1000 A/cm^2). The basic question to be resolved relates to determining the degree of (negative) electron affinity of the film materials.

- Development of a predictive capability for the stability of various boron, nitrogen, and carbon alloys and "superdense" carbons through the use of fundamental structure calculations. One question that should be answered: "Is there anything beyond diamond with useful extreme properties?"

Conclusion 3

- Attaining successful electronic devices requires successful controlled doping of diamond both by CVD and by ion implantation.

Recommendation

Basic understanding should be developed, through theoretical studies, of doping and defect formation and their influence on the band structure. Development and understanding of processes for both p-type and n-type doping should also be pursued.

Conclusion 4

The rapid growth of this emerging technology coupled with the wide variety of materials it can produce (e.g., crystalline and amorphous materials containing large or small amounts of hydrogen) has led to several different nomenclature schemes, with some resulting confusion.

Recommendation

The committee recommends that a uniform system of nomenclature be used based on the following principles:

1. Diamond films - true crystalline diamond films as produced by a variety of CVD techniques.

2. Diamond-like films (DL) are of two types:

   - Diamond-like hydrocarbons (DLHC) - amorphous films grown by a variety of ion-assisted deposition processes and the decomposition of hydrocarbon gases. These films generally contain between 15 percent and 60 percent hydrogen and have atomic number densities greater than 0.19 g-atom/cm^3.

   - Diamond-like carbons (DLC) - amorphous hydrogen-free carbon films having atomic number densities greater than 0.19 g-atom/cm^3.

1

INTRODUCTION

This study is motivated, in large measure, by recent discoveries that have permitted the growth of crystalline diamond by chemical vapor deposition at practical growth rates. Chemical vapor deposition of diamond has enormous technological potential in areas as diverse as electronics, optics, biomedical implants, abrasives, cutting tools, bearing surfaces, and heat sinks. The related diamond-like materials show great potential for tribological surfaces, corrosion protection, passivating layers, and diffusion barriers as well as in photolithography.

By way of background, annual world production of natural rough diamonds is about 94 million carats (18.7 tons). Synthetic production in weight terms is much larger, possibly 66 tons. Imports of industrial-quality artificial diamonds amount to about 51 million carats (10 tons). Sale price is slightly over $1/carat.

Vapor-grown diamond and diamond-like materials may play an important role in a wide range of industries. Their ultimate economic impact may well outstrip that of high-temperature superconductors. However, despite this promise, there are relatively few applications currently being realized.

Many of the most exciting applications of both diamond and the diamond-like materials arise from their extreme properties, or combinations of properties, with hardness sometimes unimportant or of secondary importance.

SCOPE

This report reviews the present status of vapor-grown diamond, the diamond-like materials, and related solids such as SiC and cubic BN. Current developments are considered in a broad context, and directions for future work are recommended.

The field of superhard materials is rapidly evolving and has diffuse and expanding boundaries. It is not an exaggeration to say that there has been an explosion of interest in the subject. Figure 1-1 shows the trend in numbers of scientific papers published in the past 20 years. The curve is sharply upward, with no indication of peaking.

At the risk of incompleteness, it was necessary to make some arbitrary judgments about topics to include. This inevitably reflects the experiences of the members of the committee and should not necessarily be regarded as a value judgment about the relative importance of topics.

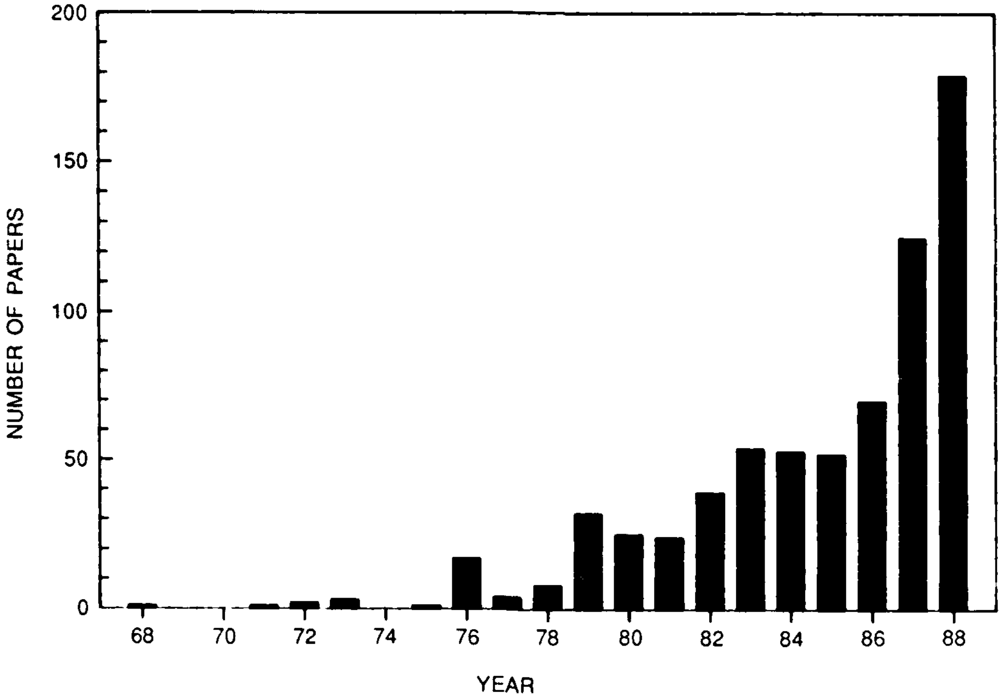

FIGURE 1-1 Number of papers published in scientific journals on low-pressure growth of diamond and diamond-like materials. (Source Yalamanchi and Thutupalli, 1988)

The types of materials considered may be categorized by their elemental composition. Most of the materials considered fall in the "composition tetrahedron" shown in Figure 1-2 and are compounds or solid solutions involving the elements boron, carbon, nitrogen, and silicon. These low-atomic-weight elements also form strong covalent bonds with hydrogen, which leads to a class of hydrogenated, typically amorphous, solids discussed later.

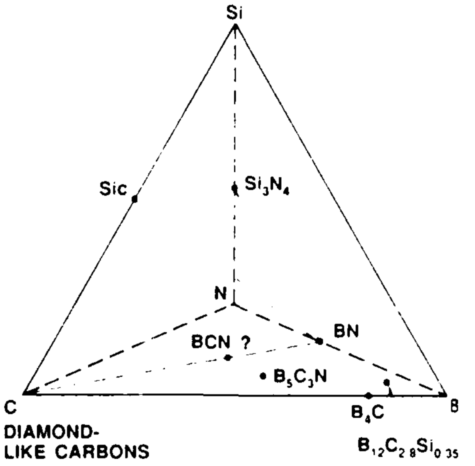

FIGURE 1-2 Hard materials in the composition tetrahedron C-B-N-Si. Other hard materials not shown include amorphous hydrocarbons and compounds with other B/C ratios, B-O compounds, and C-N compounds.

The major emphasis is on crystalline diamond and the so-called diamond-like materials. For the latter the categorization method proposed by Angus and Hayman (1988) is used; coverage is restricted to carbons and hydrocarbons with atomic number densities greater than approximately 0.19 g-atom/cm^3. The amorphous diamond-like materials have higher number densities than other carbonaceous materials and have a significant fraction of sp^3-bonded carbon sites.

Cubic BN and both hexagonal and cubic SiC are considered because they are structurally related to diamond and have overlapping areas of application. Other recently reported hard materials in the C-N and B-O systems are noted but not discussed. The committee has arbitrarily chosen not to include BeO, Al_2O_3, BP, AlN, Si_3N_4, and the garnets. No doubt these materials will compete for many of the same applications discussed in this report.

NOMENCLATURE

A confusing and inconsistent nomenclature has arisen to describe the diamond-like materials. The committee made an arbitrary choice of terms for use in this report. The generally accepted generic term, "diamond-like materials," is used to describe all carbon and hydrocarbon solids with atomic number densities greater than approximately 0.19 g-atom/cm^3. It is accurate in that the diamond-like phases have exceptional hardness, a significant proportion of sp^3 carbon atom sites, and atomic number densities between those of crystalline diamond and the adamantanes.

There appear to be two main classes of diamond-like solids (i.e., nonhydrogenated and hydrogenated). These are referred to in this report as diamond-like carbons and diamond-like hydrocarbons respectively. In some cases the abbreviations a-C (amorphous carbon) and DLC are also used to refer to the diamond-like carbons and a-*C:H* and *DLHC to refer to the diamond*-like hydrocarbons. A summary of the principal terms used to describe the diamond-like materials is given in Table 1-1.

TABLE 1-1 Nomenclature for Diamond-Like Materials

Nonhydrogenated	Hydrogenated
Used in This Report	
Diamond-like carbons	Diamond-like hydrocarbons
a-C	a-C:H
DLC	DLHC
Not Used in This Report	
Dense carbons	Dense hydrocarbons
a-D	
i-C	
Hard carbons	

BACKGROUND

Hardness is one of the oldest and yet most poorly understood of all the physical properties of solids. The theory of hardness has remained essentially a semiempirical science, at least until very recent years. Relatively few studies are available that attempt to relate hardness to basic notions of bonding and structure (Cohen, 1986; Zhogolev et al., 1981; Goble and Scott, 1985). There are useful empirical correlations of wear resistance versus lattice energy per unit volume (Plendl and Gielisse, 1962) and bulk modulus versus some function of interatomic spacing (Cohen, 1985). Similarly, hardness correlates strongly with atomic number density and with bond energy density. This is shown in Figure 1-3, which is a plot of microhardness versus atomic number density for diamond-cubic and zinc-blend solids (Angus et al., 1988). The extreme values of hardness of diamond, cubic BN, and a-C:H are clearly evident.

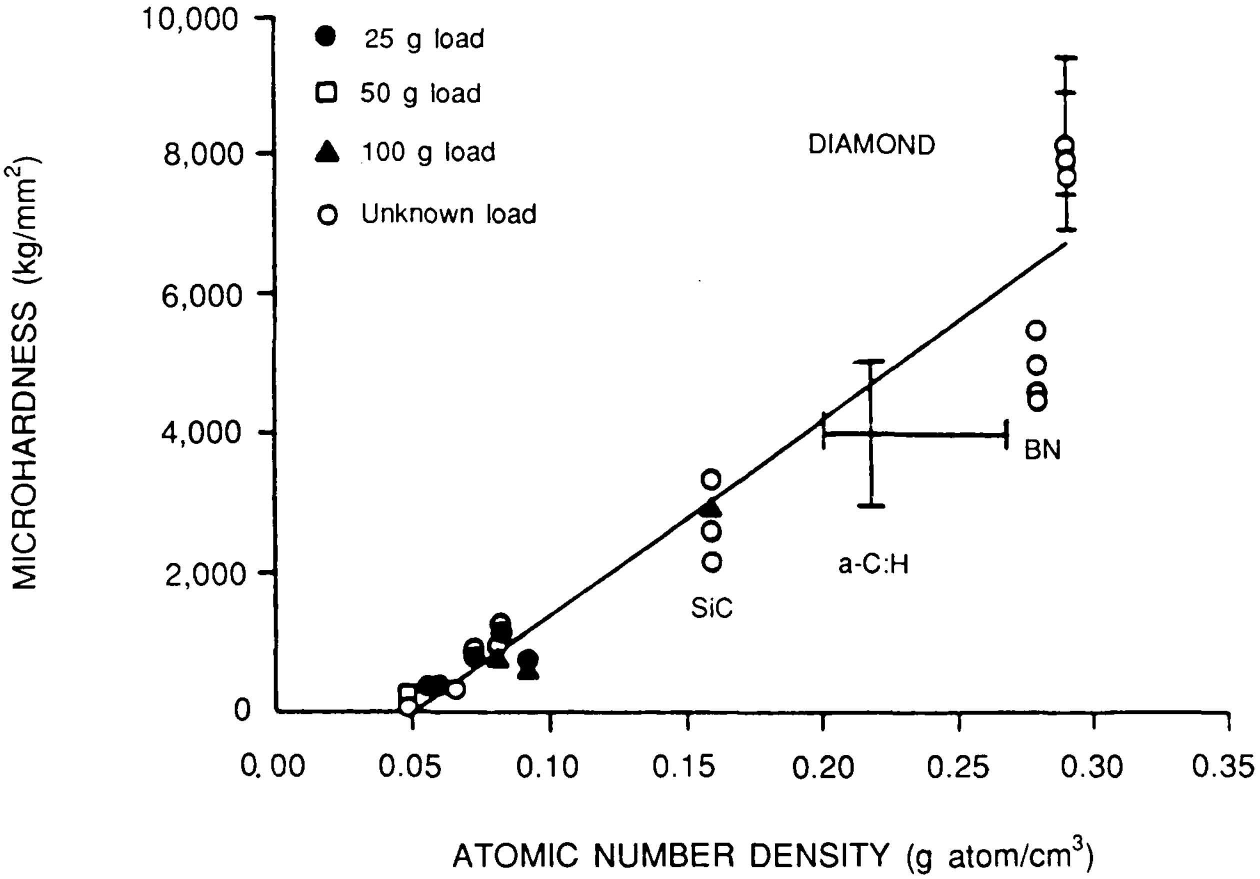

FIGURE 1-3 Microhardness versus atomic number density.

High-Pressure Synthesis of Diamond and Cubic BN

The General Electric Company was the first to reveal a successful process for growth of diamond at high pressure and high temperature (Bundy et al., 1955). Graphitic carbons in the presence of a liquid metal solvent-catalyst are brought into the temperature-pressure range where diamond is the thermodynamically stable phase and crystals spontaneously nucleate and grow (Figure 1-4). Since 1955 the growth of abrasive grain up to about 1 mm at high pressures and temperatures has matured to become a routine manufacturing procedure. About 90 percent of industrial diamond abrasives are now synthesized. In terms of size, shape, and toughness, the process provides a reproducibility and tailorability not found in natural materials. General Electric, DeBeers, Sumitomo, and the Soviet Union now provide high-pressure grit on the world market.

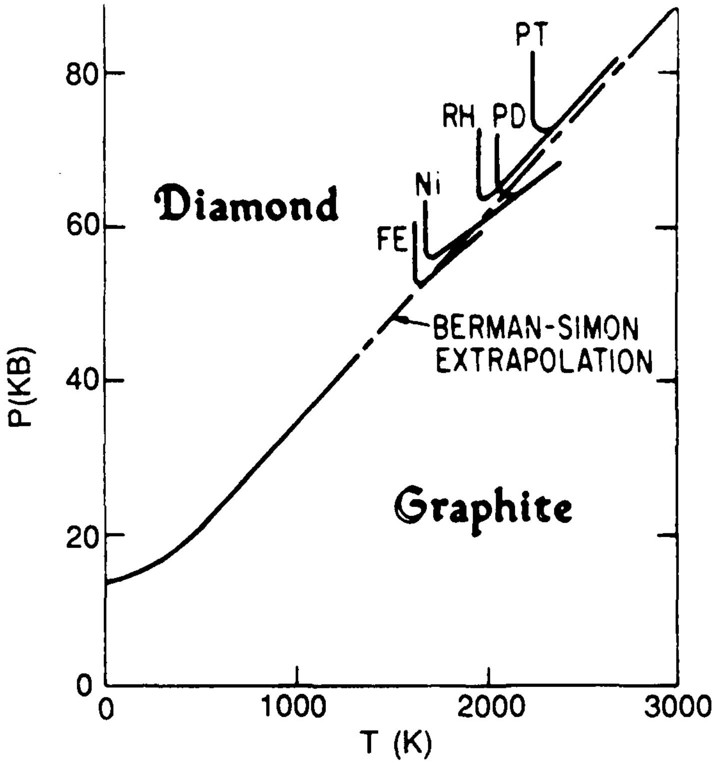

FIGURE 1-4 Equilibrium phase diagram for the carbon system. The P-T curves for several diamond-liquid metal eutectics are cross-plotted on the diagram. These curves define the minimum P-T conditions for high- pressure diamond synthesis by the solvent-catalyst method. The region for vapor-growth of diamond is located at pressures less than 1 bar and temperatures less than 1400 K.

The pressure range for high-pressure synthesis is generally 50 to 65 kb; the temperature range is from 1300 to 1700°C. The reaction mixture contains carbon (usually as graphite) in combination with the Group 8 elements, iron, nickel, and cobalt; manganese, aluminum, and boron are principal secondary elements. At the reaction conditions these systems exhibit a diamond-liquid two-phase region. Nucleation of diamond is rapid once the metal-carbon eutectic temperature is exceeded.

High-pressure diamond synthesis is a batch operation. The time cycle is determined by the desired grain size and optimization of die life. Growth rates can be very fast, but 1000 μm/hour is a useful average rate for grain sizes in the range of 50 to 1000 μm. The process becomes prohibitively expensive for sizes larger than about 1 mm, with the possible exception of crystals larger than 1 carat. Sintered materials are produced for cutting tools, wire-drawing dies, and well-drilling bits. Polycrystalline pieces up to about 50 mm in diameter, usually on a carbide base or within a carbide ring, are available.

It is possible to grow large gem-quality single crystals by a high-pressure thermal gradient process. Diamond crystals as large as 11 carats with a maximum dimension of 17 mm have been reported (Shigley, 1987). Crystals doped with either boron or nickel can also be produced. Sumitomo Corporation sells N-doped crystals at least 6 to 7 mm in maximum dimension for fabrication into cutting tools, microtome and scalpel blades, wire dies, anvils, and heat sinks.

Similar processes are used for cubic BN synthesis. The principal solvent-catalysts are alkali and alkaline earth metal nitrides and metal solvents similar to those used for growing diamond. Although cubic BN abrasive grain has been available since 1957, the first optically and electrically useful crystals were synthesized in 1987 (Mishima et al., 1987).

Metastable Diamond Growth

Metastable phases can form from precursors with high chemical potential if the activation barriers to more stable phases are sufficiently high. As the precursors fall in energy they can be trapped in a metastable state. For metastable diamond synthesis the undesired competing processes are nucleation of graphitic carbons and graphitization of existing diamond. The possibility of making diamond in the pressure-temperature range where it is thermodynamically unstable has been recognized for many years (Bridgman, 1955; Lander and Morrison, 1966); however, accomplishing practical low-pressure processes has taken decades to accomplish.

The first documented successful effort to grow diamond from vapor was initiated in 1949 by William G. Eversole at the Linde Laboratories of Union Carbide Corporation (Kiffer, 1956; Eversole, 1962). Eversole's work was contemporaneous with the earliest studies of high-pressure diamond growth. Angus in the United States (Angus et al., 1968) and Deryagin in the Soviet Union (Deryagin et al., 1968) continued these efforts, which ultimately led to proof that diamond could be grown by chemical vapor deposition from hydrocarbon gases and to some understanding of the role of hydrogen in the process. Although relatively rapid transient growth rates (0.1 μm/hour) of diamond were achieved in these early studies, graphitic carbons eventually nucleated on the diamond seed crystals, suppressing further diamond growth. Average growth rates were too low to be of commercial significance.

Several reviews describing the history of low-pressure diamond growth are available (Devries, 1987; Badzian and Devries, 1988; Angus and Hayman, 1988). These papers provide extensive bibliographies.

VAPOR GROWTH OF DIAMOND

The first reports of rapid low-pressure growth of diamond crystals on nondiamond substrates were by Deryagin's group in the Soviet Union (Deryagin et al., 1977; Spitsyn et al., 1981); however, the method of growth was not revealed. Worldwide interest in low-pressure diamond growth was stimulated by a series of remarkable papers published by workers associated with the National Institute for Inorganic Materials (NIRIM) in Japan (Matsumoto, 1985;

Matsumoto et al., 1982a,b; 1987a,b). Yaichiro Sato and Nobuo Setaka were leading figures in this effort. Methods for growth of diamond at rates of 10 μm/hour were described, and convincing characterization evidence was given. The *de novo* growth of faceted diamond without the necessity of a seed crystal was a significant advance over earlier methods.

Crystalline diamond can be grown by an astonishingly large variety of energetically assisted chemical vapor deposition processes. These may be conveniently, if somewhat arbitrarily, divided into two broad categories:

- Thermally-assisted chemical vapor deposition, for example, hot-filament-assisted processes.

- Plasma-assisted chemical vapor deposition (PACVD), for example, microwave-assisted processes.

These methods are described in detail later in this report. They can produce polycrystalline diamond films on a wide variety of substrates without the necessity of a diamond seed crystal. Although detailed molecular mechanisms are not known with certainty, all of the processes have elements in common; namely, the presence of atomic hydrogen and the production of energetic carbon-containing fragments under conditions that support high mobilities on the diamond surface.

Average growth rates of polycrystalline diamond films are tens of micrometers per hour, but growth rates on the order of hundreds of micrometers per hour have been reported in high-energy systems. (Kurihara et al., 1988). Indeed, a growth rate of 30 to 40 μm per hour has been achieved with an acetylene torch (Hirose and Kando, 1988; Hirose, and Mitsuizumi, 1988). Diamond-on-diamond epitaxy has been reported (Spitsyn et al., 1981; Fujimori, 1987) but the epitaxial layer is not of high quality, with stacking faults, twins, and even microcracks along (111) planes. It is expected that heteroepitaxy of diamond will be accomplished in the near future. The uncontrollable nucleation of diamond nuclei has prevented the growth of large (i.e., greater than 1 mm) single crystals by vapor deposition.

DIAMOND-LIKE MATERIALS

Related research has led to the discovery of a new class of materials, the diamond-like solids. The diamond-like phases are distinguished by unusual hardness and chemical inertness. These properties apparently arise from the high proportion of sp^3 carbon sites. Several recent review articles give access to this literature (Angus and Hayman, 1988; Tsai and Bogy, 1987; Angus et al., 1986).

There appear to be two classes of diamond-like phases: the diamond-like hydrocarbons (a-C:H) and the diamond-like carbon (a-C). More is known about the diamond-like hydrocarbons than the diamond-like carbons. The diamond-like carbons may, in fact, include several different types of structures ranging from microcrystalline diamond to complex, amorphous materials containing significant amounts of both sp^2 and sp^3 carbon sites.

The diamond-like materials are made by energetically assisted deposition processes--for example, from rf plasmas--by direct deposition from low-energy (~100 eV) ion beams or by condensation from plasma arcs. As in the case of vapor growth of diamond, detailed molecular mechanisms are not known with certainty. However, evidence from several sources suggests that the metastable, amorphous diamond-like structures may be stabilized by the quenching due to the cold substrate.

APPLICATIONS

Applications of Diamond

The applications of diamond will stem from its extreme properties. Diamond has the highest values of atomic number density, hardness, thermal conductivity at 298 K, and elastic modulus of any known material (Table 1-2). It is the most incompressible substance known and has a thermal expansion coefficient lower than Invar. Diamond also has a high refractive index and optical dispersion. If nitrogen is absent, diamond is extremely transparent from 230 nm to at least 40 μm in the infrared (apart from a few intrinsic absorption bands from 2.5 to 6.0 μm).

Applications of diamond as an abrasive or as a cutting tool arise from its extreme hardness and high thermal conductivity. The ability to deposit diamond films over large areas will greatly expand these applications and should lead to many others as well. Diamond films may find application as wear-resistant coatings, wire-drawing dies, coatings for drills, and bearing surfaces. It may also be possible to employ diamond coatings as impact-protection coatings for rain erosion and small-particle impact.

TABLE 1-2 Some Properties of Natural Type IIA Diamond and Vapor-Grown Diamond

Properties	Type IIA	Vapor-Grown
Hardness, GPa	≈90*	80 - >90
Mass density, g/cm^3	3.515	2.8 - 3.5
Molar density, g-atom/cm^3	0.293*	0.23 - 0.29
Specific heat at 300 K, J/g	6.195	
Debye temperature, 273-1100 K	1860 ± 10 K	
Thermal conductivity at 198 K, W/cm/K	≈20*	10 - 20
Bulk modulus, N/m^2	$4.4\text{-}5.9 \times 10^{11}$*	
Compressibility, cm^2/kg	1.7×10^{-7}**	
Linear thermal expansion coefficient at 293 K, K^{-1}	0.8×10^{-6}***	
Refractive index at 589.19 nm	2.41726	≈2.4
Dielectric constant at 300 K	5.7 ± 0.05	≈5.7

*Higher than any other known material.
**Lower than any other known material.
***Lower than Invar.

The high thermal conductivity, low expansion coefficient, and strength of diamond provide high resistance to thermal shock. Windows for very-high-power lasers may take advantage of this combination of properties. Crystallume for example, has announced the commercial availability of 6-mm diameter x-ray windows. The high thermal conductivity has led to the use of diamond as a heat sink material in electronic applications. This application, and many others, will likely be expanded by the availability of large-area diamond films.

Natural and high-pressure synthetic diamonds are already used as instrument windows in specialized research applications. This is a natural application of vapor-grown diamond films; optical elements and diamond-coated optics are long-range possibilities. However, some applications require significant reductions in surface roughness and in optical absorption.

Diamond electronics is another long-range possibility. Diamond is a wide-band-gap semiconductor (5.5 eV) and, furthermore, has a high breakdown voltage ($\sim 10^7$V/cm) and a saturation velocity (2.7 X 10^7 cm/sec), higher than silicon, GaAs, or InP. Electron and hole mobilities are approximately 1900 and 1200 cm^2/V-sec respectively. However, the use of vapor-grown diamond as an active electronic component will require greater crystalline perfection than is now available. Many electronic applications will also require growth of heteroepitaxial diamond films, which at this time has not been achieved.

Applications of Cubic BN, SiC, and Other Materials

Cubic BN has a hardness second only to diamond and is unreactive with alloys of iron, nickel, and cobalt. These properties have led to important applications as an abrasive. It has potential applications as an active semiconductor device (it can be doped both n- and p-type) and as a heat sink material.

Silicon carbide is a commercially important abrasive material that can be made in tonnage lots at 1 atm pressure. Recent advances in the growth of large single crystals of SiC may lead to applications as an active electronic device material, as a heat sink, and possibly as a substrate for the heteroepitaxial growth of diamond from the vapor.

Boron carbide is used as an abrasive (although never achieving its initial promise in this application), as an energy-absorbing material in armor, and as a moderator in nuclear reactors. It is under serious study and shows promise for high-temperature thermal electric applications.

Applications of Diamond-Like Materials

As with crystalline diamond, the applications of the diamond-like materials stem from their extreme properties. Of particular importance are their hardness, chemical inertness, smoothness, and apparent impermeability. Also, these films can be deposited on cold, temperature-sensitive substrates (e.g., hardened steel), which opens up other potential applications.

The properties of the diamond-like hydrocarbons can be "tuned" by adjusting the hydrogen composition and by adding other functional groups. It may be possible to exploit this behavior to tailor the properties for specific applications.

The diamond-like materials may find principal applications as a wear-resistant coating and as a diffusion barrier and corrosion-resistant coating. Coatings on magnetic and optical disks are the most immediate possibilities. Hermetic coatings to protect optical fibers and high-temperature superconductors are other potential applications. These materials have been used as antireflection coatings on germanium optics because of their hardness and the ability to control their refractive indexes by varying the carbon/hydrogen ratio.

Diamond-like materials are being actively developed for high-resolution submicrometer-scale lithography. Excimer laser etching has been used to produce structures as small as 0.13 μm. These materials can also be employed as a bottom layer in a two-layer resist system.

Other potential applications of diamond-like films include ultraviolet-absorbing coatings and coatings for photothermal energy conversion and photoreceptors.

INTERNATIONAL ACTIVITIES

It is difficult to make an accurate assessment of the relative positions of the various countries known to be doing research in diamond and diamond-like materials. Groups in Japan are leading in practical applications of this new technology. Whether or not they have any greater insight into the fundamental issues of nucleation and growth is much less clear. According to an article in the New York Times (October 20, 1988), American experts acknowledge that Japan now holds a commanding lead in CVD diamond technology. Statistics from industry sources provide a comparison: in the past 5 years, of 573 patents granted in the new diamond technology, 488 were awarded to Japanese companies and only 28 were awarded in the United States. Soviet workers, particularly Deryagin's group, have a long history in low-pressure diamond research (Badzian and DeVries, 1988). However, the committee is aware of no applications of this technology in the Soviet Union. This may, of course, be due to the unwillingness of Soviet researchers to divulge detailed descriptions of their efforts. DeBeers has supported low-pressure diamond synthesis, at least sporadically, since the early 1970s and currently is supporting work on CVD growth of diamond in both England and South Africa, but apparently not at the intensity of the Japanese effort.

Leadership in diamond-like technology appears to be more evenly diffused. There are leading research groups in Japan, the Federal Republic of Germany, Australia, Great Britain, and the United States.

RESEARCH AND DEVELOPMENT ISSUES

The new diamond science and technology transcend the boundaries of traditional materials science. Fundamental developments in this field will require contributions from organic chemistry, surface chemistry, plasma physics and chemistry, theoretical quantum chemistry, thin-film mechanics, and solid-state physics. A host of engineering and applied disciplines will be involved in applications work.

The basic molecular mechanisms involved in both nucleation and growth of diamond are not well understood. Special attention should be paid to those surface spectroscopies that can give insight into species and processes on the growing crystal surface. It is unlikely that high-rate growth of optical- and semiconductor-grade diamonds can be achieved without better understanding of the molecular mechanisms involved in both nucleation and growth.

Virtually all current research efforts involve growth of diamond from the vapor. Other low-pressure processes--for example, growth from liquids--should be explored as alternative avenues for growth of large, high-quality diamond crystals.

The vapor growth of diamond for sophisticated optical and electronic applications by current techniques is limited by two factors: (a) the uncontrolled formation of independent diamond nuclei during growth and (b) the appearance of growth errors during extension of the lattice. The first leads to polycrystalline films with a typical crystal size of 1 to 10 μm and surfaces that are faceted. The second leads directly to defect structures within the diamond lattice.

Diamond-on-diamond epitaxy has been achieved, and the epitaxial layers are approaching electronic-grade quality. The relationships between growth parameters and the types of defect structures produced should be explored. Heteroepitaxy on silicon, SiC, or other sacrificial substrates would also be highly desirable but has not been achieved yet as far as the committee knows. Also, achieving substitutional n-type doping in diamond is still problematical.

Fundamental theoretical studies of the types of molecular structures that lead to "hardness" and basic studies of the atomic-scale processes during inelastic deformation are appropriate. This research could lead to new superhard materials and to designed modifications of existing superhard materials.

The scale-up and engineering of plasma processes for production of diamond and diamond-like films is important for the development of practical, large-scale applications. Rapid growth of uniform, high-quality films over large areas that exhibit good adhesion to their substrates will be required for many applications. Here the application of fundamental concepts of plasma chemistry and plasma physics is in order. The deposition of crystalline diamond films at low temperatures (<300°C) would permit a host of applications involving temperature-sensitive substrates. Deposition on steel or other metals, of strongly adherent films would be a major achievement in saws, drills, and similar tools.

Growth of diamond at high pressures will continue to be an important commercial process. Basic research in the synthesis of diamond and related materials at high pressures should be supported.

The diamond-like phases should be recognized as a new class of materials. Much work on the influence of elemental composition and process variables on the structure and properties of the diamond-like hydrocarbons (a-C:H) is required before these materials can be fully exploited. Current a-C:H films are highly compressively stressed and are thermally unstable above 400°C. The structure and properties of the diamond-like carbons (a-C) and their relationship to microcrystalline diamond should be explored.

Assuming solutions to adhesion problems, the largest impact of the diamond-like phases may be in tribological coatings and as diffusion barriers. However, the influence of additional elements, functional groups, and ambient gases on friction and wear characteristics is not known. The permeability of diamond-like hydrocarbons is expected to be very low. However, careful measurements of permeability as a function of process conditions and film composition have not been made.

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2

GROWTH PROCESSES

This chapter addresses deposition processes of superhard materials as defined in Chapter 1. Although it is the discovery of diamond growth from a low-pressure vapor by enhanced CVD techniques that is the focus of this report, the wider range of materials and methods is also described.

The high-temperature, high-pressure (HPHT) techniques for growth of diamond and cubic BN, which are now over 30 years old, can be considered a mature technology. However, there are still some key scientific questions relating even to basic nucleation and growth and potential technological developments (large-area single crystals with controlled purity and perfection) that must still be explored. If homoepitaxy of diamond proves to be important, an in-country capability, or at least expertise, in the preparation of HPHT substrate may be critical.

It is the control of nonequilibrium gas phase chemistry that allows for the growth of diamond at low pressures. Over the past 10 years workers have moved from a generally held belief that no practical process for low-pressure diamond growth was possible to the current realization that nearly any method that produces a ready supply of atomic hydrogen and some carbon-containing species works. Furthermore, the crystal quality and related morphology are remarkably similar for all the various processes and their variants, even though they range from plasma-enhanced processes to heated-filament-assisted nonplasma processes. During the course of the writing of this report even an atmospheric oxyacetylene torch has been reported to produce polycrystalline diamond films. Such observations suggest a common mechanism of nucleation and growth. However, there are differences, such as the growth rates reported varying over 3 orders of magnitude (0.1 to 300 μm/hr). Also, scratching the substrate with diamond (or other abrasive) is essential for high nucleation densities ($>1/\mu m^2$) in some processes but not others (e.g., thermal plasmas and atmospheric torch). To compare the various deposition techniques, much more needs to be known about the generation and transport of critical vapor species to the growing film surface as well as surface processes during both nucleation and growth.

Key technological concerns include the deposition rate, the area that can be uniformly covered, the throwing power of the process, the range of substrates on which diamond can nucleate, the substrate temperature, and the energy efficiency of the process. Eventually a comparative parameter such as the mass deposited per unit time per unit power input could be used to compare each of the processes on an economic basis, but results are currently too sketchy. Also, each application will weight the different components of such a parameter differently.

Although enhanced CVD processes for diamond growth have created a number of new application opportunities, there are a number of limitations. These include (a) the high substrate temperature (~1000°C) for optimum crystal perfection; (b) the large grain size, which leads to optical and IR scattering, high friction, etc.; (c) contamination from etching and re-deposition of the substrate and deposition system components in contact with the atomic hydrogen; (d) the higher defect densities reported in all CVD diamond; (e) diamond's low coefficient of thermal expansion compared to most substrate materials; (f) lack of adhesion; (g) high stress; and (h) lack of large area heteroepitaxial substrates. Certainly the hope is that, through further development of current techniques plus discovery of even other deposition processes, these problems can be overcome. Of course, in formulating new applications for CVD diamond it is well to keep in mind basic limitations that are inherent for diamond materials in general. For example, the upper use temperature for conventional diamonds in air is no more than approximately 600 to 700°C, and a similar limitation is expected to apply to CVD-grown material.

For many applications the substrate temperature is the limiting factor, and often temperatures above 500°C are unacceptable. A number of physical vapor deposition (PVD) techniques, involving ion bombardment, have been developed over the past 18 years to produce these materials at close to room temperature. However, the DLC and DLHC have lower crystallinity, higher residual stress, and lower hardness. To their credit, DLC and DLHC films are smooth, dense, and reasonably hard and have a variable range of other properties such as refractive index, optical band gap, and electrical resistivity. A relatively unexplored area of deposition "space" is the use of both bombardment and chemical vapor deposition processes simultaneously at temperatures not exceeding 300 to 500°C. Such materials may have properties intermediate between the diamond and DLC and DLHC materials, possibly leading to new applications.

One final research and development (R&D) opportunity is the possibility of polycrystalline cubic BN films with grain size similar to that of diamond films. Whether analogous approaches might be successful remains to be seen. Microcrystalline cubic BN has been produced by ion-bombardment-mediated PVD processes (similar to DLC and DLHC), and this provides some hope. However, no successful attempts have been reported for crystalline cubic BN.

GENERIC AND FUNDAMENTAL ISSUES

The two principal superhard materials, diamond and cubic BN, can be synthesized by high-pressure, high-temperature (HPHT) processes in the stable thermodynamic region by static or dynamic methods in the case of diamond, or by low-pressure techniques in regions of thermodynamic metastability. The former is a mature manufacturing process and will be described first. About 90 percent of all industrial diamond used is synthesized by the HPHT process because it provides a reproducible product in terms of size, shape, and toughness (or friability). All cubic BN must be synthesized, since it does not occur naturally. Research and development effort in certain areas of this field in the United States appears to be very limited compared to activities in some other countries.

The vapor deposition of diamond now allows for preparation in many new forms--thin films over large areas, chemically bonded to a wide range of surfaces, on complex shaped surfaces, freestanding forms, powders, etc. It appears that cubic BN films with large crystal sizes (>1 μm) are possible, which would open up even further new materials opportunities. Several years ago it seemed as if polycrystalline films of diamond at practical growth rates could not be prepared at all, and now it appears that just about every technique that can provide an intense source of atomic hydrogen during growth works. This creates the frustrating situation of having too many choices. Ultimately it may turn out that there is no one best deposition method but rather that certain ones will be best for certain film forms or applications.

This section deals mainly with diamond and diamond-like materials--i.e., amorphous and nanocrystalline carbon both with and without hydrogen and with high gram-atom number densities ($\rho_n > 0.2$ g-atom/cm^3) (Angus et al., 1986)--since they are the only superhard materials for which a significant body of literature exists. The limiting value of hardness of DLC and DLHC films is still not known. Cubic BN has been prepared as a microcrystalline coating, but to date no films with crystal sizes above 200 Å have been reported, and the chemical and structural characterization of these materials is sketchy. The recent disclosure of a suboxide of boron of nominal composition of $B_{22}O$ (Badzian, 1988) as a material that can scratch diamond is also intriguing. This composition also can be prepared by reactive sputtering to have properties similar to that of the bulk material. However, such reports must be considered with caution, since even SiC has been known to scratch diamond. Superhard materials in the C-N system are yet to be explored.

If cubic BN can be successfully vapor-deposited as large crystals and polycrystalline films, it is expected that research on this material will increase dramatically, just as when diamonds were successfully deposited from the vapor and the result recognized. Deposition approaches analogous to those for diamond are under way in the United States and elsewhere.

In this report the deposition of superhard materials is categorized in a standard manner as chemical vapor deposition (CVD) and physical vapor deposition (PVD) processes. In general, CVD methods use gas-phase chemistry to control both the retention of the metastable phase when condensed on a surface and the details of the composition, impurities, defects, etc. In PVD it is usually ion bombardment processes that control the characteristics and thus the properties of the resulting metastable films. As mentioned earlier, it now seems that just about any process that efficiently produces atomic hydrogen and carbon-containing species can yield diamond films over some range of conditions. In some deposition processes both physical and chemical processes take place simultaneously, but such distinctions will not be made specifically. Very often the relative roles of the two different general processes are not well understood.

HIGH-PRESSURE, HIGH-TEMPERATURE PROCESSES

The first reproducible industrial process for making diamond was announced in 1955, and the synthesis of cubic BN was accomplished by 1957. Both phases were precipitated from solution at pressures >45 kb and temperatures >1100°C, where they are the thermodynamically stable phase. The unique chemistry for each of the two superhard materials is considered separately. A description is given of the critical mechanical equipment that makes the synthesis possible.

Materials Growth Processes

Direct Conversion

It is possible to make both diamond and cubic BN by direct conversion of graphite and hexagonal BN, respectively. This can be done both by static and dynamic processes, but for diamond the pressure range (>120 kb) and temperature are prohibitively high and not economically viable because of the limited life of carbide dies used in static processes. However, under dynamic conditions (shock), the conversion is practical, and the DuPont process provides a marketable product. Because of the short reaction time, the crystals range in size from submicrometer to several micrometers, and they are used primarily for polishing-grade material or for starting material for sintering.

For cubic BN the pressure-temperature (P-T) conditions are less severe than for diamond, and a directly converted product is available. The wurtzite form of BN, which is also hard, is made by shock synthesis and is used primarily for sintering polycrystalline aggregates.

Static or Indirect Process

The difficulties of direct conversion led to the development of processes to lower the pressure and temperature. This is accomplished by use of a solvent-catalyst system that permits growth to occur at conditions much nearer the diamond-graphite equilibrium line but at lower temperatures.

The static synthesis process consists of first raising the pressure to the desired value and then raising the temperature of the cell by resistive heating. The P-T conditions for growth are held for the desired time, and the power to the heater is decreased to zero. The pressure is then released and the cell removed for separation of the product.

The P-T conditions for both diamond and cubic BN are attained as described above, but the chemistry for the synthesis of the two materials is different. For diamond, the compositions are generally mixtures of Group VIII metals with graphite. Usually the metals iron, cobalt, or nickel are major components of the alloy with carbon, with manganese, aluminum, and boron the secondary components. The physical chemistry of these systems can be described in terms of a phase diagram of the selected metal alloy-carbon system (a T-X diagram) at pressures where diamond is a stable phase in equilibrium with a metal-rich liquid. In this system there exists a eutectic at lower P-T conditions than required for direct conversion. In these terms, the growth is from solution, and the driving force for nucleation is the difference in solubility between that of diamond and graphite under the HPHT conditions. Nucleation and growth begin as soon as the eutectic temperature of the system is exceeded. Some believe the process is better described as "catalytic," and the compromise term "solvent-catalyst" is frequently seen in the literature. There are still many things not understood about the nature of the solution and the transport in it under HPHT conditions.

The first requirement is a mechanical system that will reproducibly attain 50-65 kb and 1200-1700°C simultaneously. Since the material is produced in batches rather than continuously, it is an advantage to have as large a working volume as possible. There are several types of apparatus (e.g., uniaxial belts or girdles, tetrahedral, octahedral, and variations on the cube press, piston-cylinder) and cells (e.g., low and high aspect ratio). During the more than 30 years of experience in synthesizing diamonds, there has been a convergence in the use of uniaxial belts for manufacturing. The other methods have advantages for R&D purposes, but scale-up has generally favored the belt.

The belt consists of a central die, generally of cemented tungsten carbide, surrounded by a series of "belted" steel rings to keep the carbide in compression. Two symmetrically opposed tapered anvils are pressed toward the die hydraulically and are separated from carbide-carbide contact by a set of gaskets made from natural or synthetic pyrophyllite or soapstone-like material (Figure 2-1).

Carbide and pyrophyllite are the key materials used in this and most other high-pressure apparatus. The gasket provides mechanical, thermal, and electrical insulation and contains the cell and its reactants. The anvil-die-anvil combination is adapted to commercially available presses. The cost of setting up a large apparatus is estimated to be in the range of at least

$250,000 to $1,000,000. This equipment must be capable of repeated excursions to and from HPHT conditions. Die breakage is related to fatigue and work-hardening of the carbide dies and can be an important manufacturing cost factor. The supply and cost of carbide dies (especially for large volume) are probably key factors in limiting new entrants to the manufacturing of these materials. The attractiveness and relative simplicity of CVD as alternative processes will be obvious, as described later in this report.

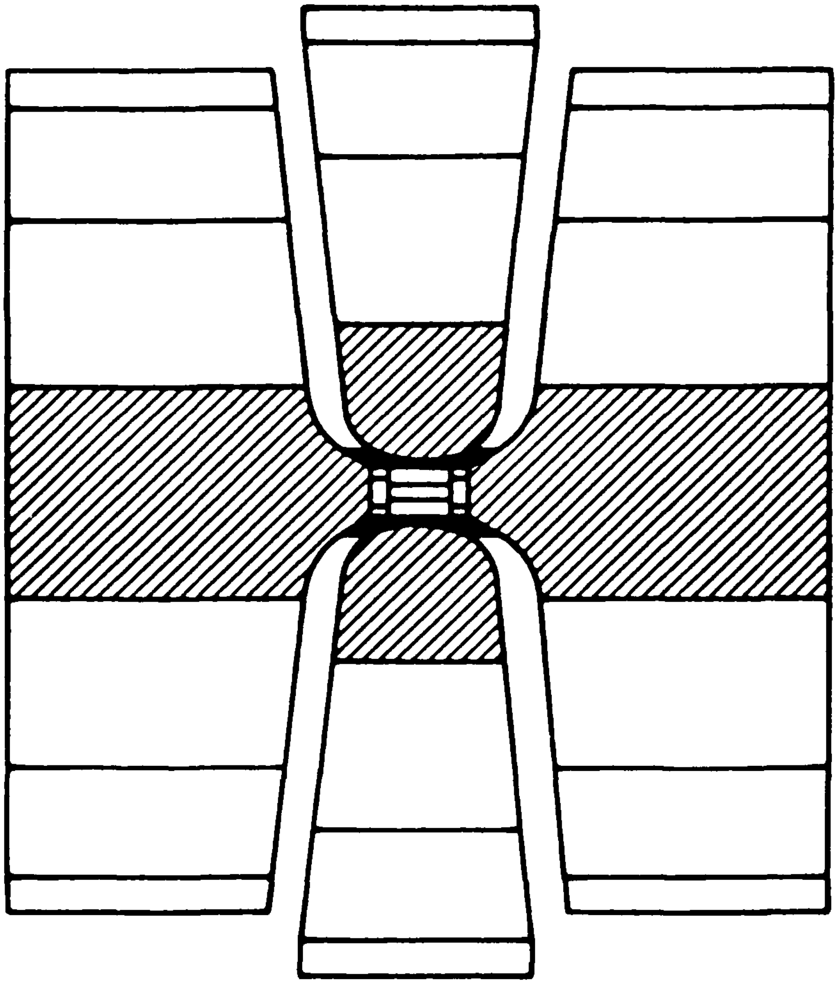


FIGURE 2-1 The Hall "belt" apparatus. Shaded areas are cemented carbide; black is gasket material.

There are many cell designs to cover the needed variations, but common to all is internal heating by passing a low-voltage high current through the cell. Direct heating usually means the current passes directly through the reactants (e.g., a mixture of iron and graphite for diamond synthesis). Indirect heating is used with nonconducting reactants (e.g., BN plus Li_3N mixture for cubic BN) by packing them in a conducting cylindrical sleeve or around a conducting core (graphite or metal). Cell variations result from the need to separate reactants from containers and to control the heat distribution.

Cubic BN Chemistry

The solvent-catalysts for cubic BN are based primarily on alkali or alkaline earth metals and their nitrides. The phase diagram for hexagonal BN with Li_3BN_2 is analogous to that of graphite with a metal. Cubic BN can also be synthesized from Group VIII metals with a bit of aluminum added and from other systems, but the water and acid solubility of the alkali and alkaline earth metals and nitrides favors easy removal of the product from these reactants.

Control of Crystal Size

The static process permits control of grain size simply by controlling the time the system remains at the desired P-T conditions. Carbon is transported from the graphite source through a thin metal film to the growing crystal. Most abrasive grain found in the marketplace is less than 1 mm in maximum dimension because the process becomes noneconomical if the growth time is too long. The practice has been to use sintered diamond when sizes greater than 1 mm are needed. The special case of large gem-quality crystals is considered below. Growth rates can be very high, but 1 mm per hour is commonly attained.

The nucleation rate can be controlled by varying pressure conditions above the eutectic temperature for both diamond and cubic BN. Nucleation can also be controlled by seeding with small diamond or cubic BN crystals.

Growth of Large Crystals

In 1970 a thermal gradient process for growing large crystals (>1 mm) in a controlled manner was developed (Figure 2-2). Using this technique, colorless, blue (B-doped), and yellow (N-doped) diamond crystals of gem quality were grown to about 6 mm in maximum dimension and about 1.3 carats weight. The crystal size at that time was primarily limited by cell size. These crystals were grown one at a time for 100 hours or more. Since that time Sumitomo and DeBeers have both scaled up the process to grow larger crystals and many at a time. Yellow crystals up to 7 mm in size are available (from Sumitomo Electric) for tools, windows, scalpels, anvils, etc. DeBeers has reported a crystal greater than 11 carats with a maximum dimension of 17 mm. The process requires large expensive equipment, which could be producing abrasive grain, so that some manufacturers have been reluctant to get involved. To improve the yield, many crystals must be grown at the same time by optimizing the use of the thermal gradient vertically in the cell of a belt apparatus. The gradient can be established in the cell with a sleeve heater, but then alloys with different eutectic temperatures must be used to allow growth in several layers in the cell. This is fairly simple for N-doped crystals, but there are fewer degrees of freedom for the aluminum alloys used to eliminate nitrogen and produce colorless and blue crystals. New alloy design is needed.

Cubic BN crystals to about 3 mm maximum dimension have been grown by thermal gradient methods, but good-quality untwinned crystals are rare. Sumitomo has taken up this challenge, and this situation can be expected to change. NIRIM (Mishima, et al. 1987) has grown cubic BN p-n junctions.

The production of large crystals is of considerable current interest for electronic, optical, and dielectric applications and should be re-evaluated in the United States, especially in light of the obvious commitment by Japanese and South African diamond manufacturers. However, if the CVD techniques continue to show promise, the difficulty of growth at high pressures may be bypassed as epitaxial techniques (perhaps on SiC crystals) are developed.

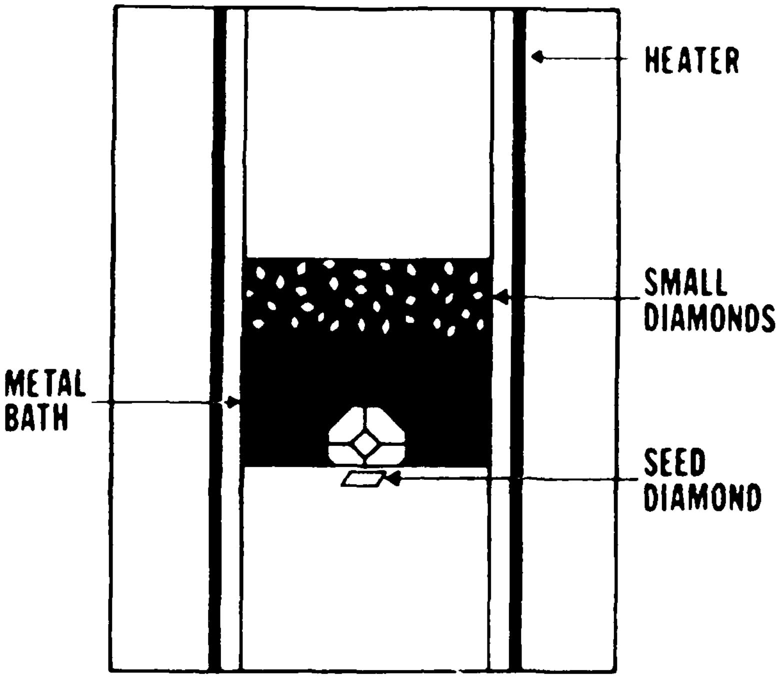


FIGURE 2-2 Cell design for growth of large crystals of diamond or cubic BN using a temperature gradient between carbon source and the seed crystal. For cubic BN, the transporting medium can also be an ionic melt.

Control of Crystal Shape

Diamond

The octahedron is the predominant growth form for natural diamond; the (100) and (110) faces are also common. It was found that the relative development of (111) and (100) could be controlled by the temperature of growth at a constant pressure. In a P-T plot of the diamond stability region (Figure 2-3), the cube (100) face predominates at the lower temperatures (near the metal-carbon eutectic) and the octahedron (111) at higher temperatures, near the diamond-graphite equilibrium curve. (This is opposite to the morphology changes in CVD diamond growth.) In between these extremes the cubo-octahedron predominates and, because this shape holds better in a binder, it is preferred. The morphology-temperature relationship is serendipitous and is essentially limited to yellow Type Ib diamond crystals, which predominate in synthesized abrasive grain. That the morphology is more than temperature-dependent is evident from results with the addition of aluminum to getter nitrogen, where only octahedra form is the fast growth mode that is characteristic of processes for abrasive grain.

Cubic BN

Similar morphological changes as a function of temperature are seen with respect to (111) and (100) faces, but there are some basic differences because of the noncentrosymmetric nature of cubic BN. The predominant face is (111) of either the (+) or (-) form, so the morphology is

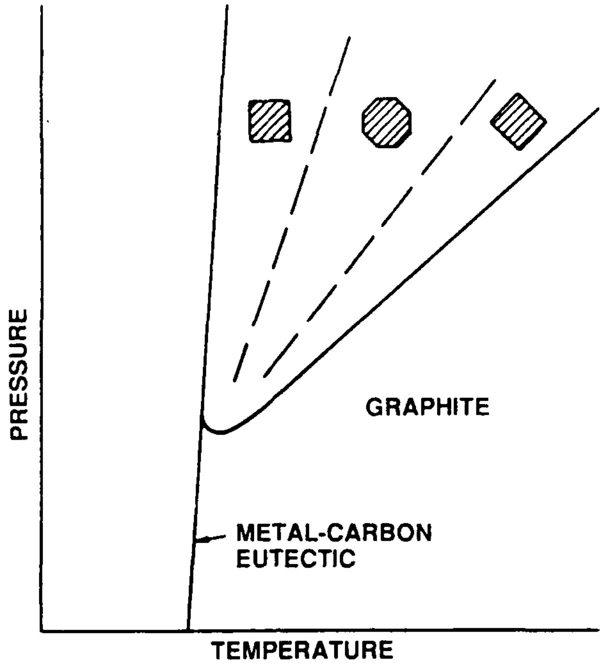


FIGURE 2-3 Morphology of diamond from metal solutions as a function of pressure and temperature. Cubes dominate at lower temperatures, octahedra at higher temperatures, and mixtures in between.

usually a tetrahedron with truncated tips. However, it is possible with equal development of these forms for an octahedron to grow. Another common morphological form of cubic BN is that of hexagonal plates.

Control of Chemistry, Doping, and Impurities

Diamond

Natural diamonds have been classified into four main types on the basis of their absorption spectra, which are dependent on the chemistry and structure of defects. Figure 2-4 shows a chemical classification of diamond based on a phase diagram. Type IA is shown as a two-phase C-N material (platelet diamond--90 percent of natural diamond and essentially unavailable from synthesis). Type IB is diamond with nitrogen in solid solution at lattice sites. Type IIA diamond is essentially pure carbon and exhibits the highest thermal conductivity. Type IIB is the p-doped semiconducting diamond with boron in lattice sites. Although many impurity elements are reported to be present in natural diamond, some are present in second-phase inclusions. The only elements that appear to be truly in substitutional sites are boron, nitrogen, and possibly beryllium. In synthesized materials the impurities are metal and graphite as inclusions and boron and nitrogen. Usually no effort is made to eliminate nitrogen when loading a cell, so all greenish-yellow crystals contain about 1000 or more ppm. If aluminum is added to remove nitrogen, a colorless crystal is obtained. If boron is added along with aluminum, the crystal is blue and a p-type semiconductor. A crystal with 10 ppm boron is very dark and opaque. Both nitrogen and boron can be nonuniformly dispersed in a crystal, usually along

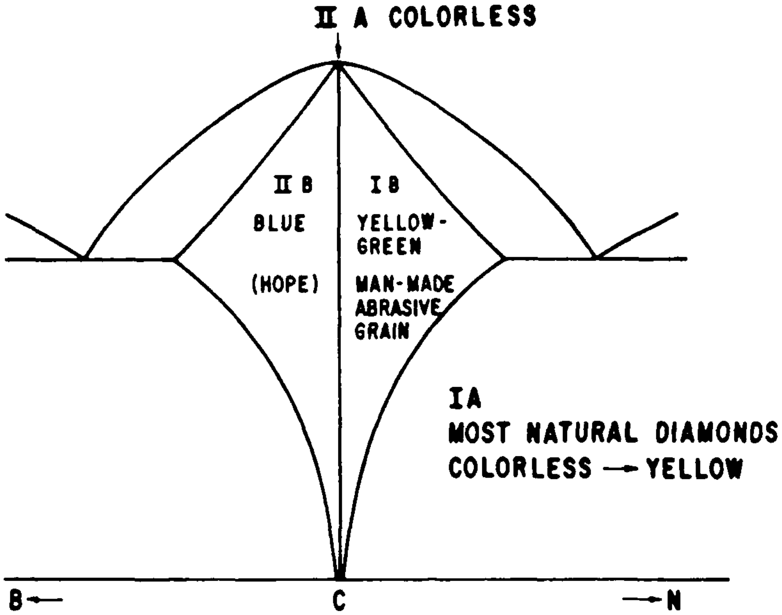


FIGURE 2-4 Schematic representation of the four principal types of diamond in terms of the systems B-C and C-N. Most natural diamonds (IA) are two-phase mixtures of platelets precipitated in the host diamond.

certain directions, and differential wear and electrical properties can be associated with the distribution. N-type doping of diamond under equilibrium conditions has not been achieved.

Cubic BN

Cubic BN can be doped to be either n- or p-type under equilibrium conditions, and a p-n junction has been reported by synthesis at HPHT (Mishima, et al., 1987). Most unintentionally doped cubic BN is amber, a color that is thought by some to be the result of excess boron. It behaves like an extrinsic semiconductor, with a decrease in resistivity on heating, as well as exhibiting a reversible thermochromism. Up to 10 ppm lithium (from the solvent-catalysts) has been measured in cubic BN, but its location in the lattice is not known. Cubic BN may also have inclusions of hexagonal BN and borides. Some products contain carbon as an inclusion, although solid solutions between diamond and cubic BN are reported. A ternary phase, BCN, is also said to exist.

Pressure-Sintered Material

Both diamond and cubic BN powder can be pressure-sintered into polycrystalline aggregates in their respective stability regions at HPHT conditions. Tools for cutting, drilling, sawing, and wire drawing have been common in the marketplace since about 1970. Dimensions of the diamond layer on a carbide substrate are at least as large as 50 mm diameter and 1 mm thick at this writing. Such "sandwich" materials can be used for wear plates but are more often cut into rectangular, square, or pie-shaped pieces for tools. Large wire die blanks, which consist of a ring of carbide around a cylinder of diamond at least as large as 14 x 14 mm, are routine trade items.

Although both diamond and cubic BN can be directly sintered, most of the compacts are made by a liquid-phase sintering process. In the simplest case a liquid metal (cobalt-rich) from the carbide infiltrates a mass of diamond grains *in situ* in the press. The liquid dissolves and reprecipitates diamond at grain contacts to make diamond-diamond bonds. The final product consists of two continuous phases: diamond and about 6 volume-percent metal. The latter can be removed by etching, leaving a diamond compact of high strength and greater thermal stability than with the metal in place. However, it is still a brittle material, and thin layers of either diamond or cubic BN cannot be expected to withstand high stresses without the carbide support. Small pieces free of carbide can replace many applications of larger diamond if properly supported in a metal binder using the same technology that is well-tested for these materials. The random array of grains in a polycrystalline aggregate is a better material than a single crystal in two respects: elimination of both anisotropic wear and cleavage. Thus, wire-drawing dies of sintered diamond are far superior to a single-crystal die in terms of die life. There is an effort to use sintered diamond as anvils in high-pressure apparatus, with the hope of attaining higher pressures and longer life than with carbide alone. As will be discussed below, polycrystalline CVD diamond films form a random, though under certain deposition conditions an ordered, array of grains that "sinter" due to the normal growth and undergrowth of individual polycrystalline grains.

Cubic BN can be sintered by analogous techniques described for diamond with some chemical modifications that are in general proprietary. The cubic BN tools are especially useful for turning ferrous-based material. The direct sintering of cubic BN from hexagonal BN is within the capabilities of static apparatus, and such materials are available. If the grain size of this material can be kept small enough, precision turning tools may be developed that will eliminate the need for single crystals of this rather friable material. The directly sintered material also has potential for heat sinks.

Polycrystalline CVD diamond is a potentially very attractive replacement as a coating or as grains because it is 100 percent diamond, with very clean grain boundaries and without porosity and second phases to disrupt thermal stability. The possibility of making unusual shapes and large sizes directly, if successful, will have considerable negative impact on the high-pressure process remaining economically competitive. One of the significant problems to be solved, however, is that of adhesion. There is room for improvement in the bonding of CVD diamond to any material.

CHEMICAL VAPOR DEPOSITION PROCESSES

It was the recognition of the role of atomic hydrogen in the vapor deposition approach that led Russian workers to the first successful growth of diamond films at commercially practical deposition rates (>1 μm/hr). Since the early 1980s a wide variety of energetically assisted CVD methods have been employed. (Before that it seemed like nothing would work and now it seems like everything works--at least any process that efficiently produces atomic hydrogen.) These are subdivided into plasma-enhanced processes and nonplasma (primarily thermally assisted) processes. Distinctions between the processes become blurred in some cases, such as in thermal plasmas.

Plasma-Enhanced Processes

A plasma is an efficient way to dissociate gas molecules to produce nonequilibrium concentrations of gas-phase species, such as the high concentrations of atomic hydrogen needed to make diamond. Plasmas can be generated by a number of energy sources (dc, rf, and microwave electric fields and flames), and the plasmas can be either cold or hot.

The main techniques with their variations are given in Table 2-1, and schematics of typical experimental setups are shown in Figure 2-5. Also given are representative references. Although these preparation methods are not discussed in detail, a few general comments can be made.

The most extensively studied process is microwave plasma-enhanced chemical vapor deposition (MPECVD). This trend has only increased over the past several years, especially in Japan (Figure 2-6). The apparent reasons are (a) the stability and reproducibility of microwave cold plasmas; (b) their energy efficiency (high plasma density, low electron temperatures, low sheath potentials); (c) the increased availability of 1-2 kW microwave (wave-guided) power supplies and applicators; and (d) the potential to scale the process to larger substrates (4-5 in.). However, the rf and dc plasma methods produce diamond films of comparable quality and, under certain conditions (e.g., substrate biasing), at much higher rates, and they are being used in commercial processes in the United States (Crystallume and Air Products).

Although strides to scale the MPECVD process have been made, it seems that rf and dc plasmas are easier to scale. It is not as clear which of these processes would have an advantage in coating nonplanar substrates or which is amenable to large batch coating such as on vertically stacked wire mesh trays for cutting tool coatings. Also, dc plasma processes at present seem to have an advantage of potentially higher deposition rates (~5X).

The thermal plasma approach generates the necessary temperature to dissociate H_2 directly in the plasma. Although the plasma nozzle is nearby, nothing is known at present as to temperatures and carbide formation at the metal nozzle or, more generally, the stability of the process. To date this process has only been used successfully in Japan by NIRIM, Fujitsu and Asahi Diamond; U.S. companies and universities are pursuing this approach. It is known that the rates can be extremely high (200-500 μm/hr) but the deposition area is small (<1 cm^2). The deposition "on-time" is thermally limited, and the uniformity and reproducibility are poor. However, if controlled, this approach could be very important.

Of the remaining plasma-enhanced techniques listed in Table 2-1, the atmospheric torch is unique and potentially the most important. Although not strictly a plasma, an atmospheric flame is simple in design, cost, and use. Hydrogen, oxygen, and hydrocarbon gases (e.g., acetylene) are simply burned, and diamond forms in the reducing part of the flame. Hirose's results in atmospheric torch deposition (Hirose and Mitsuizumi, 1988) have now been repeated in several laboratories around the world (Naval Research Laboratory, Pennsylvania State University, and Sumitomo Electric), and it is expected that other groups will be pursuing this technique.

The trade-offs among plasma stability, deposition rate, coating area, film quality (as defined by either scientific or technological criteria) for each of the plasma processes have yet to be determined. It is likely that there will be no single answer, solution, or technique; rather, each technique will find its niche (albeit, some small niches).

Nonplasma Processes

Besides the plasma-enhancement approach to vapor deposition of diamond, Derjaguin and Fedoseev (1977) recognized that high-temperature and catalytic processes could also produce a "superequilibrium" of atomic hydrogen, which appeared to be the necessary ingredient for a single-step deposition process.

TABLE 2-1 Plasma-Enhanced Chemical Vapor Deposition (PECVD) Processes for Diamond Film Growth

Technique	Deposition Rate (μm/hr)	Selected References
Microwave-PECVD - magnetic field at high pressure (>1 torr) - ECR (<0.1 torr)	0.1-5	1,2,3
rf-PECVD - inductively coupled - capacitively coupled	?	4,5
dc-PECVD - capacitively coupled - hollow cathode discharge	0.01-100	6,7,8
Thermal plasmas - dc thermal plasma torch - rf thermal plasma torch - atmospheric flame torch - vacuum arc	10-300	9,10,11

Key to References:

1. Kamo, M. Y. Sato, S. Matsumoto, and N. Setaka. 1983. Diamon synthesis from gas phase in microwave plasma. J. Cryst. Growth, Vol. 62, p. 642.
2. Saito, S., S. Matsuda, and S. Nogita. 1986. J. Mat. Sci. Lett., Vol. 5,p. 565.
3. Kawarada, H., K. S. Mar, and A. Hiraki. 1987. Larbe area chemical vapour depositon of diamond particles and films using magneto-microwave plasma. Jpn. J. Appl. Phys., Vol. 26, p. L1032.
4. Matsumoto, S. 1985. Chemical vapour deposition of diamond in rf glow discharge. J. Mat. Sci. Lett., Vol. 4, p. 600.
5. Marria, R., L. Stobierski, and R. Pampuch. 1981. Diamond syhthesis in cool plasma. Cryst. Res. Tech., Vol. 16, p. 785.
6. Suzuki, K., H. Yasuda, and T. Inuzuka. 1987. Growth of diamond thin films by dc plasma chemical vapor deposition. Appl. Phys. Lett., Vol. 50, no. 12, p. 728.
7. Pinneo, J. M. 1987. Diamond Technology Initiative Workshop, paper 4. Sponsored by the Office of Naval Research at M.I.T. Lincoln Laboratories, Boston, Massachusetts (February 2).
8. Singh, B., O. R. Mesker, A. W. Levine, and Y. Arie. 1988. Diamond synthesis by hollow cathode plasma assisted chemical vapor deposition. Proc. SPIE, Vol. 877, p. 70.
9. Koshino, N., K. Kurihara, M. Kawarada, and K. Sasaki. 1988. 1988 MRS Spring Meeting, Symposium D Extended Abstracts, p. 95. M. Geis, G. H. Johnson, and A. R. Badzian, eds.
10. Matsumoto, S., M. Hino, and T. Kobayashi. 1987. Synthesis of diamond films in a FR induction thermal plasma. Appl. Phys. Lett., Vol. 51, p. 737.
11. Hirose, Y., and Kondo. Spring 1988. APL Meeting, Abstracts, p. 434.

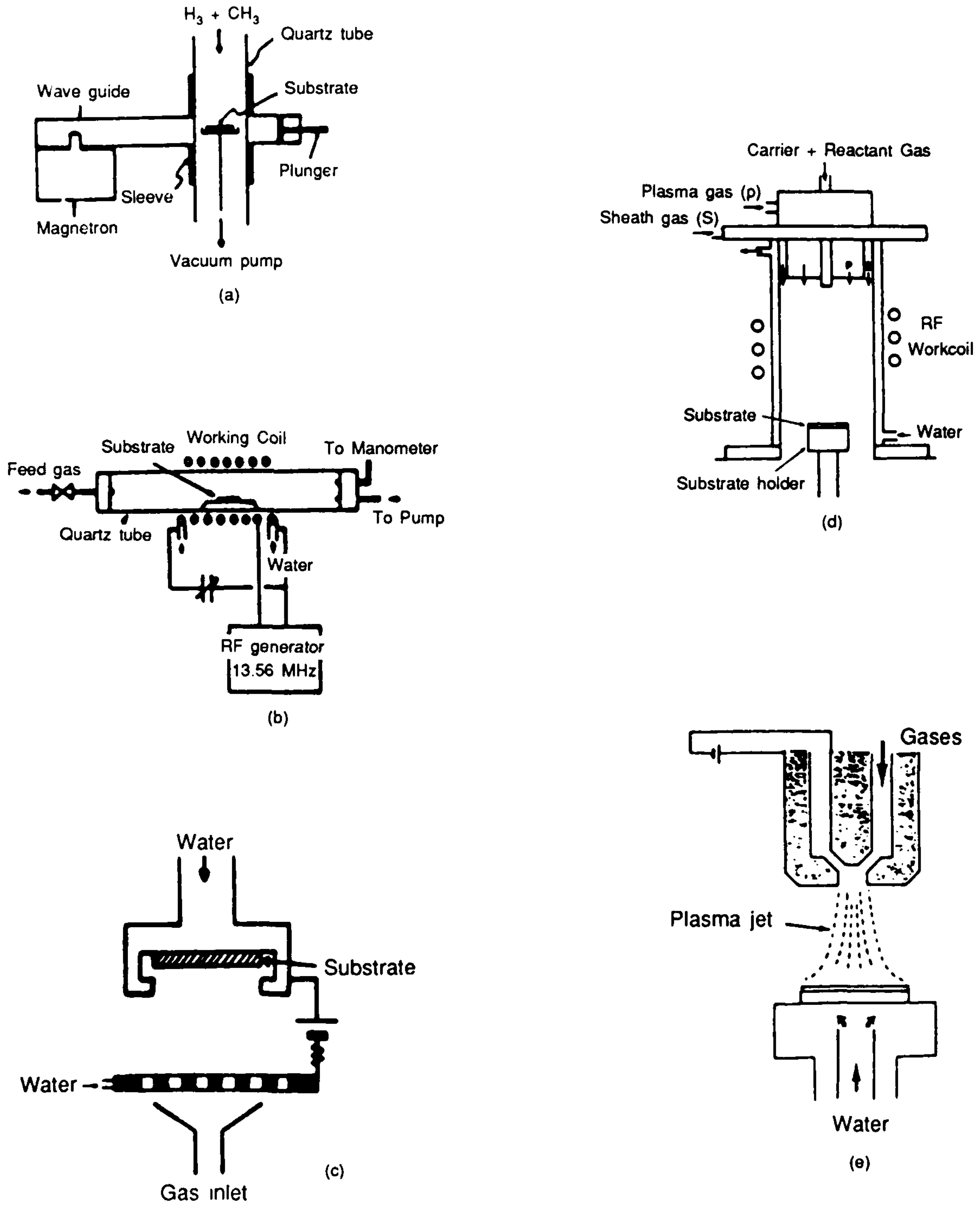


FIGURE 2-5 Schematic diagrams of various plasma-enhanced CVD techniques for diamond growth: (a) microwave PECVD (Kamo et al., 1983); (b) rf PECVD (Matsumoto, 1985); (c) dc PECVD (Suzuki et al., 1987); (d) rf thermal plasma CVD (Matsumoto, 1985); (e) dc thermal plasma CVD (Koshino et al., 1988).

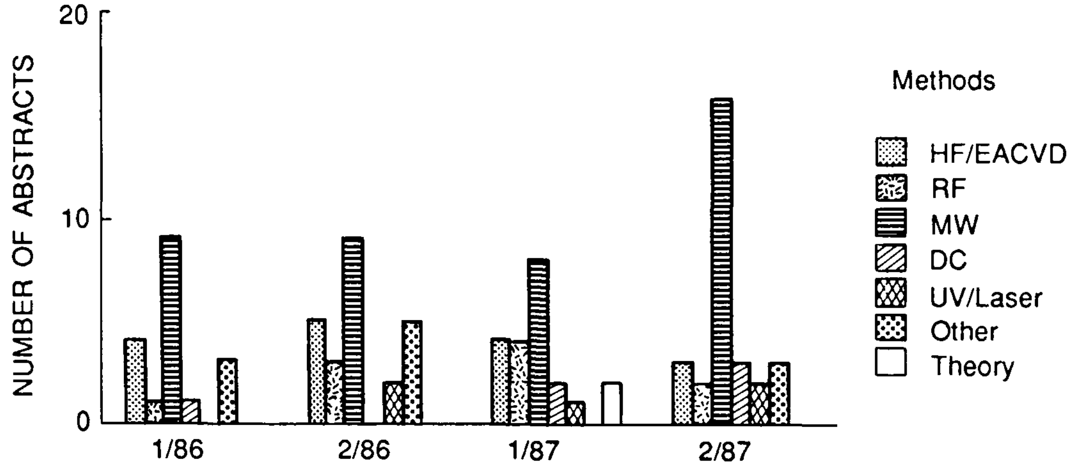


FIGURE 2-6 Statistics of abstracts published at the meetings of the Japanese Applied Physics Society on different preparation methods for diamond thin films (Bachmann et al., 1988).

Other than a patent by Vickery (1973) and the recent paper by Badzian et al. (1988), the idea and use of catalytic processes in diamond vapor growth has not been explored. These approaches may prove to be important from an energy (economy) viewpoint, and thus more work is justified. However, chemistry control is always difficult to unravel, and adding catalytic mechanisms to an already complex and poorly understood process involving atomic hydrogen and hydrocarbon species will require considerably more time and effort.

Thermally enhanced processes would appear to be the easiest to understand experimentally (Figure 2-7) and conceptually. The optimum conditions for diamond growth involve, among other factors, a substrate temperature of about 1000°C and a high percentage of atomic hydrogen. Since this latter factor cannot be achieved at the 1000°C substrate surface, a secondary filament in close proximity to the substrate is an option. In fact, this approach is the simplest and most effective to date. The nonplasma methods are listed in Table 2-2.

The heated filament approaches can have some severe limitations due to hydrogen incorporation and carbide formation of the refractory metal filament (usually tungsten or tantalum). The filament may form the carbide before diamond growth starts (delay time up to hours) and then is brittle and sags or distorts during deposition. This leads to deposition conditions that are nonstable and difficult to reproduce. The small-bore-tube approach seems to minimize these effects, and the gas flow both over the heated filament and at the substrate can be better controlled. The filament temperature is generally 2000 to 2300°C, and thermochemical calculations show that between 5 and 10 percent of H_2 is dissociated to atomic hydrogen at those temperatures.

Hybrid Processes

The combination of plasma formation and particle bombardment (e.g., due to self-biases and imposed biases at the growing film) will need to be considered. Although it is considered separately in the next section of this report, it may very well be the blending of plasma chemistry with ion bombardment that produces the most practical coatings--superhard, tough, and adherent to metal and ceramic substrates.

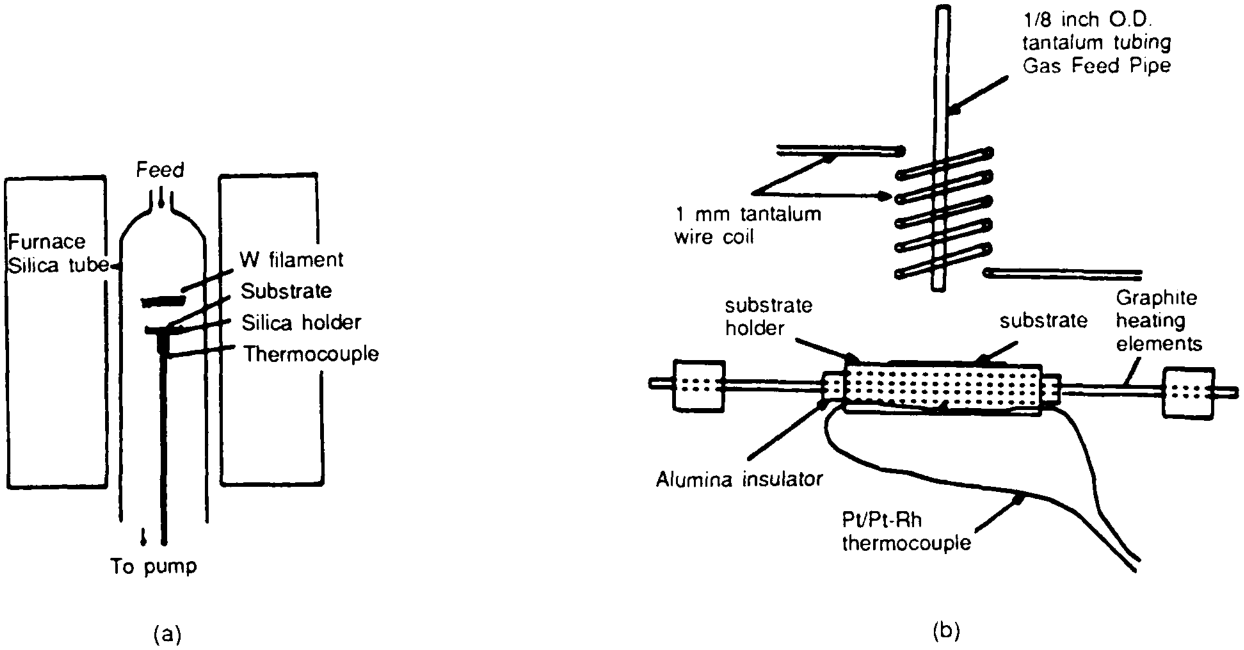


FIGURE 2-7 Schematic diagrams of two different nonplasma approaches for diamond growth: (a) heated-filament-assisted CVD (Matsumoto et al., 1982 (a, b); (b) heated-tube-assisted CVD (Yarbrough and Roy, 1988).

TABLE 2-2 Nonplasma Deposition Processes for Diamond Film Growth

Techniques	Deposition Rate (μm/hr)	References
Heated-Filament CVD - wound filament - small-bore tube - substrate biasing	0.1-20	1,2
Laser-enhanced CVD	?	3

__Key to References:__

1. Matsumoto, S., Y. Sato, M. Kamo, and N. Setaka. 1982a. Vapor deposition of diamond particles from methane. Jpn. J. Appl. Phys., Vol. 21, p. L183.1.

Matsumoto, S., Y. Sato, M. Kamo, J. Tanaka, and N. Setaka. 1982b. Chemical vapor deposition of diamond from methane--hydrogen gas. Proc. 7th Int. Conf. Vac. Metallurgy, Tokyo, p. 386.

2. Yarbrough, W. A., and R. Roy. 1988. Spring MRS Meeting Extended Abstracts, Symposium D, p. 33. M. Geis, G. H. Johnson, and A. R. Badzian, eds.
3. Kitahama, K., K. Hirata, H. Nakamatsu, S. Kawai, N. Fujimori, T. Imai, H. Yoshino, and A. Doi. 1986. Synthesis of diamond by laser-induced chemical vapor deposition. Appl. Phys. Lett., Vol. 49, p. 634.

Vapor-Liquid-Solid (VLS) Growth

The growth of diamond whiskers has been reported (Derjaguin et al., 1968), but no significant further work appears to have been done in the intervening 20 years. It was claimed that the diamond whisker growth proceeded by the VLS process, but it is not known how the conditions differed from those used to grow graphite whiskers. In the latter case, iron beads approximately 100 to 200 Å in diameter provide transport of carbon from the vapor to the growing tip of the whisker under conditions not too far removed from CVD diamond growth. Careful experiments are needed to determine what factors encourage diamond whisker growth and the possible role of hydrogen in the process.

Critical CVD Growth Parameters

Diamond crystals and films with the highest perfection have been grown by controlling the gas-phase chemistry. Although many of the details of the fundamental nucleation and growth processes are still unknown (see later section), the critical deposition parameters of nucleation and growth have been explored extensively over the past several years. Interestingly, with few exceptions, the critical parameters are similar for all of the various techniques described covering a wide range of gas activation. Thus, unless noted, the general parameters apply to all of these diamond deposition approaches.

Substrates and Their Preparation

Diamond has been nucleated and grown on a wide range of substrates, including metals, semiconductors, graphite, insulators, and even fused silica glass. Although the present evidence is inconclusive, stable carbides at the diamond film-nondiamond substrate interface appear to be important. The origin of the carbide may be due to direct chemical reaction between the activated gaseous species intentionally introduced into the system and the metal element in the substrate or to gas species originating from atomic hydrogen etching of the deposition reactor wall or the substrate.

There is usually a delay time between the start of the deposition to the point where individual crystallites are seen and the time when they grow together to form a continuous film. The most effective methods for increasing the nucleation density and decreasing the delay time for nucleation and growth have been to either scratch or seed the surface with diamond powder or add metal impurities (Si, Ti, B) in the gas phase. In the first case, the diamond crystals littered on the substrate surface are, of course, excellent nucleation sites for immediate diamond growth. Epitaxial growth of diamond on diamond has been demonstrated by Spitsyn and coworkers (1981), and Geis (1988). Other nondiamond powders (e.g., cubic BN, SiC, TaC) have been used to "seed" the surface (Bachmann et al., 1988).

Substrate Temperature

For the diamond films with the highest level of crystal perfection, the substrate temperature is usually in the range of 900 to 1000°C. This result seems to be independent of deposition technique (either PECVD or TECVD), and in all cases the film morphology consists of approximately 1- to 5-μm-size crystallites in films about 5 μm thick. The temperature obviously limits substrates to rather refractory materials.

Diamond films with crystallite sizes of approximately 2000 Å have been reported at substrate temperatures around 650°C while 100- to 200-Å-size crystallites occur for substrate temperatures less than 600°C but greater than 450°C. The optimum temperature for crystal perfection is similar to that for the maximum in film growth rate.

Gases and Gas Composition

A large number of hydrocarbon gases have been used to deposit diamond. Although there are no reported significant differences in the resulting films, methane has been the gas of choice. In nearly all reported cases, large hydrogen gas dilution (e.g., about 1 percent CH_4 in H_2) is necessary with a trade-off between high rates (at about 5 percent CH_4) and crystal size and perfection (at about 0.2 to 0.5 percent CH_4). Recently diamond films of apparent comparable quality have been grown from CO. For CO, dilution with hydrogen appears radically different. Good-quality diamond films are obtained at 50 percent CO concentrations and even greater.

Gas Flow Rate and Pressure

The largest diamond crystals are obtained at pressures from 20 to 100 torr in both the plasma-assisted and thermally-assisted processes. In the case of PECVD, at low gas pressures, SiC formation increases while the plasma starts to become unstable at pressures above 100 torr. In the optimum range (especially at 50 to 100 torr) the plasma volume is small enough so it is not in contact with the reactor tube wall (typically 38- to 50-mm-diameter tubes for MPECVD). The film quality and deposition rate are relatively insensitive to the flow rate, which is typically 50 to 1000 sccm.

Additions to Gas

Very little systematic work has been reported on either inert or reactive gas additions to the H_2-hydrocarbon gas mixtures. More work is clearly needed.

Position of Substrate

In all reports on PECVD diamond the substrates are immersed in the plasma or separated only by the dark space sheath in dc and rf plasmas. Remote plasma deposition in MPECVD has not been reported as yet, but the possibility cannot be discounted. For thermally assisted processes the substrate generally is placed about 1 cm from the heated filament (or tube or thermal plasma nozzle). Remote deposition at distances greater than several centimeters has not been reported. Whether this is related to the lifetime of active species (atomic hydrogen and hydrogen-containing radicals, ions, or molecules) is yet to be explored.

Parameters Specific to Individual Processes

In the case of heated-filament CVD the filament temperature is typically 2000 to 2300°C. Although the gas flow over and near the filament should be critical, this has not been controlled to date. For thermal plasmas the results are sketchy, but gas temperatures of 3000 to 10,000 K are reported. Although the high deposition rates and excellent quality are encouraging, the apparent lack of film reproducibility (N. Koshino, personal communication) may simply reflect the lack of control of the process at present.

Size of Substrates

To make diamond deposition commercially feasible, high deposition efficiencies are needed. One approach is to deposit over large areas, and for many applications (e.g., optical windows, semiconductor wafers, large numbers of cutting tools) this is essential. For substrate diameter greater than 5 in., uniform substrate heating at approximately 1000°C for optimum diamond growth will become a major problem. Although microwave plasmas have the advantage of stability and efficiency of production of plasma species, the geometrical constraints of coupling microwave energy to a plasma volume are significant. However, work in this direction is ongoing in both the United States and Japan. The ability to scale up dc and rf deposition processes is easier than with microwave; they seem less restrictive and have been used successfully in the a-Si:H solar cell field, for example. Scaling up of the heated-filament CVD method is a matter of constructing an array of heated wires and tubes, with the main drawback being the uniformity of deposition thickness and properties.

Electric and Magnetic Field Effects

Biasing of the substrates during dc plasma deposition results in diamond formation when positively biased and in carbide formation when negatively biased. The mechanism is not known, not even whether it involves only electrons or both electrons and ions (positive and/or negative). If high-resistivity diamond films are eventually made, then dc plasmas will not work due to space charge buildup. If a positive bias on the substrate is essential, then this could be a limitation.

For microwave plasmas the electron cyclotron resonance (ECR) condition (875 gauss) for energy coupling has been used. At high pressures (>1 torr) ECR does not occur due to gas phase collisions, but positive results have been claimed regarding the ability to increase the extent of the plasma so as to scale to larger substrates. At the lower pressures (<0.1 torr) where the ECR condition is valid, diamond growth has been reported at low temperatures (650°C). This area of research of high plasma density deserves further investigation.

To the extent that electric and magnetic fields allow for the acceleration, deceleration, and deflection of active plasma species, these process controls will allow merging between chemistry-controlled and bombardment-controlled growth of diamond. It is expected that this area will prove to be scientifically and technologically important.

Fundamental Issues in CVD Processes

There have been few reported studies that directly address the fundamental issues of nucleation and growth of vapor-deposited diamond films and the resulting film's structural and chemical defects. This section, therefore, deals more with speculations and attempts to identify critical areas of research. As is to be expected for an emerging material technology, knowledge of how to deposit films far exceeds the understanding of fundamental mechanisms and kinetics of nucleation and growth.

Nucleation

Since diamond is a metastable solid, the issue of nucleation involves not only that of diamond but also graphite and the hexagonal polytype of diamond, lonsdaleite. Furthermore, planar defects associated with the {111} planes in diamond--stacking faults, twinning, and introduction of planar graphite planes between the (111) planes of diamond--have all been observed (Badzian et al., 1988; Davis et al., 1987). The free-energy differences of these carbon phases are relatively small, so that kinetic factors, size effects, surface reconstructions, etc., during nucleation could easily be more important than thermodynamic factors.

The widely varying morphological forms reported (Matsumoto and Matsui, 1983) for vapor-deposited diamond--cube, cuboctahedra, twinned cuboctaheda, pseudo-icosahedra, decahedral, Wulff polyhedra--are not all found in natural or HPHT synthetic diamond crystals. There appear to be, however, some similarities between HPHT and vapor-deposited diamond. In both instances, stable carbides may provide favorable centers for diamond nucleation and subsequent growth. Whether this is a requirement for heterogeneous nucleation on nondiamond substrates remains to be seen.

Badzian and DeVries (1988), and others have reviewed the chemical kinetics model for diamond vapor deposition developed by Derjaguin and Fedoseev (1977) and Fedoseev and coworkers (1984). They start from thermodynamic calculations that show that the equilibrium pressure of carbon vapor over a diamond is about 2 times higher than over graphite. In the absence of other factors, graphite nucleation is more probable than diamond. The Russian scientists considered ways to overcome this inclination. In this approach, which considers chemical kinetics in the context of classical nucleation theory, there are several key points. First, the presence of a diamond surface (e.g., autoepitaxy or diamond-seeded surface) increases the probability of diamond nucleation. Second, there should be a small range of conditions over which the nucleation rate of diamond is greater than that of graphite, although this is not well defined (Figure 2-8). Third, H_2 dilution decreases the growth rate of graphite more than diamond. And fourth, atomic hydrogen etches graphite faster than diamond. Thus, the Russian literature concluded that a single-step process for making diamond was possible, as shown in Figure 2-9. In Figure 2-9 note that (a) in the case of CH_4 pyrolysis at certain supersaturation conditions, the specific growth rate of diamond (υ_d) is higher than that of graphite (υ_g), but both increase together; (b) in the presence of $H^\bullet$, *etching of diamond is insignificant, but the etching* of graphite is dominant; and (c) for mixtures of CH_4 and $H^\bullet$ there are conditions of pressure and temperature where growth of diamond is significant and graphite is etched. In this competition, graphite nucleation and growth will essentially cease or will be covered by the diamond phase (Badzian and DeVries, 1988).

Data on diamond deposition rate as a function of temperature (Derjaguin et al., 1968) show a maximum at about 1000°C (under a limited range of conditions), which is consistent with this model.

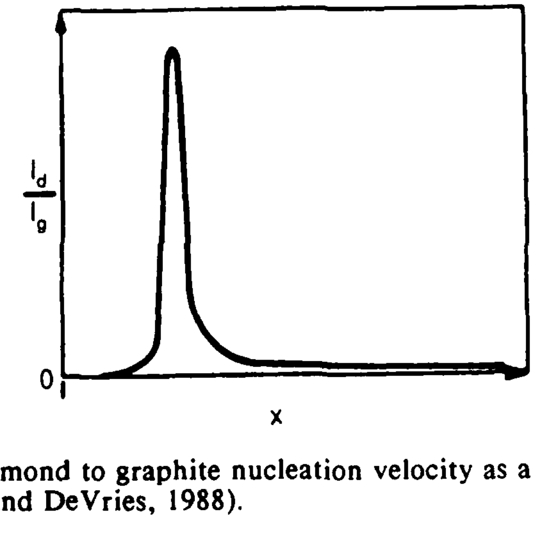


FIGURE 2-8 Ratio of diamond to graphite nucleation velocity as a function of supersaturation x (arbitrary units) (Badzian and DeVries, 1988).

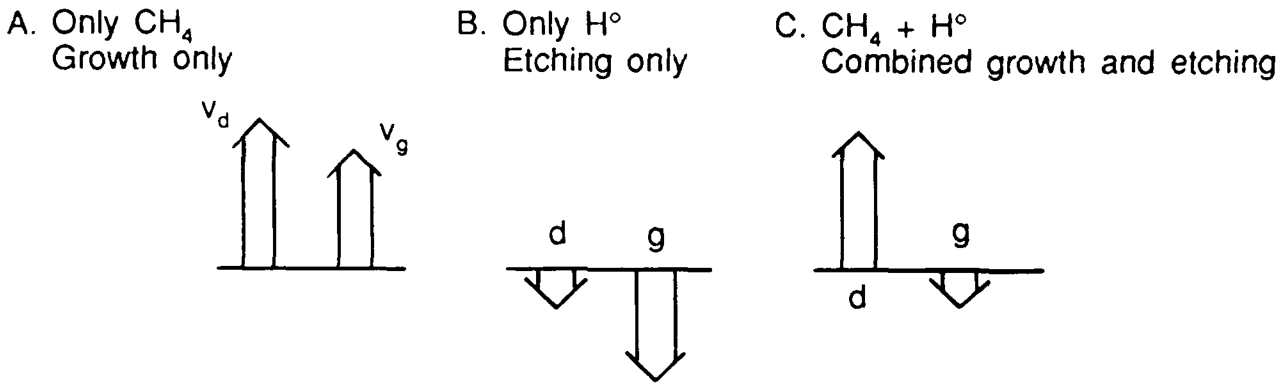


FIGURE 2-9 Relative growth and etch rates of diamond and graphite in the presence of a hydrocarbon (CH_4) and atomic hydrogen (Badzian and DeVries, 1988).

Badzian and Devries (1988) extend this approach by considering surface reconstructions and relaxations on the (111) surface of diamond, which are known to occur also in the 900 to 1000°C range (Pate, 1986). Other phenomena and properties that critically depend on temperature in this same range include adsorption and desorption of hydrogen, etch pit orientation, coefficient of static friction with metals, and oxidation rate. Based on this set of circumstantial evidence as a whole, a nucleation model that requires a critical temperature was suggested.

Clearly, the nucleation stage in diamond growth poses the most important questions that will have to be answered before there is significant progress in solving practical problems of low-defect-density polycrystalline films, high purity, homoepitaxy, heteroepitaxy, and controlled morphology. Yet the current models of nucleation are primarily speculative, with a minimal amount of conclusive results reported. There is still no real understanding of critical nucleus size and crystallographic orientation; effect of impurities; catalytic effects (if any); intermediate layers (e.g., distinct or graded, stable carbides, hydrogenated); defect generation, propagation, and elimination; and gas-phase nucleation.

At an even more basic level, we still do not know enough about the detailed surface chemistry and crystallography in this carbon-hydrogen system to know whether diamond growth is the thermodynamically unexpected or expected structure. It has been suggested recently (Machlin, 1988) that there is a thermodynamically stable region for diamond in the C-H system and that the diamond could be the expected phase to nucleate and grow under certain low-pressure conditions.

Growth Mechanisms

Before understanding diamond nucleation and growth from a vapor, a mechanistic and chemical kinetics model must be developed. The key to any model will, of course, be a knowledge of the species at the growing film surface. Derjaguin and Fedoseev (1977) first suggested that CH_4•H complexes dominate in diamond growth (and CH_3 radicals dominate for graphite growth) in conventional (nonenhanced) CVD processes from hydrocarbon gases. Recently, two alternative mechanistic models have been proposed that attempt to take into account both thermal and plasma enhancement of the hydrocarbon CVD process.

Tsuda et al. (1986) and Marria et al. (1981) have proposed methyl radicals as the dominant growth species, while Freuklach and Spear (1988) suggest acetylene molecules. In both models, quantum chemical calculations for the transition states have been carried out (Tsuda et al., 1987; Huang et al., 1988). Although the acetylene-based mechanism is more energetically favored, other mechanisms cannot be discounted.

Optical emission, mass spectrometric (Harris et al., 1988), and infrared absorption spectroscopy (Celli et al., 1988) measurements of gas-phase species during enhanced CVD diamond growth have shown that both CH_3 and C_2H_2 species are present in sufficient quantities to account for diamond growth. Harris et al. (1988) showed that, other than those two species, CH_4 and C_2H_4 are the only other species present in large enough quantities to account for diamond deposition. Their mass spectroscopy study of species present in the heated-filament-enhanced CVD as a function of filament distance from the substrate is shown in Figure 2-10. More work is required before a definitive judgment can be made regarding the dominant growth species; however, progress is being made.

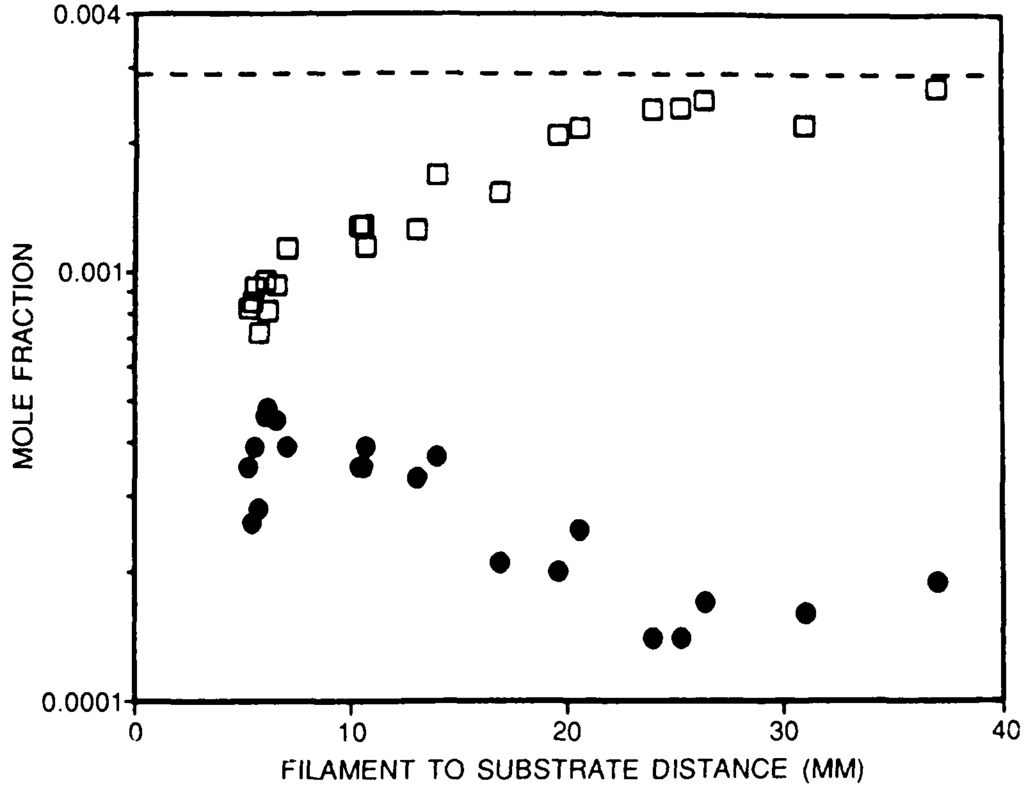


FIGURE 2-10 CH_4 (open squares) and C_2H_2 (solid circles) mole fractions at the growing diamond surface as a function of distance between substrate and filament. The CH_4 and C_2H_2 signals include contributions from CH_3 (small) and C_2H (negligible), respectively. The dashed line shows the input CH_4 mole fraction (Harris et al., 1988).

Some of the important aspects of diamond film growth that remain essentially unanswered are:

- Species on the growing film surface.
- Role of atomic hydrogen on the different crystallographic faces of diamond during growth.
- Surface structure during film growth.
- Catalytic processes, if any.
- Surface kinetics and surface diffusion.
- Ion, electron, and radical bombardment during film growth.
- Synergistic effects of surface chemistry and bombardment.
- Growth rates--e.g., rate-limiting process(es); effect of impurities.

Impurities

The current vapor-deposited materials are extremely impure, especially by semiconductor standards. Atomic hydrogen, which is a necessary ingredient in diamond film deposition, is a highly reactive element. Since silicon substrates and fused silica reactor tubes and bell jars are often used, silicon is a common impurity. Levels of 0.2 atomic percent silicon have been reported (Badzian et al., 1988) for films with close to optimum characteristics. It is expected that deposition techniques that provide sufficient $H^{\bullet}$ at the growing film surface and minimize $H^{\bullet}$ interactions with the substrate and containment vessel will be developed for those applications requiring low or controlled levels of impurities. At that point the purity of the starting gases will become important.

The main nonmetallic impurity is hydrogen, with the lowest levels reported (Lanford, 1987) being 435 ± 79 ppma. The only systematic measurements reported (Hartnett, 1988) show that there is an inverse relation between [H] in film and the H_2 concentration employed during deposition, with the lowest level (see above) prepared in a 0.5 percent H_2-CH_4 gas mixture. In some instances (Lanford, 1987), the [H] concentration was over 1 atomic percent, and yet the films still showed the diamond diffraction pattern.

Silicon impurities have been related to an 80-fold increase in nucleation rate and a 2 to 3 times increase in growth rate (Badzian et al., 1988). However, the Raman spectra indicate an associated increase in the 1332 cm^{-1} and a strong, narrow band luminescence peak near 6000 cm^{-1}. The origin of this luminescence band is still not understood, although an increase in the silicon content has been suggested to be related to the presence of silicon in octahedral holes of the diamond lattice (Hartnett, 1988).

The elimination and then controlled addition of impurity atoms is expected to be an important aspect in both the scientific understanding and the technological development. Little information has been reported to date.

Defects

Essentially nothing is known about point defects in CVD diamond films (vacancies, interstitials, voids, or substitutional elements), either extrinsic or impurity-related. Theoretical and high-resolution TEM (Glass et al., 1988) studies are expected to help understanding.

Planar defects such as microtwins, stacking faults, and graphite inclusions have been viewed by medium- and high-resolution TEM (Glass et al., 1988). However, their relation to preparation conditions, impurities, etc., is unknown. Other defects such as dislocations and grain boundaries have not been fully investigated.

Since defects are important to essentially all film properties, considerable emphasis will have to be placed here. Nucleation and renucleation are expected to be related to defects and impurities. At present only a little is known about the most obvious defects associated with stacking faults.

Morphology

Although a wide range of techniques have been used to deposit diamond films, the film morphologies reported are similar. Also, in all cases the most structurally perfect crystals occur over a narrow range of process parameters, as described earlier. The diamond crystals grow as cubes, octahedra, cuboctahedra, and single and multiple (111) twins and intergrow as polycrystalline layers with morphologies ranging from well-defined facets to poorly defined rounded shapes, highly irregular forms, etc. The crystal facets in many of the diamond films show layer-like growth as expected from surface diffusion to steps and re-entrants (Badzian et al., 1988) and appear similar to crystals grown rather fast under high supersaturation conditions.

One of the problems facing diamond thin films is the fact that, at the conditions for growth of the most structurally perfect crystals, the faceted top surface of a typical 5-μm-thick film shows a distribution of facet sizes usually centered around 1 to 2 μm. Such films are highly scattering, thus limiting optical applications as well as optical analysis techniques such as spectroscopic ellipsometry and IR and optical transmission. Rough films are also unsuitable for many tribological applications as well. There are two approaches to obtaining smooth films: essentially zero nucleation density (single-crystal films) and extremely high nucleation density (submicrometer grain-size films). For applications in which mechanical properties and deposition on a nondiamond substrate are important, the latter approach is better. However, associated with fine-grain-size diamond films appears to be an increasing percentage of nondiamond material, as indicated by their Raman spectra (see Chapter 3). Certainly, as the morphological units get smaller, the internal surface area (internal morphology) increases, and the volume of material affected by these surfaces can be a significant fraction of the total volume, especially when the crystallite size approaches 200 to 100 Å.

To what extent this phase purity problem is important remains to be seen. Certainly the answer for each application is expected to be different, and trade-offs will have to be made. Other properties expected to be related to morphology (both internal and external) are adhesion, internal stress, friction, chemical stability, interdiffusion, electrical conductivity, and thermal conductivity.

An evolutionary growth model for diamond films is expected to be important as attempts are made to design and engineer films for specific applications. A complete description and understanding will entail a number of the fundamental issues already discussed--nucleation, intermediate layers, renucleation, intergrowth of crystals, evolutionary selection, and effects of impurities and defects. A knowledge of how to control nucleation rate and density, and perhaps to vary the growth rate in a deliberate manner during the early growth stage or throughout the process (e.g., continuously graded or periodically graded to make multilayers), will be a desirable goal in future studies.

Diamond film morphology (often referred to as microstructure) has at least five facets, namely, (a) growth cones, (b) grain size, (c) grain shape, (d) grain orientation, and (e) defects. Growth cones are a very common feature of many different types of deposition processes and, in fact, are a common occurrence in deposition of some of the materials discussed in this report, e.g., SiC. Growth cones commonly affect a variety of properties, usually in a negative fashion. Being collections of grains of very limited misorientation, they can commonly lead to anisotropy of properties, i.e., different properties through the thickness than in the place of the coating. They typically exacerbate surface roughness and surface finishing and limit fracture toughness and, especially, strength due to their acting as pseudo-large grains, and their boundaries or frequent locations for accumulation of impurities, as well as possible porosity entrapment. Both of the latter factors, of course, can have other negative affects, e.g., on thermal conductivity.

Grain size has a variety of effects that can be either good or bad. Hardness typically decreases with increasing grain size, even in quite hard materials, e.g., SiC and B_4C. Wear resistance follows a similar trend, again as shown in such hard materials as SiC and B_4C. It is not clear whether fracture toughness has any significant dependence on grain size in cubic materials, but tensile and compressive strengths clearly do, again with larger grains giving lower strengths. Clearly, for some of the electronic semiconductor applications, grain sizes must be large enough to give a single crystal region of sufficient size for the semiconductor junction to have its proper effects.

Finally, grain size also plays a role in resultant surface finish. Larger grains tend to lead to rougher as-deposited surfaces and also often limit the quality of surface finishing that can result from machining. Grain shape, in particular the issue of whether or not columnar grains are formed, can also be important, since columnar grains may lead to lower transverse fracture toughness, i.e., easier transverse cracking. On the other hand, columnar grains may lead to enhanced transverse thermal conductivity.

Defects ranging from point, line, and planar lattice defects to voids and impurity particles can all play a role in a variety of properties ranging from electronic to thermal to mechanical. Generally, defects are detrimental to most of these properties; they can in some cases, however, be either neutral or beneficial (e.g., lattice defects can be beneficial to hardness.

Film morphology has also been related to residual stresses in PVD fibers, although not in a quantitative manner. Generally dense, fine-grain-size fibers are in a high state of compressive stress, whereas coarser grain fibers often are closer to a neutral stress state or even slightly tensile. Such stresses are, again, a very common problem in deposited coating. Such stresses are frequently observed to be serious problems in some of the materials discussed in this report, e.g., SiC. Another possible important source of such residual stresses may be stoichiometry variations, which might thus be less severe in diamond coatings, but certainly could continue to be a similar problem in BN coatings. Such stresses become of increasing concern and seriousness as both the thickness as well as the lateral dimensions of the coating increase. Hence, these can become an important issue in scaling-up for many applications.

PHYSICAL VAPOR DEPOSITION PROCESSES

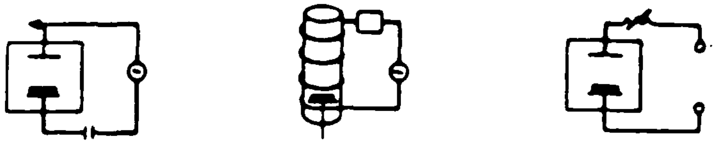
During the past approximately 35 years, many methods involving ion-assisted deposition for the production of a variety of superhard materials have been studied. These processes have all attempted to take advantage of the production of metastable materials by the condensation of energetic particles. The energetic particles have come from plasma sources, ion sources, and sputtering sources. Very hard materials that are amorphous, by x-ray diffraction, can be made by these processes. Small crystallites of single-crystal material have been reported from these ion-assisted deposition processes. However, success in producing macro-polycrystalline materials has been limited.

In these processes the energy provided is by exchange with energetic particles rather than from thermal sources. Thus these materials can be grown on relatively low-temperature substrates. In the case of diamond-like carbon films, the coatings have been reported to possess high electrical resistivity, high hardness, low coefficient of friction, and a relatively high transparency in the infrared. Optically transparent films have been reported (Lettington et al., 1987; Wort and Lewis, 1987), and consequently many applications for these coating have been directed toward optical systems.

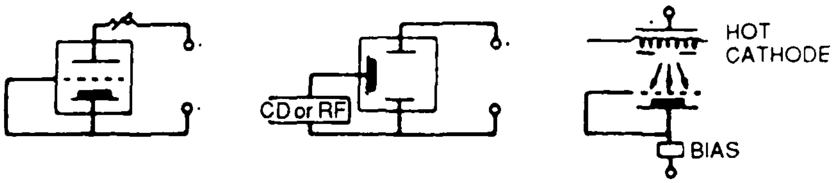
Basic Processes

Many processes have been evaluated for the production and deposition of energetic or ionized particles. Angus and coworkers (1986) classified the different preparation techniques as to whether hydrocarbon gases or solid carbon sources are used. These are shown schematically in Figures 2-11 and 2-12, respectively. Table 2-3 (as modified from Weissmantel, 1985) is a compilation of many references related to this work. Examination of this body of work reveals that basically three processes have been exploited for formation of these materials: (a) extraction of ions from a plasma essentially in the same region and pressure regime as the sample; (b) extraction or repulsion of ions from a plasma created in a region physically or electrically separated from the sample location; and (c) use of ions to sputter material from a target to the sample.

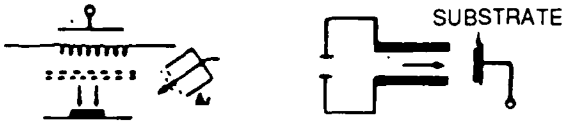
Figure 2-13 shows a typical ion plating configuration for the generation of ions and their propulsion to the substrate and growing film. In this case, electrons emitted from a hot cathode create a plasma discharge region or sheath in which molecules are introduced either through a gas inlet or through evaporation by a separate e-beam evaporator. These volatile molecules are ionized in the plasma discharge region and extracted from the region by the potential between the substrate and the plasma potential. Reactive and inert gas ions bombard the surface at a potential related to the bias potential applied between the substrate and plasma potential zone. The ion energy spread is wide due to collisions at the gas pressures used for generation of the plasma. An oscillating potential can be applied to the anode grid in order to increase the electron flight path and hence increase ionization efficiency. Depending on the bias voltage, the hydrocarbon molecules, and the chamber pressure, film growth rates have been measured in the 50 to 100 Å/sec range. Commercial equipment is available that employs this technology for production of diamond-like coatings, and related systems have been employed to coat substrates up to 1 m^2 in size.



a. RF parallel plate b. RF inductive discharge C. DC glow discharge



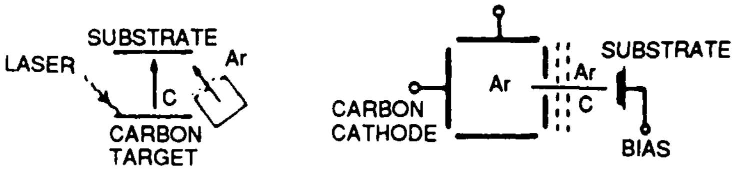
d. DC glow discharge with biased screen e. Triode f. Hot filament discharge



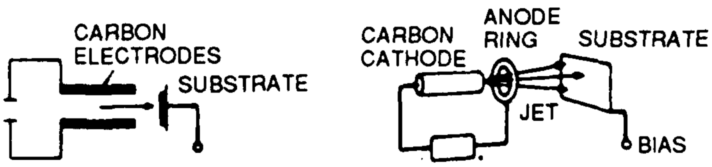
g. Hot filament discharge with auxiliary ion beam h. Pulsed discharge rail gun

FIGURE 2-11 Processes for growing carbon films from hydrocarbon gases (Angus et al., 1986).

a. Dual beam sputtering b. Single beam sputtering



c. Laser evaporation with auxiliary ion beam d. DC glow discharge with accelerating grids



e. Pulsed discharge rail gun f. Vacuum arc-discharge runs off cathode material

FIGURE 2-12 Processes for growing carbon films using solid carbon (Angus et al., 1986).

TABLE 2-3 Decomposition Data for DLC, BN, and Related Composites

Technique	Reactants	Approximate Deposition Pressure (Torr)	Ion Energy (eV) or Sample Bias	Comments	References
DC Plasma Deposition	C_2H_2	10^{-3}-10^{-4}	-	Glossy films	1,2
	C_2H_4,(Ar)	1.2x10^{-2}	2000-5000 V	Black hard films	3-5
	C_2H_2	0.9	300- 400 V	Yellow or brown inert films	6,7
RF Plasma Deposition	C_4H_{10},(CH_4,C_3H_8)	0.2	100-1900 V	Hard insulating films, depending on parameters	8-14
	C_2H_2	0.5	-	Yellow-brownish insulating films	15
	C_2H_6,(C_2H_2,C_2H_4,C_3H_8)	7x10^{-2}	500-1000 V	Hard insulating films, $p = 1.9$-$2.0\ g/cm^3$	16-18
	C_2H_4	7x10^{-3}	10-1400 V	Very low friction coefficients	19,20
	C_3H_8	.15	400- 700 V	Optical coatings	21
	C_6H_6	2.2x10^{-2}	400-1800 V	Optical and protective coatings	22,23
	CH_4,C_2H_6	7x10^{-3}	500-2000 V	Coatings with diamond-like properties	24,25
	CH_4	3x10^{-2}	540 V	Investigations on kinetics and structure	26,27
	CH_4,C_2H_2,C_2H_4	7x10^{-2}	-	Particle conglomerates or films containing microcrystals	28
	C_3H_8(Ar)	-	-	GeC interlayer to improve adhesion	29
		7.5x10^{-6}	10-1400 V	Study of tribology properties	30
Sputter Deposition	C,(Ar,Kr)	1.5x10^{-4}	-	Ion-beam sputtering	31-36
	C,H_2,(Ar)	.4	-	Ion-beam sputtering with H^+ participation	37,38
	C,CH_4,(Ar)	1.5x10^{-4}	200-1000 eV	Dual-ion-beam sputtering	33,38-43
	C,(Ar)	4.5x10^{-3}	0- 300 V	RF bias sputtering	44
	C,C_2H_2,(Ar)	1x10^{-3}	-	Hybrid process: dc magnetron sputtering and plasma decomposition	45-50
	C,C_4H_{10}	3.7x10^{-2}	0- 100 V	Hybrid process, low-stress films	51
	Ar	3 x10^{-2}	150 V	Ion beam sputter with assist beam	52
	Ar	7.5x10^{-3}	-	Magnetron sputter at various power levels	53
	Ar	7.5x10^{-3}	0- 150 V	Unbalanced magnetron with bias	54
	-	-	-	Fibrous carbon source	55
Ion Plating Techniques	C_6H_6 (Tetraline, antrhacene)	2.2x10^{-4}	20-5000 V	Deposition rates of 30-100 nm/min at low pressures	8,38,56-58
	C_6H_6,Al,Si,Ti,Cr	2.2x10^{-2}	200-3000 V	Preparation of Me/i-composites	38,59-64
	C,CH_4,(Ar)	-	3000-5000 V	Columnar film morphology	
Ion Beam Deposition	C,(Ar)	3.7x10^{-5}	20- 100 eV	Very hard, inert, transparent films	9,65-70
	C,CH_4	-	900 eV	Epitaxial layers on diamond	
	CH_4	7.5x10^{-2}	20- 800 V	Hard films containing micro-crystals	71
	C,(Ar)	5 x 10^{-9}	30- 100 eV	Mass filtered ion beam, small crystallites	72
	C,(Ar)	7 x 10^{-7}	10-1000 eV	Mass filtered ion beam, high resistivity coatings	73
	CO	5 x 10^{-10}	1- 300 eV	Mass filtered ion beam	74
	CH_4(Ar)	2 x 10^{-4}	100 eV	Dual ion beam deposition	75
	CH_4(Ar)	5 x 10^{-5}	90- 250 eV	Single beam direct deposition	76

TABLE 2-3 Decomposition Data for DLC, BN, and Related Composites (Continued)

Technique	Reactants	Approximate Deposition Pressure (Torr)	Ion Energy (eV) or Sample Bias	Comments	References
Other Techniques	C,(Ar)	-	0- 980 eV	Laser evaporation with ion bombardment	34,77
	CH_4	0.37	-	Pulsed plasma process	78
	C,(Ar)	750	-	Ion generation from randomly moving arc spot, high deposition rates	79
	C(Ar)	1×10^{-6}	-	Coaxial carbon plasma gun	80
Deposition of i-BN	BN,N_2,(Ar)	$7.5x10^{-3}$	-	RF sputtering, stoichiometric films	81,82
	BN,N_2,(Ar)	$4.5x10^{-3}$	0- 100 V	RF bias sputtering, inert, dense films	83
	B,N_2,NH_3,(Ar)	$1.5x10^{-3}$	0-3500 V	Ion plating combined with electron beam evaporation	21,32,38,56, 60
	BH_3,B_2H_6,N_2,NH_3	-	-	Plasma decomposition	84-86
	B_3,N3,H_6,(Ar)	$2.2x10^{-4}$	200-1000 V	Plasma decomposition	32,56,87
	B,N_2	$7.5x10^{-6}$	40 keV	Electron beam evaporation of B with nitrogen ion bombardment	88,89
	B,N_2	5×10^{-7}	2- 25 kV	Boron E-beam evaporated, nitrogen ions	90
	$B_3N_3H_6$	5×10^{-4}	-	Stoichiometric BN	91
	BN,Ar	-	-	FAB dual beam sputter deposition	92
Review Articles	-	-	-	Review of UK RSRE applications	93
	-	-	-	A review of recent work on hard DLC films	94
	-	-	-	DLC for thin film media for magnetic recording	95

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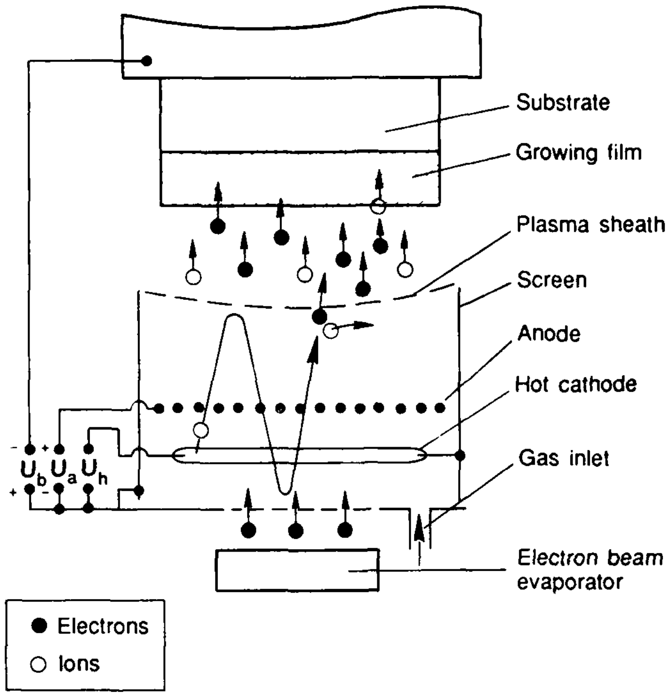

FIGURE 2-13 Ion plating configuration.

An alternative approach to the ion plating technique is the use of an rf-plasma-assisted CVD system also using a voltage bias on the sample holder. A typical configuration is shown in Figure 2-14. Radio frequency energy of 13.56 MHz is applied to the lower electrode. This creates a plasma between the lower electrode and upper electrode that is at rf ground potential. Superimposed on the rf potential is a negative bias, typically 300 to 1000 V. This results in bombardment of the lower electrode (holding the samples) by energetic species extracted from the plasma. An alternative configuration of this same technology allows the sample electrode to self-bias due to the very different mobilities of electrons and ions. This will also result in energetic bombardment of the samples.

This configuration has seen significant development for the production of optical coatings. One application has been for the deposition of hard a-C:H coatings on germanium substrates. Equipment has been constructed for coating objects up to 1 m in diameter.

Figure 2-15 shows the original sacrificial cathode ion source developed for direct ion beam deposition of diamond-like carbon coatings. In this process, a high-voltage discharge is initiated between the carbon cathode and carbon anode in the ion source. Argon is supplied to this discharge, and the resulting charged argon ions sputter the negative electrode, introducing sputtered carbon into the plasma discharge. Ions of argon and carbon are extracted through an orifice by appropriate electronic extraction optics and are impinged on the sample held in a second vacuum chamber at substantially lower pressure. This technique results in amorphous carbon coatings with little or no hydrogen. In addition, the low vacuum pressure of the deposition chamber results in a more uniform ion energy profile. Small crystallites (up to 5 μm) of diamond have also been produced by this technique.

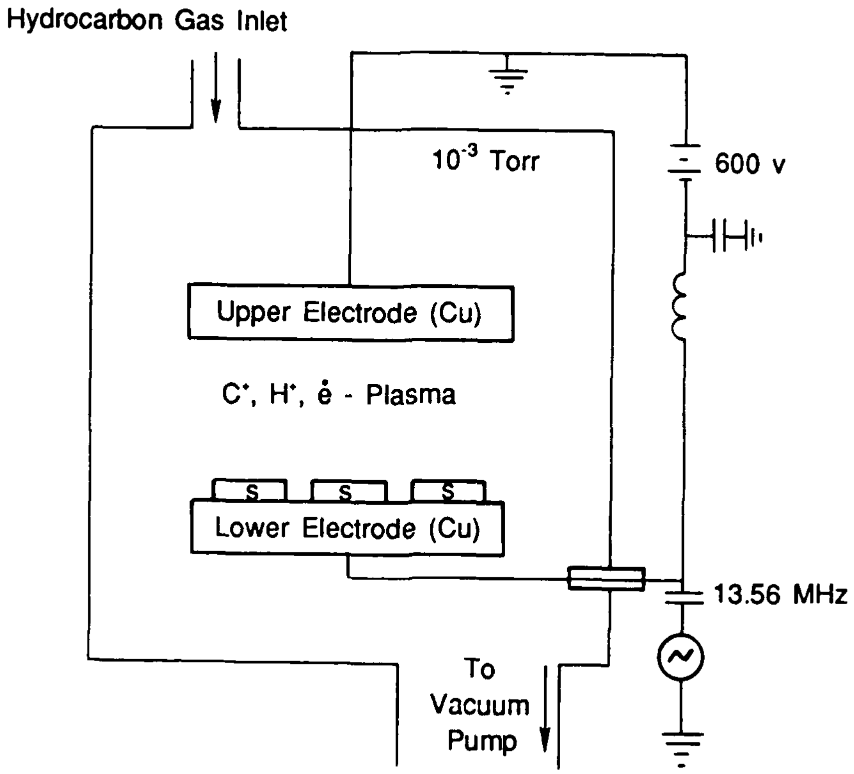

FIGURE 2-14 rf plasma configuration.

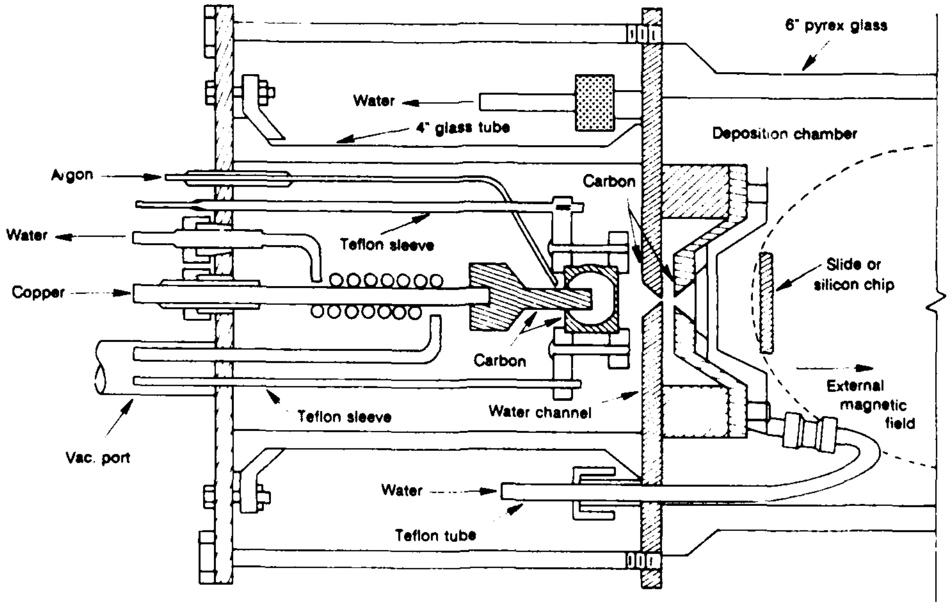

FIGURE 2-15 Direct ion beam deposition from solid precursor configuration.

Another manifestation of the single ion beam direct-deposition approach is shown in Figure 2-16. In this technique, a standard Kaufman-type ion source is employed for the generation of energetic carbon and argon ions. Because a hydrocarbon feed is used, substantial quantities (up to 30 atomic percent) of hydrogen are incorporated into the resulting amorphous coating. This inclusion of hydrogen can be beneficial in tailoring the refractive index of the resulting material. In addition to diamond-like carbon, this technique has also been employed for the production of cubic BN coatings.

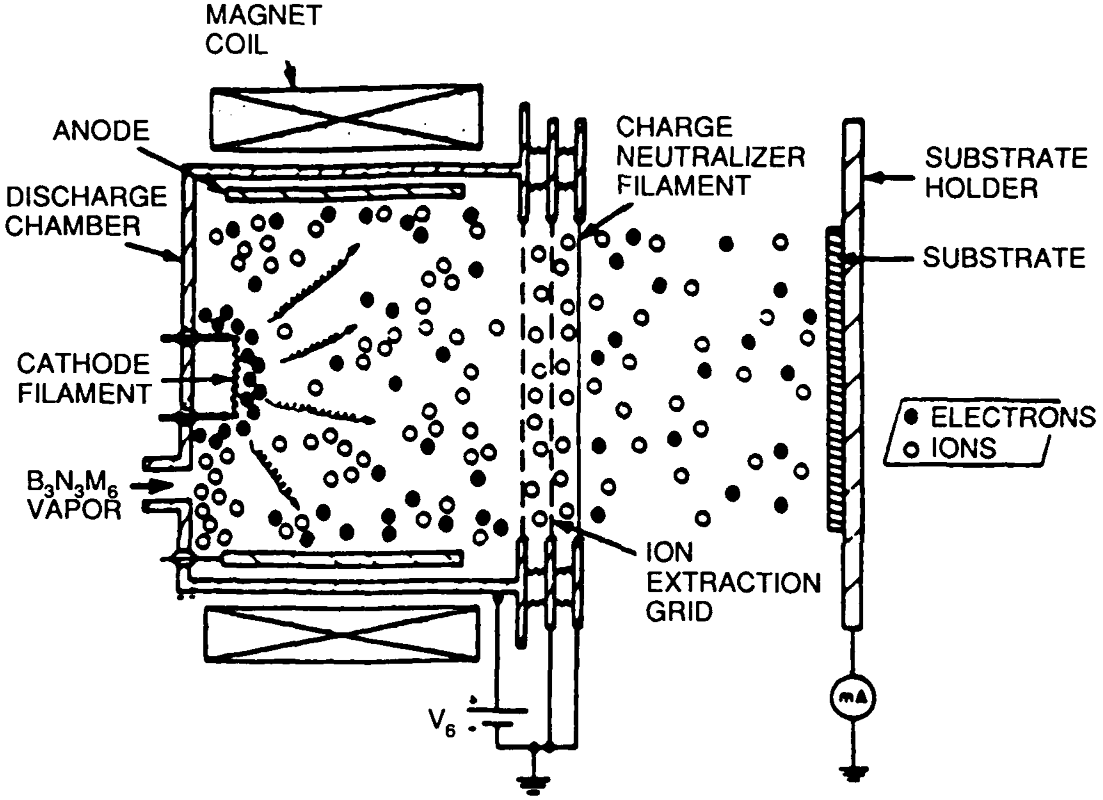

FIGURE 2-16 Direct ion beam deposition from gaseous precursor configuration (Holland and Ojba, 1978; and Berg and Anderson, 1979).

Figure 2-17 shows a modification of the single direct ion beam deposition configuration. In this technique, originally developed by workers at NASA's Lewis Research Center (Mirtich, 1981) and other laboratories, a second ion source is typically operated at higher ion energy than the depositing source. The resulting films have been shown to be clearer than diamond-like films produced from a single beam ion source using volatile precursor molecules.

Another modification of the dual ion beam system is shown in Figure 2-18. In this system, carbon is sputtered from a graphite target by the first ion source. The sputtered carbon is allowed to deposit on the substrate with or without secondary ion bombardment. A second ion source, operated at a lower ion energy, can be employed to further bombard the sample surface. This results again in films with improved mechanical and optical properties. This technique has also been employed for the production of cubic BN films.

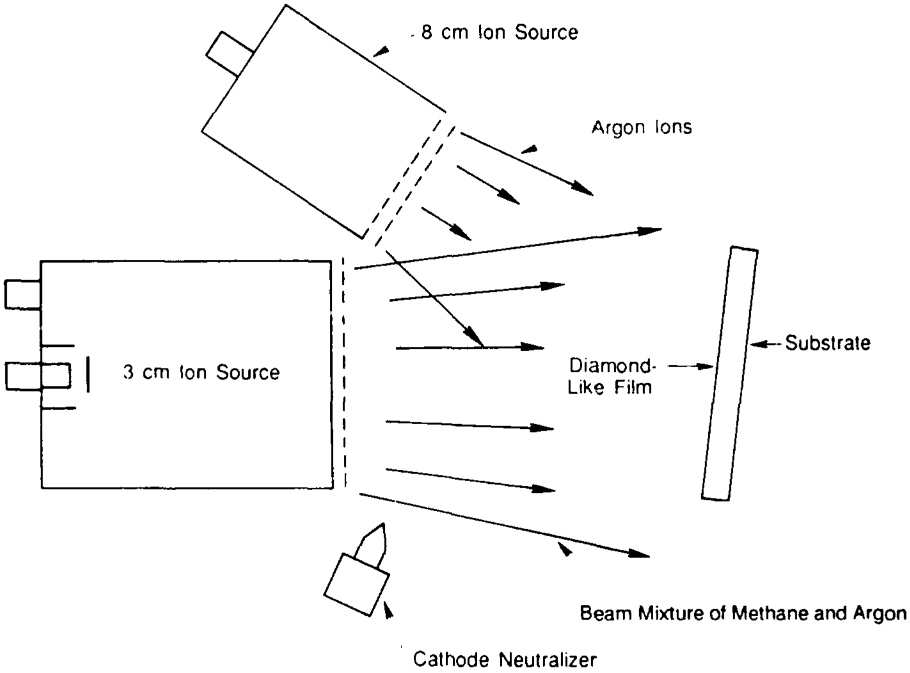

FIGURE 2-17 Dual ion beam deposition configuration (Mirtich, 1981).

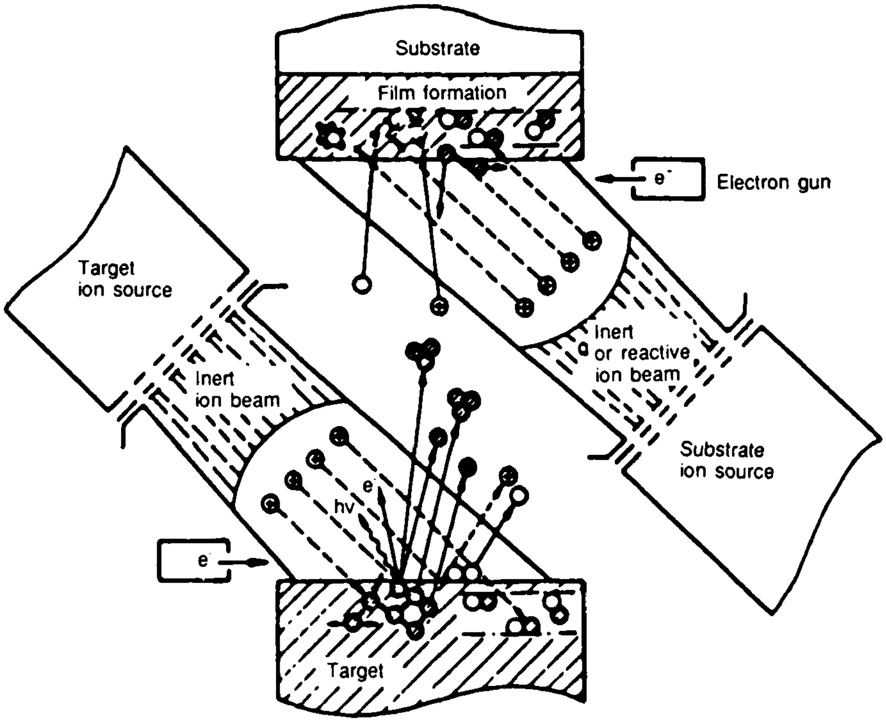

FIGURE 2-18 Ion beam sputtering with ion beam assist configuration.

Critical Growth Parameters

Amorphous diamond-like carbon and cubic BN thin films have been produced by ion-assisted processes primarily through close control of ion energy. Many of the fundamental processes involving the nucleation of these films, the critical role of the impinging ion energy, and the relative roles of deposition ions (i.e., CN_n^+) versus argon ions are still not well understood despite extensive study over many years. However, it is abundantly clear that a new class of materials with very interesting physical, electronic, and optical properties can be produced by this technology. The following sections point out some of the considerations necessary in producing these materials.

Substrates and Film Nucleation

Since it is possible to operate ion-assisted processes at temperatures below 100°C, a wide variety of substrates have been studied in the deposition of these amorphous thin films. Substrates tested include a wide variety of optical materials (CR 39 optical plastic, polycarbonate, glass, quartz, sapphire); infrared-transmitting optical materials, including germanium, zinc sulfide, and zinc selenide; a variety of hard substrates including normal steels, tool steels, and cemented carbide substrates; and a variety of electronic-grade materials. Although thin films can be produced on this wide variety of substrates, the adhesion properties of the coatings and their resistance to abrasion vary widely. Generally, sputtering of the substrate prior to deposition is employed to improve adhesion properties. In addition, thin interlayers such as germanium on ZnS have also been used to improve adhesion (Lettington et al., 1987).

The processes involved in the initial nucleation of the coating vary, depending on the deposition process. Generally, coatings produced by ion plating techniques and those produced by ion beam sputtering nucleate quite easily, and films grow rapidly thereafter. However, films produced by direct ion beam deposition show a significant influence of substrate type on initial coating nucleation. Seeding techniques such as those discussed in the earlier section entitled "Substrates and Their Preparation" are not generally employed for these amorphous coatings.

Deposition Pressure

As can be seen from Table 2-3, at least two distinct regions of process pressure are used in depositing these coatings. Coatings produced by ion plating and related techniques, wherein the gas discharge is in the same pressure regime as the sample, employ chamber pressures in the millitorr region. Direct ion beam deposition techniques, on the other hand, utilize pressures in the submillitorr region. Because of this fundamental difference, coatings produced by ion plating typically grow at faster rates but have poorer optical and electronic properties than those produced by ion beam processes.

Ion Energy Considerations

Perhaps the single most widely studied process parameter employed in producing ion-assisted coatings is control of the energy of the incident energetic particles. These studies have clearly shown that many of the resulting film properties can be directly related to the control of particle energy. Ion plating and related techniques typically use sample bias voltages of 500 to 1500 V. Because of the relatively high gas pressures utilized in these processes, the actual energy of particles impacting the surface is considerably less. In addition, a wide spread of particle energies can be expected in these techniques.

Direct ion beam deposition processes have focused on ion energies ranging from 50 to 150 eV. Careful control of ion energy in high-vacuum systems employing mass filtering of carbon ions has been shown to produce crystalline diamond materials up to several micrometers in size (Chaikovskii et al., 1981).

Size of Substrates

Process equipment for coating substrates up to 1 m in diameter has been constructed for ion plating and related deposition systems. Until recently, the area coated by direct ion beam processes has been restricted by the unavailability of large-area ion beam source technology. Most of the experimental work has been conducted utilizing sources capable of covering areas ~15 cm in diameter or smaller. Recently, however, commercial ion beam sources have become available up to 38 cm in diameter. In addition, ion sources up to 1.5 m in diameter have been constructed at the NASA Lewis Research Center. The availability of large-coverage-area ion sources will accelerate development of direct deposition of these materials.

Fundamental Issues in PVD Processes

Ion-assisted PVD processes take advantage of the production of metastable species by the condensation of energetic particles. The energy contained in the condensing particle is employed in preferentially rearranging the bonding structure on the material surface. Much of the fundamental chemistry and physics occurring on the surface is still not well understood. However, some issues are clearly important, and a variety of theories have been advanced to explain the nature of these resulting unique materials.

Growth Mechanisms

As particles of varying energy impact on a solid surface, a number of basic processes can occur, including recoil of the particle from the surface, ejection of material from the surface caused by the impact (sputtering), sticking of the particle to the surface, also with resulting energy transfer from the particle to the solid surface, and implantation of the particle into the surface with resulting energy transfer. A variety and combination of these processes may well be occurring in many of the deposition approaches used for making amorphous diamond-like carbon and other hard materials.

In the case of the production of diamond-like carbon, it is important to understand why carbon atoms are deposited in the tetrahedrally bonded (sp^3) structures versus the non-sp^3 bonded carbon structure. One theory proposed to explain this observed result is that of preferential sputtering (Spencer et al., 1976). Under the conditions used in the deposition of these coatings, an arriving energetic particle is most likely to either recoil from the surface, condense on the surface, or eject material from the surface. Studies done by Angus and coworkers (1986) and by Miyazawa and coworkers (1984) indicated that impinging energetic particles may have sufficient energy to preferentially sputter non-sp^3 bonded carbon materials. Consequently, over a given time period the material remaining on the surface will contain a preferential enrichment of sp^3 structures.

The second proposed concept for the stabilization of sp^3 bonded structures involves the high transient temperatures and pressures that appear in the immediate vicinity of an impacting energetic particle. Weissmantel (1981) proposed that transformations into sp^3 structures can occur during these short-lived pressure and temperature events. Although the correctness of this theory has been debated, it appears clear that the growth surface is undergoing energetic bombardment of sufficient energy for a variety of transformations to occur.

It does appear that, whatever the detailed mechanism of formation, the final structure of diamond-like hydrocarbons is close to that predicted for completely constrained, random covalent networks.

Microstructure

Diamond-like carbon films have been shown to contain a variety of hydrogen contents and range of atomic structures. The majority of the dense films have been found by x-ray examination to be amorphous. Sometimes small crystallites have been identified, particularly in films produced by ion beam processes. These crystallites have been identified as having both graphite and diamond structures.

OTHER DEPOSITION PROCESSES

It is interesting to speculate that if part of the diamond-making process involves the stabilization of the surface, whether it be in the equilibrium or metastable regions, then there may be other ways of doing this. There are two claims in the category of synthesis in the presence of a liquid phase under metastable conditions: (a) the report of overgrowths on diamond in a molten salt in the presence of nickel (Patel and Cherian, 1981); and (b) the breakdown of Al_4C_3 in the presence of a carbon halide in a molten salt (French and French, 1981, 1982). The latter definitely produced fine-grained hard powders. Although there has been adequate time for the use of such processes if they were indeed successful, there appears to have been no consummation of what are obviously exciting results. These should be reexamined.

Another regime for study is the C-H-O system in the pressure range up to about 20 kb. There is an apparent convergence in the literature on the reality of carbon deposition from this system in nature in liquids essentially immiscible with silicates.

Yet another approach to making diamond (and other high-pressure phases) at atmospheric pressure is the solid (graphite)-solid (diamond) transformation process mediated by intense laser irradiation of a loose, free-falling powder. Fedoseev and coworkers (1983) were the first to report successful experiments by this process using a CO_2 laser, and recently Alam and coworkers (1988) have confirmed these results using both CO_2 and Nd-YAG lasers. The current drawbacks to this approach are the low conversion efficiency of the transformation process and the fact that powder and not continuous films are produced.

OTHER SUPERHARD MATERIALS

Silicon carbide is considered a superhard material in the context of this report. It is about one-third as hard as diamond and comparable to cubic BN. Cubic BN is about half the hardness of diamond and is the second hardest material known. Corundum, α-SiC, is the hexagonal (6H) phase that normally forms; it has been produced commercially for many years by the Acheson process. Generally these crystals form dark platelets of low purity. High-purity transparent SiC is more difficult to obtain because of difficulty in purity and stoichiometry control, but crystals of 1 x 5 x 5 mm have been produced.

There are a large number of hexagonal and rhombohedral polytypes and only one cubic (3C) polytype, β-SiC. The β-phase has been produced by vapor deposition processes, and various procedures have been developed for heteroepitaxial growth on large-area silicone substrates based on various buffer layers to satisfy the mismatch in lattice parameter and thermal expansion coefficient. Thick layers have been successfully prepared by a number of workers (e.g., Nishino et al., 1980; Liaw and Davis, 1985).

Although high-purity heteroepitaxial films could be achieved, they still contain a high defect density of microtwins, intrinsic stacking faults, and antiphase boundaries. Recent results from the North Carolina State University group (see extensive review by Davis et al., 1988, which also discusses diamond films deposition) of the deposition on Acheson-type α-SiC [both Si (0001) and C (0001) faces] show that these defects could be essentially eliminated, with the only remaining defect being of the double-positioning-boundary (DPB) type. And even these DPB defects could be eliminated by 3° off-axis tilting of the substrate. However, in this latter case the resulting film is α-SiC and not β-SiC.

Silicon carbide films can be doped both n- and p-type, and this combined with its high thermal conductivity and electrical field breakdown strength, makes it an excellent material for electronic devices. The potential electronic and nonelectronic uses of this new high-purity and low-defect density material are just beginning to be explored.

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3

CHARACTERIZATION TECHNIQUES RELEVANT TO SUPERHARD MATERIALS

Many different types of analytical techniques have been used to characterize the superhard materials. More traditional methods such as optical microscopy, optical absorption, x-ray diffraction (XRD), x-ray fluorescence (XRF), and Auger spectroscopy, have proved very useful in ways that have been discussed at length in other publications (Field, 1979; Sze, 1983; Tsai and Bogy, 1987). The special characteristics of the superhard materials and their unusual growth methods, however, have led investigators to rely heavily on a number of less commonly used techniques. This chapter provides background regarding the nature of these techniques and the information they provide and points out the need for new characterization methods. The areas covered include techniques for characterizing phases present, surface structure, chemical composition, and properties such as thermal, electrical, and optical. The need for fundamental studies of the diamond-like materials is also discussed.

STRUCTURE STUDIES

Determination of the different carbon phases incorporated in diamond and diamond-like carbon materials is of importance for controlling the growth or deposition conditions. Several techniques are sensitive to differences between carbon phases, including Auger electron spectroscopy, electron energy loss spectroscopy (EELS), and Raman spectroscopy (Solin and Ramdas, 1970). Since Auger and EELS are surface analysis techniques, they are sensitive only to the first 3 nm of the surface and hence incapable of characterizing the bulk of the material. Raman spectroscopy appears to be the analytical tool of choice because the diamond Raman peak at 1332 cm^{-1} is easily distinguished from peaks related to other forms of carbon, as shown in Figure 3-1. A detailed investigation of the Raman spectra of films prepared under various deposition conditions, correlated with Auger and EELS data, should lead to the development of standard reference materials for calibrating instrumentation in the field (as opposed to the research laboratory).

In addition to the Raman signal, a photoluminescence signal may also be present. This fluorescence background arises generally from defect centers within the films and therefore could provide an analytical tool for their identification. This may be important for films to be used in electronic or optoelectronic applications because free carrier properties such as carrier lifetime and mobility may be affected by them. The presence of the fluorescence signal does introduce a

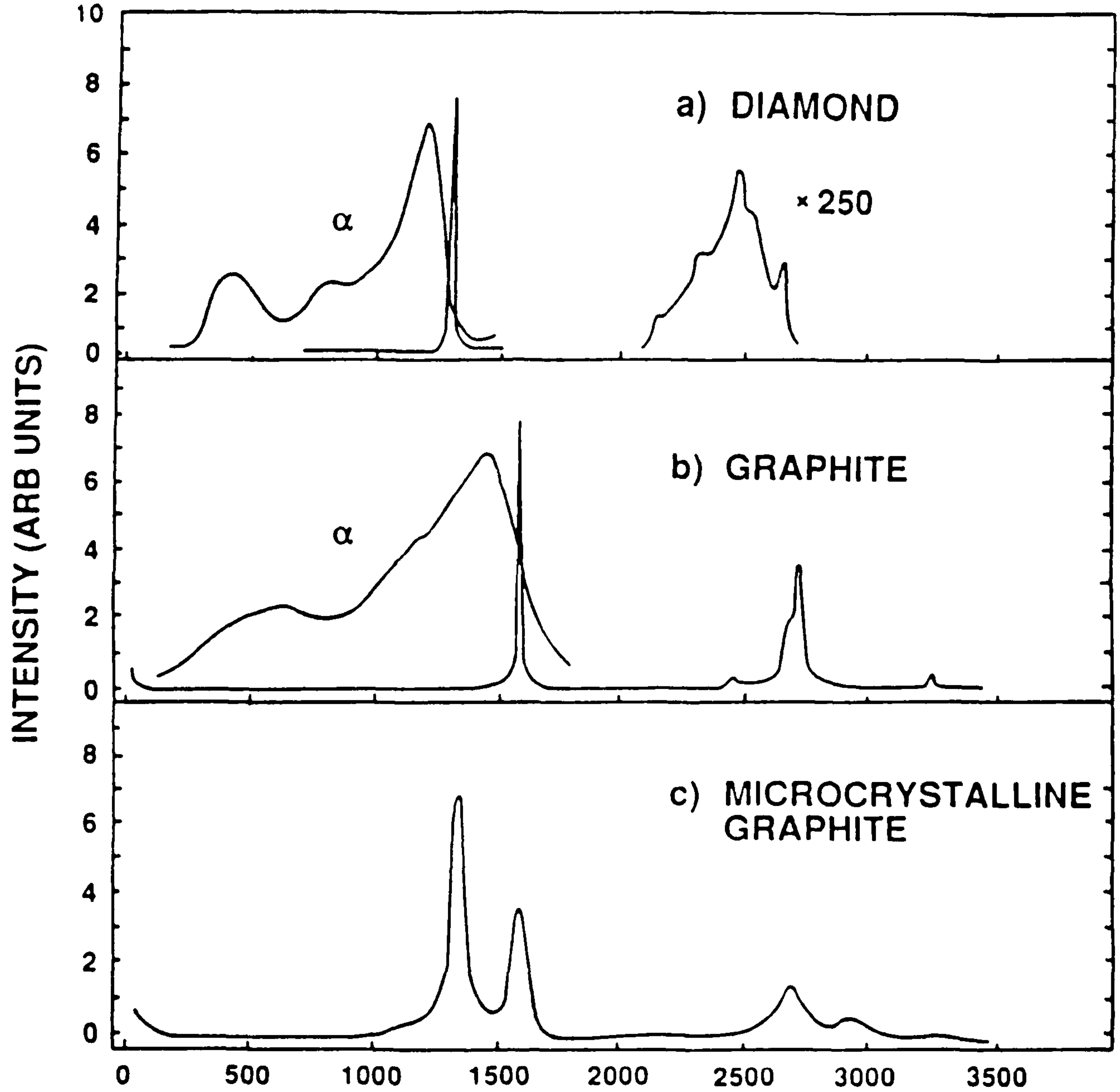

FIGURE 3-1 Raman spectra of (a) diamond, (b) graphite, and (c) microcrystalline graphite. The solid lines in (a) and (b) represent the first- and second-order spectra of crystalline diamond and graphite respectively. The broad line labeled α in (a) is the spectrum of α-Si scaled to the diamond frequency to represent the spectrum of amorphous diamond, while the broad line labeled α in (b) is that due to amorphous graphite (Nemanich et al., 1988).

problem, however, since it represents a background signal that must be subtracted from the Raman signal. If the fluorescence signal is large, experimental uncertainties introduced in the subtraction process could limit the ability to make the Raman data quantitative for this application.

The most critical single parameter for understanding the nature of the diamond and DLC materials is the sp^3/sp^2 ratio. Diamond is characterized by sp^3 bonding between atoms, and graphite is characterized by sp^2 bonding. The sp^3/sp^2 ratio can be determined by several techniques, including nuclear magnetic resonance spectroscopy (Hoch and Reynhardt, 1988), electron energy loss spectroscopy, and optical measurements of the dielectric function. Also of great interest is the distribution of hydrogen over the different types of carbon sites (CH, CH_2, and CH_3). This can be determined using Fourier transform infrared spectroscopy (FTIR). The diamond-like materials are typically amorphous, and the local environment around each carbon atom may provide information of interest. This can presumably be accomplished by neutron or x-ray diffraction techniques. Extended x-ray absorption fine structure spectroscopy (EXAFS) may also be useful in this context. The concentration of dangling bonds (free radical sites) may be measured by electron spin resonance (ESR).

The diamond-like materials often exhibit a medium-range order, which may be small clusters or microcrystallites. High-resolution transmission electron microscopy will undoubtedly be of value in characterizing these features.

Surface Characterization

The surface structure of diamond is extremely stable and is responsible for some of its interesting properties (e.g., low coefficient of friction and negative electron affinity). Characterization techniques useful for examining the structure of diamond surfaces may be conveniently divided into three categories, depending on whether they measure geometric structure, electronic structure, or chemical composition. A summary of these techniques follows.

Geometric Structure

The classical methods for studying the geometric structure of crystalline surfaces are low-energy electron diffraction (LEED) and high-energy electron diffraction (HEED). These methods are well known and require no discussion here.

Grazing angle x-ray scattering can also be used to give information about geometric surface structure. To apply this technique to monolayers, one requires a synchrotron x-ray source--e.g., the Brookhaven source--and very low scattering angles.

In recent years the scanning tunneling microscope (STM) has been developed. It is an extremely powerful method that can resolve individual atoms on surfaces but cannot be applied to insulating materials. The scanning force microscope, on the other hand, does not require a conducting substrate; however, its resolution is significantly less than that of the STM. The expectations are that the scanning force microscope will be able to provide atom resolution within the next few years.

Electronic Structure

The electronic structure of adsorbed species on surface can be studied by angle resolved photoelectron spectroscopy. Either x-ray or ultraviolet photons can be used. The angular and energy distribution of emitted electrons gives direct information on the electronic structure of the surface, from which geometric structures can also be inferred. Auger spectroscopy may also be useful.

Ultrahigh-vacuum ellipsometric spectroscopy can be used to investigate the electronic structure of surfaces. It can provide a measure of the dielectric coefficient tensor and its frequency dependence at optical wavelengths. This provides information about surface electronic states. In principle, the IR region can be done as well.

Chemical Composition

There are, of course, a number of other well-known surface analytical methods that give information on the composition, and sometimes bonding, in the near-surface region. These are secondary ion mass spectroscopy (SIMS), Auger spectroscopy, photoelectron spectroscopy and electron spectroscopy for chemical analysis (ESCA). For highly insulating materials, secondary neutral mass spectroscopy (SNMS) may be useful.

Dynamic Processes

Inelastic scattering processes give information on the motion of scattering centers. Both inelastic neutron scattering and inelastic laser light scattering can be applied to the study of diamond surfaces. Molecular beam scattering from diamond surfaces, perhaps using C^+ or H^+, also might be considered. Scattering intensity as a function of angle and energy will give information about dynamic processes on the surface.

Fourier transform infrared spectroscopy is an extremely powerful method for analyzing the vibrational modes of absorbed species. FTIR is now capable of monolayer sensitivity by means of double-reflection infrared and attenuated total reflection techniques. Raman spectroscopy can also be done in a Fourier transform mode and may prove useful for studying nucleation processes.

High-resolution electron energy loss spectroscopy can also be used to obtain information on the vibrational structure of absorbed species.

Molecular Modeling

Molecular modeling methods are powerful tools for the study of surfaces. Both static structural problems and dynamic processes may be studied. For example, molecular mechanics and more advanced *ab initio* quantum mechanical techniques can be used to study the state of reconstructed crystalline surfaces. Random, diffusive processes on surfaces can be modeled using stochastic methods directly--e.g., through the general Langevin equation for generating trajectories and various Monte Carlo algorithms. Also, molecular dynamic techniques can be used to develop trajectories, from which dynamics can be studied. Supercomputers are required for advanced work in either of these areas.

ELEMENTAL COMPOSITION

It is astonishing that a majority of reports on the DLC and diamond materials still do not include a measurement of the elemental composition of the films. Of particular importance is the amount of hydrogen. Hydrogen can be conveniently determined by ^{15}N nuclear reaction analysis (NRA), which provides a depth profile of hydrogen concentration. Hydrogen can also be determined by helium forward scatter spectroscopy, but with a higher detection limit. Analysis of heavy elements is conveniently done by Rutherford backscatter spectroscopy (RBS). Auger spectroscopy is also useful for elemental analysis, and when combined with sputtering can give composition profiles as well. However, both RBS and Auger spectroscopy have detection limits on the order of 10^{-3} atomic percent. When lower detection limits are required secondary ion mass spectroscopy or neutron activation is useful. Finally, combustion analysis can provide measurements of hydrogen, carbon, oxygen, and nitrogen for samples of milligram size.

FUNDAMENTAL MECHANICAL MEASUREMENTS

Surprisingly few measurements of the fundamental mechanical properties of CVD diamond and diamond-like materials have been made. Of particular interest would be the measurements of the modulus of elasticity, the thermal expansion coefficient, the thermal conductivity, and the level of internal stress. All of these mechanical properties are of fundamental importance for many proposed applications.

The films appear to be very impermeable; however, there are no accurate measurements of the permeabilities of these materials. Applications of diamond and diamond-like materials as diffusion barriers, corrosion protection layers, and vapor barriers will depend on the permeabilities.

A simple and very instructive property that should be routinely measured is the mass density. When combined with the knowledge of elemental composition, this permits placing the material of interest in the field of atom number density versus atom fraction hydrogen (Figure 3-2). This type of plot provides a convenient way for categorizing different classes of hydrocarbons and carbon. Similar compounds, for example the *n*-alkanes (AL), fall in tight groupings of the diagram. Diamond, DI, is at the upper left-hand corner. The adamantanes, AD, which are 10 and 14 carbon atom molecular diamonds, are at the lower right of the diamond-like hydrocarbon (a-C:H) grouping. The diamond-like hydrocarbons (filled symbols) range from approximately 0.20 to 0.60 atom fraction hydrogen and have number densities greater than 0.19 gram-atom per cubic centimeter. The vertical dashed lines show the theoretical composition range predicted for fully constrained, random hydrocarbon networks. The atom number density of a-C-H increases with hydrogen content, in contrast to the behavior of conventional hydrocarbons. This increase is caused by the increase in average coordination number of carbon from 3 to 4 as the amount of hydrogen is increased. The diamond-like carbons (a-C) appear to be a different class of material, with little or no hydrogen and with atom number densities from approximately 0.19 to 0.28 gram-atom per cubic centimeter. These densities indicate significant sp^3, tetrahedral, bonding. The amorphous carbons (AM) are dominated by sp^2, trigonal, bonding and can be formed by laser or electron-beam evaporation. Other symbols are AC, oligomers of acetylene; AD, adamantanes; AR, polynuclear aromatics; and GR, graphite.

There are indications from several sources that the diamond-like materials are inhomogeneous. In particular, variations of elemental composition and properties with depth of the film are suspected. This question is rarely addressed but should be considered when assessing film properties. The interface between diamond or diamond-like materials and various substrates

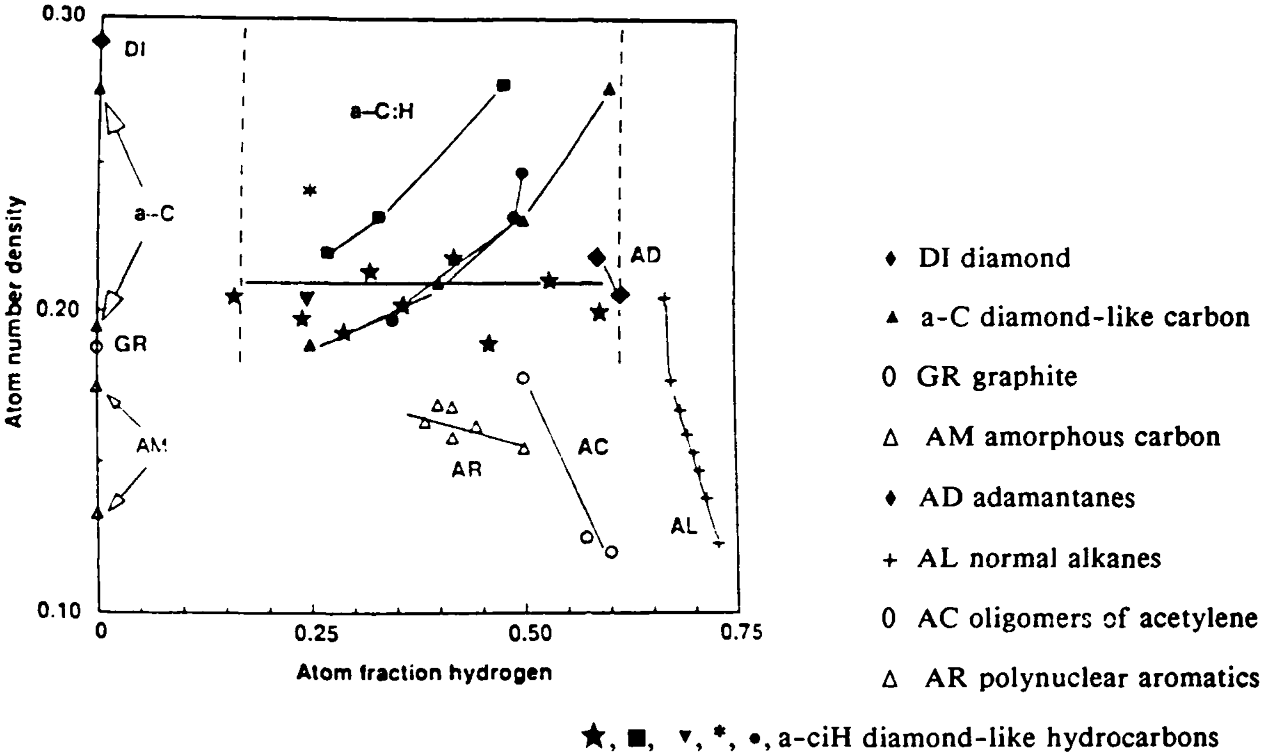

FIGURE 3-2 Atom number density versus atom fraction hydrogen (Angus and Hayman, 1988).

is also of great importance. The strength of adhesion and the nature of this interface will often be the dominant factors in determining whether these materials can be used in specific applications. Recent work on the performance of brittle coatings (Evans, et al., 1983) has relevance to diamond.

Scratch and Hardness Tests

Although the quantitative meaning of a scratch test can be obscure, the qualitative results can be useful as an indicator of relative wear and hardness. It is fairly simple to set up comparative materials for scratch tests: Sapphire (Al_2O_3), cemented WC, SiC, B_4C, cubic BN, and diamond separately mounted metallographically and polished can be used as a base on which the unknown is rubbed (usually a circular motion enhances distinction of new scratches from background). More sophisticated techniques like motion of a diamond point over the sample surface can sometimes be made more quantitative. Indentation techniques on thin films are difficult and should be viewed with skepticism, particularly when the unknown is essentially as hard as diamond. Careful observation of the scratch itself is also sometimes qualitatively helpful in relative hardness evaluation.

Woodell abrasion resistance is a somewhat more quantitative measure of hardness based on relative wear of different materials as determined by measurement after simultaneous abrasion under controlled loads. The technique is not as convenient as a simple scratch test (Woodell, 1935).

THERMAL CONDUCTIVITY

Many of the applications of superhard materials, especially CVD diamond, will rely heavily on their high thermal conductivities (Figure 3-3). Recent work has shown that the thermal conductivity of CVD diamond depends strongly on the hydrogen/methane ratio used in the microwave plasma CVD process and that the measurements correlate strongly with the DLC 1332 cm^{-1} peak in the Raman spectrum (Ono et al., 1986). It has also been shown that the thermal conductivity of CVD diamond below room temperature is significantly lower than that of natural diamond crystals (Morelli et al., 1988), possibly because of the small crystallite sizes in CVD diamond. This variability makes it imperative that the thermal properties of CVD diamond be well characterized, not only as a means of establishing design parameters for specific devices but also because it may be possible to use thermal measurements as a means of monitoring the deposition process.

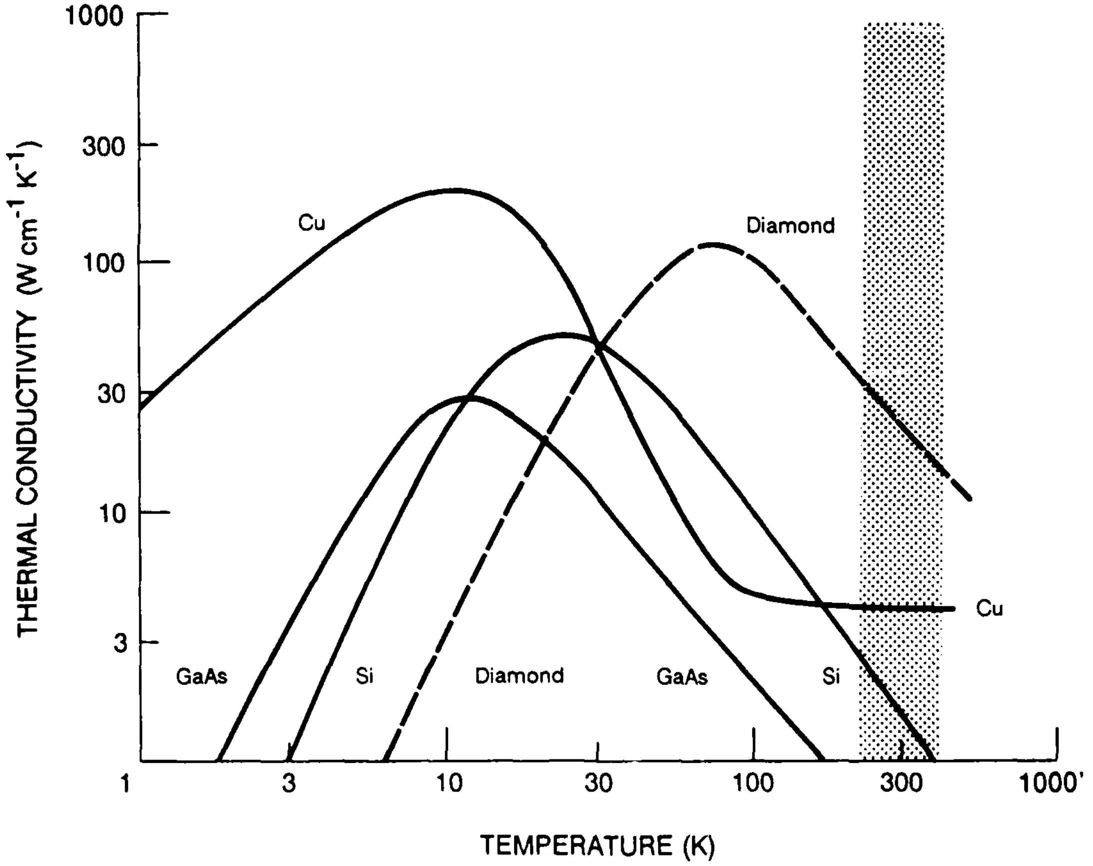

FIGURE 3-3 The thermal conductivity of various materials as a function of temperature. The vertical band represents the temperature region from -25 to 125°C.

Measurements of thermal properties are important at temperatures below and above room temperature. Diamond has the highest thermal conductivity of any known material at room temperature. The temperature range between 20 and 250 K is important not only because thermal data can provide a measure of the quality of the diamond but also because diamond has considerable potential for applications as a superconductor of heat in this temperature interval. Measurements above room temperature are desirable because electronic devices made of diamond are expected to operate at elevated temperatures.

The methods of Ono and coworkers (1986) and Morelli and coworkers (1988) are cumbersome and would probably not be suitable for routine measurement; both employ delaminated CVD diamond films, which are highly brittle. In the Ono method the film strip is suspended in vacuum between two heated supports. The temperature distribution along the length of the sample is measured by means of a thermograph, which monitors the specimen through a CaF_2 window. From an approximate solution of the steady-state heat diffusion equation, the thermal conductivity of the film can be calculated.

The Morelli method is more conventional and allows for measurement of thermal conductivity as a function of temperature down to 20 K. Thermocouples are attached to a strip of delaminated diamond film suspended in a cryostat, and one end of the film is heated to establish a thermal current in the film. From a measurement of the temperatures at two points along the film and other parameters, the thermal conductivity can be calculated.

Several methods based on thermal wave generation and detection appear promising for measuring the thermal properties of diamond films. These methods yield the thermal diffusivity, A, which is related to the thermal conductivity, k, by

$$A = k/C\rho$$

where C = specific heat and ρ = density.

The first method is called photothermal radiometry (Konstad and Nordal, 1980). In this technique, a laser beam (CO_2 or argon-ion) modulated at a frequency, f, is focused onto the surface of the diamond film, thus heating the surface and causing a thermal wave to propagate into the film. The temperature at the surface is measured with an infrared detector, typically liquid-nitrogen-cooled InSb. The temperature at the surface depends not only on the direct heating from the laser beam but also on thermal energy that returns to the surface because of reflections at the film-substrate interface. (Reflections may also result from defects within the film.) Thermal waves are highly damped, with the penetration depth varying inversely with the square root of f. Thus, by varying f, one can probe to different depths of the film, thereby affecting the amount of thermal energy reflected from the film-substrate interface. By measuring the phase of the surface temperature as a function of f, one can obtain the thermal diffusivity of the film and, hence, the thermal conductivity. The phase of the thermal signal is measured with a vector lock-in amplifier. Measurements can be made over a temperature range of 20°C to 900°C by conducting the experiments with the specimen in a furnace (Frederikse and Ying, 1988).

With pure diamond films 0.1 to 1 mm thick, frequencies in the range 1000 to 4000 Hz are needed. In the case of thinner films, the frequencies required can be significantly higher, and consequently the measurements can be more difficult to perform. In this case, a variation of the technique could be used. For example, instead of measuring the effect of propagation of heat normal to the film surface, one could measure the effect of heat propagation parallel to the surface. This type of experiment can be done at significantly lower frequencies.

Another method that can be used is the optical beam deflection technique (Boccara et al., 1980). Here again, the film surface is heated by a focused, modulated laser beam. In this method, a probe helium-neon laser beam skimming the surface of the specimen is deflected by the thermal gradients in the air, which act as a probe of the specimen temperature. The deflection is measured by a quadrant detector. By translating the probe beam position relative to the heated spot on the film surface, one can obtain not only the thermal diffusivity of the film but, in addition, the thermal anisotropy in the film.

The thermal properties of diamond are most sensitive to defects near 77 K, the temperature at which the thermal conductivity of pure diamond has a maximum. At this temperature phonon scattering begins to limit the thermal conductivity, and above this temperature only large concentrations of defects would be important. Thus, thermal measurements are expected to yield excellent data regarding defect densities in diamond films. In this case, methods based on the work of Morelli and coworkers (1988) appear to be most appropriate. Residual stress can be a consequence of the thermal history.

ELECTRICAL AND OPTICAL CHARACTERIZATION

The performance of semiconductor materials in electronic and optoelectronic devices such as transistors, detectors, light-emitting diodes, lasers, and optical switches is dependent on the extrinsic electronic states in the material. These states may be deliberately introduced into the material by processes such as doping and ion implantation, or they may be present because of unwanted impurities and defects introduced during processing. Important parameters regarding these states are concentrations and spatial distribution of defect and impurity states; energy levels within the band gap; carrier (electrons and holes) capture rates, release rates, and mobilities; recombination rates and branching ratios for radiative and nonradiative decay; and quantum efficiencies for luminescence and photoconductivity. Some of the techniques that can be used to probe the defect-related electronic states that lie within the forbidden gap of diamond and SiC and how these states affect the electronic properties are as follows:

- **Cathodoluminescence imaging and spectroscopy**. These experiments can be carried out in a scanning electron microscope. Cathodoluminescence is optical emission from defect-related or intrinsic electronic states resulting from excitation by an electron beam. By combining scanning-electron imaging with luminescence spectroscopy, information about point defects and impurities, extended defects (e.g., dislocations, stacking faults), and crystal growth habits can be correlated (Collins, 1987). In addition, cathodoluminescence imaging can be correlated with secondary-electron or other imaging modes of the electron microscope that may provide complementary information about crystal growth and morphology. Cathodoluminescence images and spectra in CVD diamond have been able to identify defect centers that have been observed in bulk diamond (Boccara et al., 1980).

- **Electrical conductivity**. This measurement provides information about the electrical activity of dopant species. The activation energies of impurities are investigated by measuring the temperature-dependence of the electrical conductivity. As part of this research, various methods of attaching electrical contacts to the specimens will require investigation.

- **Photoluminescence and photoconductivity excitation spectroscopies**. These techniques are used to study defect-related optical absorption. An arc lamp or flash lamp with high UV output, combined with a scanning monochromator, or a tunable excimer-pumped dye laser can provide the means for exciting photocarriers above the band gap. The absorption process is observed either by measuring the total luminescence signal as a function of the incident photon energy or by observing the wavelength-dependence of the photoconductivity. Time-resolved photoluminescence and photoconductivity also provide information about carrier (electron or hole) lifetime and mobilities.

A wide variety of defect centers have been identified in natural diamond by means of photoluminescence and cathodoluminescence. Some of these defects such as the neutral vacancy and nitrogen-carbon interstitial complexes have now been observed in CVD diamond. It is important that extensive investigation of these defects and their abundance in CVD diamond be carried out.

As is true with other new fields, progress in understanding behavior is impeded by the lack of a "standard" materials of known purity and structure. This is especially true in investigating electronic behavior; the distribution of standardized samples to various laboratories would be a boon.

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4

APPLICATIONS

New methods for producing superhard materials have enormously enhanced their potential applications in both old and new areas of technology. These applications generally will depend on a combination of properties. For example, the use of SiC and diamond as new semiconducting electronic materials will depend both on their electronic properties and on their thermal properties. Application of diamond as a substrate for electronic packaging takes advantage of a very high thermal conductivity for large heat dissipation, very high electrical resistivity for excellent electrical insulation, and low permeability for environmental protection of devices.

Tables 4-1, 4-2, and 4-3 list the combinations of properties that make superhard materials desirable for a wide range of applications. Six categories of materials have been chosen: single-crystal diamond, polycrystalline diamond composite, polycrystalline diamond film, diamond-like materials, SiC, and cubic BN. Specific applications are discussed in more detail in the following sections.

TABLE 4-1 Mechanical and Thermal Applications of Superhard Materials

Application	Property Utilized	Material
Bearings, journals	ABCDEF	23456
Barrier coatings	BC F	3456
Heat sinks	F	123456
Cutting tools	AB DEF	123456
Surgical blades, microtomes	A D	1 3456
Knives, cutting blades	AB DE	1 3456
Abrasives	A F	23 56
Medical implants	ABC E	34
Wire drawing dies	AB DEF	123 5

Legend

A - Hardness	1 - Diamond, single-crystal
B - Chemical stability	2 - Diamond, polycrystalline composite
C - Permeability	3 - Diamond, polycrystalline film
D - Young's modulus	4 - Diamond-like materials
E - Friction coefficient	5 - Silicon carbide
F - Thermal conductivity	6 - Cubic boron nitride

TABLE 4-2 Electronic Applications of Superhard Materials

Application	Property Utilized	Material
Transistors		
High-performance	F LM	1 56
High-temperature	BC F LMN	1 56
Radiation-hard	F J LM	1 56
High-power	F LMN	1 56
Negative electron affinity cathode	J L	1 3
Electrical insulators	B JK M	1 3456
Substrates, heat sinks	F K M	1 3
X-ray masks	ABCD G	1 34
Direct-write microelectronics	AB	4
Magnetic disks, heads	AB E	1 4
Hifh-voltage switches	F K M	1 56
Thermistors	F J	1 3 56
Packaging	A C F K M	1 34

Legend

A - Hardness
B - Chemical stability
C - Permeability
D - Young's modulus
E - Friction coefficient
F - Thermal conductivity
G - X-ray transmission
H - Infrared transmission
I - Visible transmission
J - Ultraviolet transmission, large band-gap
K - Electrically insulating
L - Semiconductivity
M - Dielectric strength
N - Carrier velocity\mobility

1 - Diamond, single-crystal
2 - Diamond, polycrystalline composite
3 - Diamond, polycrystalline film
4 - Diamond-like material
5 - Silicon carbide
6 - Cubic boron nitride

Many of the potential applications of superhard materials are currently limited by conditions during synthesis and by the properties of the resultant product. In the case of diamond films, limiting factors are high substrate temperatures during deposition; large surface roughnesses that are undesirable for many mechanical and optical applications; poor adherence to substrate materials; and stresses in the films that can lead to delamination and substrate fracture.

Other applications require single crystals or epitaxial films. Single-crystal diamond films have been grown homoepitaxially on diamond; however, epitaxial growth on other materials, which would be highly desirable, has not yet been confirmed. For electronics, one must be able to dope with electrically active species to produce both n-type and p-type conductivity. In the case of diamond, there is a problem of how to incorporate substitutional n-type dopants.

Finally, CVD deposition of polycrystalline bulk material, as opposed to thin film material, requires high deposition rates. Although high deposition rates have been reported in the literature, uniform deposition of high-quality material over large areas has not yet been achieved.

TABLE 4-3 Optical and Optoelectronic Applications of Superhard Materials

Application	Property Utilized	Material
Windows, lenses, mirrors	ABCD F HIJ	1
X-ray windows	ABCD FG	1 3456
Mirror substrates	ABC F	1
Heat sinks	F KM	1 3 56
Optical emitters, lasers, LEDs	F J L	1 56
Optically activated switches	F J LMN	1 56
Ultraviolet detectors	J L	1 6
Optical waveguide	C HI O	1 3

Legend

A - Hardness
B - Chemical stability
C - Low permeability
D - Young's modulus
E - Friction coefficient
F - Thermal conductivity
G - X-ray transmission
H - Infrared transmission
I - Visible transmission
J - Ultraviolet transmission, large band-gap
K - Electrically insulating
L - Semiconductivity
M - Dielectric strength
N - Carrier velocity\mobility
O - *Refractive index*

1 - Diamond, single-crystal
2 - Diamond, polycrystalline composite
3 - Diamond, polycrystalline film
4 - Diamond-like material
5 - Silicon carbide
6 - Cubic boron nitride

MECHANICAL APPLICATIONS

Bearings and Journals: Coatings and Monolithic

Single-crystal diamonds have been used as bearings and wear-resistant surfaces (as for phonograph needles) and more prominently for wire-drawing dies. This last use has been taken over by polycrystalline sintered diamond, which eliminates the problems of anisotropic wear (due to differential hardness) and weakness due to cleavage of single crystals. These compacts are available from the principal diamond manufacturers as layers up to several millimeters in thickness and 50 mm in diameter on cemented carbide or as cylindrical slugs of diamond at least 14 mm in diameter by 14 mm high. They are used as the "filling" in the hole of a doughnut of cemented tungsten carbide. These slugs are used primarily for wire-drawing dies, which are precision products with controlled grain size that improve the surface finish of wire. Tungsten carbide with a coated layer of sintered diamond is a proven product for well-drilling and cutting tools. Diamond-carbide composites are also used for bearing surfaces, but there is great opportunity for further innovative applications.

In their manufactured form, these compacts contain several percent of a metal phase as a result of the liquid sintering process. This phase imposes a maximum operating temperature of about 750°C. Above this temperature, catastrophic cracking failure occurs because of thermal expansion mismatch and incipient graphitization. It is possible to remove almost all of the metal phase by acid leaching, thus eliminating this cracking failure mechanism. However, the temperature limitations of graphitization and oxidation of diamond are still present. Cubic BN can be used at higher temperatures than diamond. Surface fluorination is being used to enhance the oxidation resistance of diamond (Margrave, et al., 1988).

Some of the advantages seen for CVD diamond layers in bearing and wear-surface applications are higher thermal stability, which will aid both in use and in brazing to substrates; essentially theoretical density (no metal phase, no porosity from metal removal); ability to make intricate shapes; and potential of making smooth, mirror-like surfaces without polishing.

The high thermal conductivity of some of the superhard materials (diamond, cubic BN, SiC) can decrease wear significantly by rapid transfer of heat from hot spots caused by localized frictional heating. Diamond and diamond-like materials both have shown small coefficients of friction (<0.05), which also acts to minimize frictional wear (Koskinen et al., 1985; Miyake et al., 1985).

In the case of diamond-like materials, the coefficients of friction depend on the relative humidity (RH). Up to about 1 percent RH, the coefficients are very low (0.01-0.02); however, above 1 percent RH the coefficients increase rapidly, reaching 0.2 at 100 percent RH (Tsai and Bogy, 1987). The coefficient of friction of diamond is less sensitive to moisture. In the case of diamond, adsorbed hydrogen appears necessary to maintain the low coefficient of friction. However, in a vacuum environment or at high temperatures, this hydrogen layer will desorb, resulting in a significantly higher coefficient of friction.

Although diamond-like films are very smooth, CVD diamond usually has a rough surface that would act to abrade an opposing part. Deposition of smooth CVD diamond films would solve this problem. The nonreactivity of superhard materials in corrosive environments and at high temperatures makes possible the fabrication of bearings and journals that can operate in adverse environments such as those found in nuclear reactors.

The ability to deposit diamond, DLC, and cubic BN in thin film form should allow for coating large surface areas for abrasion and wear resistance. Thus, for example, it may be possible to produce diamond-coated ways, spindle bearings, and shafts on milling machines and lathes. The decrease in wear of such components would result in equipment that maintains small machining tolerances over significantly greater periods of time than at present.

Barrier Coatings

Nonreactivity in corrosive environments, at high temperature, and in the presence of ionizing radiation may make it possible to use some superhard materials as protective barrier coatings in adverse environments. Their low permeability would prevent diffusion of reactive species to the substrate material, thus preventing substrate degradation. High thermal conductivities would diffuse hot spots, preventing localized high temperatures from reaching the substrate.

Cutting Tools: Drills, Bits, Cutters, Saw Blades

Precision turning tools made of polycrystalline diamond are still of limited value because the grain size is larger than the desired surface finish in most cases. This is less of a problem in direct-converted polycrystalline materials (i.e., graphite converted directly to diamond without solvent catalysts, or hexagonal BN converted to cubic BN). CVD diamond and cubic BN are very attractive for this application because of the possibility of having very-fine-grain material or single crystals deposited and bonded directly onto the tool material.

Surgical Blades and Microtomes

Single-crystal diamond is already used for microtome blades and surgical knives. The sharpness of the blade allows cutting of biological tissue without significantly depressing the tissue (minimum springback), and the hydrophobic surface of diamond prevents sticking and dragging. The production of large synthesized single crystals was at first aimed primarily at this market and the turning tool market. The limitations here are primarily associated with the difficulty of grinding and polishing uniform edges. It is expected that eventually the CVD process could be used to produce a uniform edge directly, without a polishing procedure, and thereby solve this problem.

Knives and Cutting Blades

There are applications for diamond cutting blades in a wide variety of industries. For example, the orange juice industry requires cutting blades that maintain their sharpness for an extended length of time. Dull blades waste the juice in the oranges. At the present time, these cutting blades, which are made of a hard stainless-steel alloy, require sharpening every 30 days. If the blades could last for a full cutting season of 9 months without sharpening, considerable savings would result. Coating the cutting blades with diamond or DLC would appear to be one way of extending the time between sharpenings.

Abrasives

Diamond grain and cubic BN abrasive grain were the first synthesized superhard materials products. Sintered polycrystalline materials followed. Manufacturers in about 14 countries make good-quality abrasive grain that ends up mounted in various media for cutting, grinding, and sawing applications. Grain sizes range from submicrometer scale to almost 1 mm. The larger sizes are used primarily for rock cutting and shaping. Synthesized abrasive grain can be provided reproducibly with controlled properties--size, shape, toughness. It is for this reason that about 90 percent of industrial diamond is synthesized and 10 percent is natural.

The potential of CVD diamond for abrasive grain is now being evaluated by various manufacturers. It will probably find a unique niche in the market by virtue of its purity, shape (i.e., flakes and sheets are possible), and polycrystalline nature. Its defect structures may give CVD diamond different and perhaps better abrasive properties.

Medical Implants

Ion beam-deposited DLC coatings have been studied for their use in biological implant systems (Aisenberg and Chabot, 1974). The coatings produced were found to have an extremely smooth surface, high surface tension, and slight electronegativity (Adamson, 1982). In addition, the samples were found to have a low gas permeability and high adhesion to the substrates tested. Results of vena cava, renal embolus, and *ex vivo* tests indicate a high degree of thromboresistance for these materials. These results combined with the durability of the materials suggest that they could be useful as coatings for medical implants, including artificial joints. One would expect that diamond coatings would perform in a similar manner. The high surface energy of diamond, which causes it to be hydrophobic, allows it to resist bacterial and viral attachment, since surface energy relates to surface tension (Adamson, 1982).

Additional Technological Impacts

A wide variety of technologies would benefit from the use of superhard materials. These include bearings for cruise missiles and helicopter rotors; diamond-tipped bonding tools for electronic leads; oil-drilling bits; gourmet knives; thermal and rocket engines; loudspeakers with extended frequency response (first commercial application of DLC films); coatings for dissipating heat and ionizing radiation in fission and fusion reactors; diamond-coated storage containers, such as beakers, for holding highly reactive, corrosive chemicals; gears; seals.

ELECTRONICS

Superhard semiconductor materials are expected to have an enormous technological impact on electronics, especially in the areas of high-power, high-performance transistors (Bazhenov et al., 1985; Geis et al., 1987; Prins, 1982; Setaka, 1986; Moazed et al., 1988). Two recognized figures of merit exist for evaluating semiconductor materials (Johnson, 1965; Keyes, 1972). The first of these (chronologically), formulated by Johnson, applies to the evaluation of semiconductors for performance as high-power microwave and millimeter-wave amplifier materials. Its principal parameters are the saturated charge carrier velocity (i.e., the velocity at which charge carriers move through the semiconductor at very high electric fields) and the dielectric breakdown strength. Table 4-4 lists the relative ranking of Johnson figures of merit of important semiconductor materials. (Parameters necessary to estimate the Johnson figure of merit for BN have not been available.) Obviously, the high-temperature semiconductors exhibit great potential for improving the performance of microwave and millimeter-wave power amplifiers.

TABLE 4-4 Relative Figures of Merit for Electronics

	Ratio to Silicon	
Material	Johnson[1]	Keyes[2]
Si	1.0	1.0
GaAs	6.9	0.5
InP	16	0.6
α-SiC	694	
β-SiC	1138	5.8
Diamond	8206	32

[1] High-power, high-frequency microwave amplifiers.
[2] Dense integrated circuit applications.

Keyes figure of merit:

$$\frac{\sigma_T \ V_{SAT}^{1/2}}{K}$$

Johnson figure of merit:

$$\frac{E_B V_{SAT}}{\pi}$$

where

α_T = thermal conductivity

V_{SAT} = saturation velocity

E_B = breakdown voltage

K = dimensionless quantity

Keyes formulated a figure of merit for choosing semiconductors for dense integrated circuit applications. Principal parameters used in this formula are the dielectric constant, saturated velocity, and thermal conductivity. Table 4-4 also lists the relative ranking of Keyes figures of merit for the same set of semiconductors; again, the parameters for BN are not certain enough for use at this time. Here also one sees clearly the superiority of β-SiC and diamond.

To have successful electronic device applications, doping of diamond is essential. Recent results indicate that p-type doping is easily achieved with boron by incorporation using CVD; continued improvements are seen in both CVD and in ion implantation techniques. At the writing of this work, progress is also seen in n-type doping of diamond, both by ion implantation and CVD techniques.

Ion implantation utilizing low-temperature carbon damage with overlapping boron implantation followed by rapid thermal annealing produced successful boron doping comparable to CVD methods. Preliminary work on n-type doping shows encouraging results. Theoretical studies predict that lithium, sodium, phosphorus, and antimony are excellent candidates for n-type doping.

Other areas of major potential impact of superhard materials are electrical insulators, high-temperature transistors, negative electron affinity cathodes (Himpsel et al., 1979), electronic heat sinks, advanced projection photolithography, direct-write microelectronics, transistors resistant to ionizing radiation, and coatings for magnetic disks and magnetic read-write heads for protection from head crashes.

High-Power Transistors

The output power that a transistor can deliver to a load resistance is proportional to the square of the voltage across the load. Superhard materials such as SiC, BN, and/or diamond exhibit dielectric breakdown strengths of 4×10^6, 1×10^7, and 2×10^7 volts/cm respectively. This compares to silicon breakdown at 5×10^5 volts/cm. The tenfold increase in breakdown strengths of the superhard materials translates into potential power output increases of 100-fold over silicon devices. This advantage is of particular importance in phased array antenna modules--especially for air search and space search surveillance radars. Other advantages accrue in replacements for vacuum tubes. Cathode wear-out is the primary failure mechanism for microwave and millimeter-wave vacuum tubes (traveling-wave tubes) in satellites.

High-Performance (Rapid-Response) Transistors

Several factors affect transistor speed. Among them are dielectric constant, charge carrier mobility, and charge carrier velocity. The dielectric constant determines the parasitic capacitance of the transmission lines on integrated circuits. Phase distortion and propagation speed are adversely affected by a large parasitic capacitance. The dielectric constants for diamond and SiC are 5.5 and 9.0, respectively, compared to 12 and 13 for silicon and germanium, respectively. Speed/frequency performance is inversely related to the dielectric constant; therefore, the superhard materials provide advantages in applications involving supercomputers and solid-state power amplifiers in the microwave and millimeter-wave spectrum.

Modern transistors require lithographic resolutions of less than 1.0 micrometer and are characterized by charge carrier channel regions of similar dimensions. These very short channel lengths lead to electric field strengths of 50,000 volts/cm in logic devices and even greater fields in analog devices. Since the superhard materials have lower atomic mass than more conventional semiconductors, the energies of the optical phonons that scatter the charge carriers are much higher. The velocities at which the charge carriers (i.e., electrons and holes) are scattered by optical phonons is thus much higher, and charge carrier transit time across the transistor channel is therefore shorter than in semiconductors characterized by higher atomic mass. Transit time gain factors of 2 to 3 over silicon and GaAs are possible. This translates directly into a proportionately higher frequency response.

Although charge carrier mobilities exhibited by diamond and SiC are generally lower than those of conventional semiconductors (an exception is the hole mobility of diamond, which is 3 times the hole mobility of silicon), this limitation can be circumvented by using cascade-structured devices, wherein the charge carrier velocity entering the second stage of the device is near saturated velocity. In this manner the average velocity of electrons in diamond and SiC can be much higher than that of even GaAs.

A final speed and frequency advantage of diamond and SiC over III-V semiconductor devices arises because the superhard semiconductors do not exhibit a region of negative differential conductivity. As such, the charge carrier velocity remains high, even at high electric field strengths. This equates to higher-power microwave and millimeter-wave amplifiers.

High-Temperature Transistors

The large forbidden band-gaps of diamond, SiC, and cubic BN enable them to continue to act as semiconductors at extremely high temperatures without experiencing charge carrier degeneration. Temperatures as high as 650°C have been demonstrated for β-SiC; BN and diamond should perform at even higher temperatures. Practical upper operating temperatures will be limited primarily by degradation in the metallization used for ohmic and Schottky contacts to the semiconductors.

High-temperature transistors will be particularly advantageous in spacecraft. In unmanned spacecraft, the systems required to cool conventional silicon devices to 125°C could be largely eliminated if operating temperatures of 325°C were permissible. These cooling systems can occupy up to 60 percent of the volume of an unmanned satellite. Thus the use of semiconductors such as SiC, cubic BN, and/or diamond could significantly reduce the system volume, weight, and cost. However, the advantages, compared to silicon and GaAs, may be offset because the mobilities of the negative free carriers (holes) appear to decrease more rapidly with increasing temperature than those of silicon and GaAs.

Radiation-Hard Transistors

The binding energies between the atoms of superhard crystals are much stronger than those of the more conventional semiconductors. Therefore, their vulnerability to heavy particle (ion) bombardment is less than that of conventional semiconductors. Furthermore, because of their higher band-gaps, fewer electron-hole pairs are generated per impinging photon; again this translates into greater immunity to alpha, beta, and gamma radiation. Definitive tests on diamond and BN devices have not yet been conducted because of the embryonic state of the art. Preliminary tests on synthetic epitaxial and natural diamond indicate a factor of 100 improvement in the damage resistance over that of silicon to 1.5 meV electrons. Initial Japanese tests on β-SiC devices have shown them to be immune to a radiation dose of 10^7 rad equivalent in silicon, radiation sufficient to damage most silicon devices. If fused silica is used as the insulator for SiC devices, the fused silica and not the SiC will be the limiting factor in radiation immunity. Fortuitously, AlN is lattice-matched to SiC and may be useful as a heteroepitaxial insulator, enabling SiC to operate in a potential well of the single-crystalline AlN insulator. If so, it may be possible to fabricate insulated-gate field-effect transistors that do not have the limitations of present SiO_2-based silicon devices. Similarly, diamond devices may be made to operate in a potential well created by lattice-matched cubic BN insulators. A significant amount of research will be required before these aspects of inherent radiation hardness can be confirmed.

The combination of radiation hardness and high-temperature capability of superhard materials may make electronics practical within or near nuclear reactors.

High-Voltage Electronics

High-voltage electronics made from superhard semiconductor materials would have greater reliability than vacuum tubes, the components most likely to fail in high-voltage circuits. This would be extremely important for phased array antenna modules and satellites. Megavolt switches would be reliable because superhard materials have high breakdown voltages. This would facilitate implementing high-voltage dc transmission of electricity.

Reliable Electronics

The predominant failure mechanism in power semiconductors is the migration (diffusion) of dopant impurities. The superhard semiconductors have a decided advantage in this respect. The diffusivity of dopant impurities in the superhard materials at temperatures well above the melting point of silicon is equivalent to the diffusivity of dopants in silicon at 125°C. At temperatures well above 400°C, impurity diffusion in the superhard semiconductors is negligible. The predominant failure mechanism will be solely that of the metallization. The use of metal silicides and metal carbides is expected to significantly improve resistance to even this degradation mechanism. However, low diffusivity may be a problem when trying to obtain uniform semiconductor doping.

Negative Electron Affinity Cathodes

Diamond is believed to have a negative electron affinity (Himpsel et al., 1979). This should make possible efficient electron emitters for a variety of applications, such as electron guns with cold cathodes and micrometer-sized vacuum tubes that would have power and frequency performance far superior to that of conventional semiconductor devices.

Electrical Insulators

Superhard semiconductor materials generally possess large forbidden band-gaps and therefore are good electrical insulators. Natural diamond, for instance, can exhibit dark resistivities greater than 10^{20} ohm-cm resistance. In synthesized diamond, resistivities vary between 10^{9} and 10^{10} ohm-cm, depending on the growth process used. The insulating properties of semiconducting heterojunctions must, however, be considered on a case-by-case basis. Depending on how the band-gaps align, the material with the wider band-gap may not necessarily be an insulator for both electrons and holes. The view of semiconductor-insulator interfaces must be modified to a concept of assessing materials in potential wells. Diamond-like materials can have resistivities exceeding 10^{12} ohm-cm.

Heat Conductors

Most of the superhard materials useful for electronic applications also have high thermal conductivities. For example, natural diamond has a value of 20 $\mathrm{Wcm^{-1}\,K^{-1}}$ at room temperature (Ono et al., 1986). Since natural diamond contains both carbon 12 and carbon 13 isotopes, its thermal conductivity is not optimized. Isotopically pure carbon 12 diamond should have a thermal conductivity that is greater by a factor of 2, but experimental verification of this prediction is needed.

BN, SiC, and AlN are also good thermal conductors and are of use in a variety of applications. These materials are most useful in single-crystal form, heteroepitaxially bonded to the material to which they are to be used as heat sinks. However, heteroepitaxy is believed to be limited to lattice-matched materials with similar chemical bonding. BN is only lattice-matched to diamond, and SiC is only lattice-matched to AlN and GaN. Most applications will require other forms of bonding, such as soldering.

Unlike copper, the superhard heat sinks are generally electrically insulating in nature and can be used for removing heat without the complicating requirement of an additional electrically insulating layer. The high heat-removal capability of these materials should permit the fabrication of integrated circuits with significantly increased component densities.

X-Ray Masks for Advance Projection Photolithography

X-ray wavelength masks offer the possibility of achieving significantly higher-density electronics. These masks must be thin to prevent absorption of the x-ray radiation and yet must be optically transparent for visual observation. Large areas of thin unsupported diamond films will be required.

Direct-Write Microelectronics

Coating of electronic chips during processing with diamond-like coatings can be used to pattern the electronic circuit directly--for example, by electron beam etching.

Magnetic Disks and Read-Write Heads

Magnetic disks and read-write heads are susceptible to damage when the head comes into contact with the magnetic medium. The result can be destruction of the disk, the head, and valuable stored data. This problem is becoming even greater as attempts are made to increase the density of data on the storage medium, requiring smaller head-to-disk gaps. The disk and head must be protected with a wear-resistant, low-friction coating. Much of the earlier discussion concerned with friction and wear in bearings and journals is applicable here. Coating of disks and heads with DLC has been the subject of extensive study, and a considerable payoff in saved data may be realized (Tsai and Bogy, 1987).

Additional Technological Impacts

Additional advantages of superhard electronic materials include in situ electronic sensing and signal processing in chemical reactors, automobile engines, engines in heavy industrial equipment, rocket engines, nuclear reactors, etc; low-cost microwave ovens; higher-speed supercomputers; nuclear radiation dosimeters and detectors with great potential for use in radiation biology and medicine; and thermistors.

OPTICS AND OPTOELECTRONICS

The desirability of superhard materials as optical materials stems from their unique properties. Their advantages apply both to monolithic optics and to optical coatings. Their primary advantages lie in their hardness and chemical inertness, which would make optical components fabricated from these materials resistant to adverse conditions such as abrasive environments caused by dust and rain, chemically corrosive environments, reactive environments as in plasmas, and high-temperature environments. In addition, particular materials would have other advantages. The wide band gaps of diamond and cubic BN make them candidates for ultraviolet optics, and their low mass numbers make them candidates for soft x-ray windows. High thermal conductivity, high Young's modulus, low thermal expansion coefficient, and high fracture toughness make diamond an important candidate material for optical components in high-photon-flux environments, such as in free-electron lasers, because of its resistance to thermal fracture and its ability to dissipate heat rapidly. Table 4-5 shows the figures of merit for thermal stress resistance of diamond relative to those of several important optical materials. Diamond is clearly superior to the other materials, from both a practical and a theoretical point of view.

Several major problems must be overcome before diamond optics in the near-infrared, visible, and ultraviolet will be widely used. In the case of single-crystal diamond, only limited sizes are available, perhaps up to 2 cm in diameter. CVD diamond could be used in monolithic optics (such as lenses, windows, and domes), provided deposition rates were sufficiently high. In the case of CVD diamond, however, the limitations are optical scatter arising from polycrystalline morphology and surface roughness and absorption resulting from graphitic or diamond-like species, lattice defects, and other impurities within the diamond phase.

Crystalline diamond and diamond-like materials have many potential uses as coatings for infrared optics. In principle, diamond shows no first-order absorption in the infrared; the absorption observed is due to second-order processes, defects, and impurities. Diamond coatings are potentially applicable for use from the nonvacuum ultraviolet through the infrared, except for a region of absorption between 2.5 and 6 μm, but optical scatter limits such use in currently produced CVD diamond. However, at wavelengths beyond approximately 10 μm, transmission measurements suggest that this material may have adequate transmissivity to be useful in the longwave infrared region.

TABLE 4-5 Figures of Merit for Thermal Stress Resistance

Material	R_T	Source
Silicate glass	2.3×10^2	a
Sapphire	3.4×10^3	a
Fused silica	4.3×10^3	a
Diamond (300 K)	9.4×10^5	b
(80 K)	1.3×10^7	b
(300 K)	3.8×10^8	c
(80 K)	5.4×10^9	c

a. From Krupke et al. (1986), in which a flaw size of 50 μm was assumed.
b. Based on parameters in Field (1979) and assuming a flaw size of 50 μm.
c. Theoretical value based on parameters in Field (1979).

$$R_T = \frac{\sigma_f \, \kappa(1-\nu)}{\alpha E}$$

where

R_T = figure of merit
σ_f = fracture strength
κ = thermal conductivity
ν = Poisson's ratio
α = linear thermal expansion coefficient
E = Young's modulus

The use of CVD diamond as an optical film material has the limitation of requiring high substrate temperatures (greater than 600°C) during deposition, which restricts the number of substrate materials that can be used. Adhesion to the substrate is another problem, and, when the diamond does adhere, differential contraction during cooling can lead to delamination and crazing. Diamond-like films, on the other hand, can be deposited at much lower temperatures (approximately 150°C), but they too exhibit adhesion problems and may also contain large internal stresses that can cause delamination of thick coatings from substrates. Hydrogen-free DLC coatings have much less residual stress than the DLHC type, however.

Some of the early adherence problems have been addressed with good results. For example, the adherence of diamond-like films to infrared-transmitting substrates such as ZnS and ZnSe is improved dramatically by depositing an amorphous germanium-carbon layer between the substrate and the overlying diamond-like coating (Lettington et. al., 1987; Wort and Lewis, 1987).

This combination of hard coatings can impart good wear erosion and abrasion resistance to ZnS and ZnSe and can be adjusted in thickness to provide an antireflection coating as well.

In addition to their potential use as optical coatings and monolithic optics, superhard materials have potential uses as mirror substrates, optical and optoelectronic heat sinks, laser sources, light-emitting diodes (visible and ultraviolet), high-speed optically activated electronic switches, ultraviolet detectors, optical waveguides, and fiber optic coatings.

Monolithic Windows and Lenses

The ability to deposit high-optical-quality CVD diamond at high deposition rates will make it possible to produce windows and lenses for the infrared, visible, and ultraviolet that are durable in extreme environments. In addition to the environmental advantages of diamond, its high refractive index makes it an attractive lens material because lenses with high refractive power can be made significantly thinner and hence lighter. Furthermore, simple antireflective coatings can be easily made for diamond optics, especially for the ultraviolet, because the antireflection condition is more easily satisfied than for other substrate materials. For example, a single-layer antireflection coating, to work efficiently, must have a refractive index close to the square root of the substrate refractive index, a condition difficult to achieve for substrate refractive indices less than 1.9. The refractive index of diamond at 0.589 μm is 2.418; a film with an index of 1.555 would make an almost perfect antireflection coating, a value easily obtainable with optical glasses. In addition, diamond and DLC make good infrared antireflection coatings for substrate materials such as GaAs, silicon, and germanium.

Single-crystal diamond has particular advantages as a high-power laser window or output coupler, such as is required in a free-electron laser. Because of its superior thermal shock resistance and its large heat-dissipation capability, it may make possible very compact free-electron lasers. With diamond windows the areal power density could be higher, resulting in greater total power for a given beam size. If the windows are cooled to liquid-nitrogen temperatures, the heat-dissipating capability of diamond windows would be even greater. Thus, an effort to produce large, high-optical-quality single-crystal diamond either by high-pressure techniques or by CVD processes would be extremely desirable.

X-Ray Windows

Because of the low atomic numbers of the elements in diamond, DLC, DLHC, and BN, these materials exhibit low x-ray absorption, making them excellent x-ray windows. Because of its high strength, diamond can be made very thin, thus lowering its absorptivity even more. In the soft x-ray region, diamond would be expected to replace beryllium. Commercialization of diamond for energy-dispersive anaylsis windows for energy-dispersive x-ray analysis is expected shortly.

Mirror Substrates

High thermal conductivity and high strength make diamond an excellent substrate material for mirrors intended for high-average-power laser radiation. The high strength would allow for thinner substrates and hence lighter mirrors. This will be practical when large-diameter, thick deposits can be made at reasonable deposition rates.

Heat Conductors

Diamond, SiC, cubic BN, and AlN can act as heat-conducting substrate materials for optoelectronic applications such as laser diodes, where significant heat may be developed. In this case the constraints are similar to the electronic ones discussed earlier. The use of superhard materials as mirror substrates, as discussed above, takes advantage of their large thermal conducting capabilities.

Optical Emitters, Lasers, and Light-Emitting Diodes

SiC and cubic BN, because of their large direct band-gaps, emit optical radiation at significantly shorter wavelengths than conventional III-V materials. BN has recently demonstrated emission in the ultraviolet. Furthermore, it is expected that light-emitting diodes can be made from these materials. In diamond, direct laser action is expected to be more difficult because it is an indirect band-gap material. However, laser action has been exhibited by color centers in diamond (Rand and DeShazer, 1985a, b) in the visible region; thus, diamond can act as a laser host material. Calculations indicate that, by applying a large uniaxial strain to diamond, it can be converted to a direct band-gap semiconductor. Whether such a large uniaxial strain can be produced and maintained in practical devices is highly problematical. Perhaps it can be accomplished by making diamond one component of a strained-layer superlattice. Other possibilities for laser action in diamond are intra-atomic energy transitions (2d and 4f) in impurity ions within the diamond or within a heterojunction p-n junction. Ultraviolet lasers made of superhard materials offer greater storage density capability on compact disks because the laser light could be focused to smaller spot sizes.

Optically Activated Electronic Switches

Recent experiments have shown that diamond can act as an optically activated electronic switch (Bharadwaj et al., 1983; Young et al., 1983; Glinski et al., 1984; Huo et al., 1986). Because of its high breakdown voltage, diamond can withstand very high voltages without electrical breakdown. Illumination by intense excimer laser radiation leads to switching times on a nanosecond time scale and smaller.

Ultraviolet Solar-Blind Detectors

In the region between 180 nm and 300 nm, the ozone layer reduces the reflectance of the earth over 3 orders of magnitude below that of the visible and near-infrared. In the region of 140 to 180 nm, the reflectance is further reduced by an additional 200-fold. Below 140 nm, aural spectra dominate. For exoatmospheric "targets" a truly solar-blind region is the window at 140 to 180 nm. Although the band-gap of cubic BN is not now known with certainty, it is expected to lie within this window. Since BN has now been synthesized in its cubic form, the exciting possibility exists that BN can be used not only as a solar-blind detector but also as a coherent (laser) illuminator as well. Diamond should be blind to radiation at wavelengths longer than 225 nm and thus can be used to capitalize on the more than 3 orders of magnitude ozone-created reduction in the solar reflection of the earth. SiC has too low a band-gap to be useful in solar-blind applications.

Optical Waveguides

The high refractive index of diamond makes it a candidate optical waveguide material. Because it is a centrosymmetric material, it will not exhibit an electro-optic effect; thus, it might be useful either as a passive waveguide material or as an acousto-optic material. Furthermore, the refractive index of diamond is between the refractive index of GaAs and related III-V compounds used as optical sources and that of $LiNbO_3$, a modulator material. Thus, diamond can act as a transition waveguide between components made of these two classes of materials.

Fiber Optic Coating

Fiber optics are subject to abrasion and chemical degradation from moisture. The strength of silica-based fibers is severely lowered by water vapor. Hard, impervious coating materials are needed to protect these fibers. Both diamond and diamond-like carbon are hard, providing abrasion resistance. In addition, because they are dense and chemically impervious, they can be used to hermetically seal a fiber from the environment. Fiber optics coated with DLC are effectively sealed against water-vapor penetration. This will be especially important for the new heavy-metal halide fibers that exhibit low absorption in the infrared but are particularly susceptible to environmental degradation, especially moisture. Optical communications systems, including military systems, rely heavily on fiber optics.

Optical Coatings

High-Power Laser Mirrors

Laser mirrors are subject to degradation from a variety of sources: They are subject to intense optical radiation, which causes a form of dielectric breakdown owing to the high optical electric fields present; they are subject to thermal shock and degradation as a result of heating by the intense optical radiation; they are subject to attack by reactive species such as fluorine in excimer lasers; they are subject to plasma erosion in lasers with gas discharges; and they are subject to environmental degradation from dust and moisture when they act as the output coupler to the external environment. Furthermore, many lasers operate in the ultraviolet, where there is a lack of hard coating materials possessing high refractive indices. Because of the high refractive index of diamond and its resistance to environmental attack, the development of low-optical-loss diamond coatings in single layers and in multilayers with other lower index materials such as SiO_2 would considerably ameliorate these problems. The high refractive index of diamond should make possible antireflecting and high-reflecting mirrors with fewer layers and with greater survivability than current mirrors.

Protective Coatings

Many optical components are subjected to extreme environmental factors that cause component degradation. Much of this degradation occurs in environments of critical importance to the nation's defense. Aircraft fly through dust and rain, which abrade and erode aircraft canopies; tanks and personnel operate in dusty and moist environments that degrade viewing ports, binoculars, periscopes, rangefinders, target designators, and goggles; radomes and IR-domes are subjected to dust and rain impact and abrasion and may be heated to elevated temperature because of atmospheric friction.

Heating of radomes in re-entry vehicles can be a problem because the high temperatures generated in the atmosphere can cause the radome material to become conducting, which prevents the transmission of microwave energy owing to absorption. In this situation diamond radomes would have four advantages: because of its large band-gap, diamond would remain insulating to elevated temperatures; the low dielectric constant of diamond results in low reflectivity of microwave energy because of a lower impedance mismatch with the air; the high thermal conductivity of diamond would permit generated heat to dissipate over a larger area, thus lowering peak temperatures; and oxidation of the diamond surface would cause production of CO and CO_2, with the result that the chemical composition of the radome surface would remain unchanged.

From a commercial viewpoint, superhard protective optical coatings would be useful on almost all optical surfaces. Diamond-coated eyeglasses, windshields, and windows could significantly maintain visibility by decreasing the susceptibility to scratching. The lifetimes of optical disks would be significantly extended. Improvement by a factor of 6 in scratch resistance has been obtained for plastic lenses coated with DLC.

Antireflection Coatings

Antireflection coatings of diamond or DLC would have considerable advantages. Silicon and GaAs solar cells coated with diamond would exhibit greater efficiency because of reduction of reflective losses, while at the same time the cells would be resistant to degradation from the environment. DLC coatings have been deposited on silicon solar cells with an increase in cell efficiency of 40 percent and on germanium windows, resulting in excellent transmissivity. The advantage of DLC coatings over diamond is that the refractive index of DLC can be tailored to suit a particular application. Values of refractive index between 1.8 and greater than 2.1 are obtainable by varying the deposition conditions. Moreover, DLC coatings show a negligible surface roughness.

Additional Technological Impacts

Additional advantages that may arise from the application of superhard materials to optics include environmentally stable interference filters; missile detection sensors; and detectors resistant to ionizing radiation.

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5

RESEARCH AND DEVELOPMENT ISSUES AND OPPORTUNITIES

Superhard materials are increasingly important industrial materials whose uses are currently enhancing productivity in metalworking, oil production, and mining. Several of these materials are also emerging as key materials for future advanced electronic and optical systems. It is important to point out that in this latter area the United States is not in a leadership position. There are, however, several research and development efforts in this country directed toward fabrication of high-temperature transistors based on diamond and SiC for possible use as sensors. Other efforts address the use of diamond-like films for wear-resistant coatings on magnetic disks and optoelectronic devices and components, for masks for use in fabricating distributed feedback lasers, distributed Bragg reflectors, filters, modulators, and couplers.

During the committee's deliberations it was clear that, in the area of diamond and diamond-like film technology, the U.S. efforts have been dependent on following the technologies first demonstrated in Japan and the USSR. For example, Sumitomo is beginning to market large-area thick films of cubic BN for use as heat sinks for solid-state devices, even though its thermal conductivity is approximately one-third that of diamond. As another example, Showa Denko (press release, Showa Denko, Tokyo, 1988) in collaboration with Nippon Institute of Technology, has developed a high-speed process for the synthesis of diamond thin films on silicon wafers.

In the area of high-pressure synthesis of diamond and cubic BN, the processes for doing this were invented, developed, and commercialized in the United States. These technologies have become mature and subsequently diffused globally. An example of this is the list of countries in which there is commercial synthesis (high-pressure, high-temperature) of diamond and/or cubic BN: Czechoslovakia, France, East and West Germany, Greece, Ireland, Japan, Peoples Republic of China, Poland, Romania, South Africa, Sweden, Soviet Union, and the United States. Unless the United States invests efforts in developing innovative processes and new materials in this area, it faces the prospect of the field of superhard materials and their applications following the unfortunate precedents of the steel and semiconductor device industries. This would further exacerbate the nation's negative trade balance and create yet another import-dependent critical industry.

Many applications of superhard materials require well-controlled properties. For mechanical applications this necessitates control of hardness, surface roughness, and adhesion to substrates. In thermal applications, control of thermal conductivity is required. Electronic and optoelectronic applications require control of absorption coefficient, carrier concentration, carrier lifetime, and defect-state densities. Research is needed first to control the deposition process to tailor these properties and to scale-up the processes, then to understand how the processing parameters affect the material structure and properties, and finally to formulate measurement methods for characterizing the properties of the material for specific applications.

Accordingly, this chapter focuses on key research and development issues identified with growth of superhard materials, their characterization, and their application. Although the emphasis in this report is confined to the low-pressure, lower-temperature (LPLT) processes now being developed, the established high-pressure, high-temperature (HPHT) process should now be examined in the light of emerging thin-film processes to see if knowledge of LPLT processes can be applied to the HPHT process.

GROWTH PROCESSES

The critical R&D issues associated with growth processes, particularly thin film growth, are discussed in this section within two broad categories--chemical vapor deposition (CVD) and physical vapor deposition (PVD). For CVD, the chemical aspects of the overall process dominate, whereas in PVD, several physical aspects of the process need to be considered.

CVD Growth

For the case of vapor-deposited diamond films, control of the deposition process requires understanding the chemistry of the diamond formation process. This in turn requires studies directed toward (a) understanding the nucleation and growth mechanisms as a function of substrate material and substrate surface orientation, (b) knowing the atomic and molecular species present in the gas phase, (c) finding means for doping in a well-controlled manner, (d) understanding how deposition parameters affect film morphology during homo- and heteroepitaxial deposition, and (e) determining the chemical and structural perfection (i.e., impurity and dopant distribution and degree of twinning). Understanding these epitaxial issues may lead to the growth of high-quality large area single-crystal films.

Other research and development issues include the following:

- The surface properties of films as they relate to bonding and adhesion to other materials need to be determined. Currently, diamond adheres to diamond or carbides. This work could lead to additional understanding and control of film morphology as well as increasing film adherence to other substrates and to growth of the larger-area heteroepitaxial single-crystal films important for electron devices. Grading the layers to arrive at the desired surface or layer so as to minimize strain resulting from substrate and thermal mismatch is another issue within the context of this item.

- Chemical purity and obtaining dopant homogeneity of diamond and diamond-like films as a function of growth technique, growth parameters, and doping need to be established and understood. Doping by ion implantation has not resulted in semiconducting films but might be successful for oriented single-crystal films.

- Methods of lowering growth temperatures must be determined. For example, low-temperature deposition of ZrB_2 and HfB_2 films by thermal decomposition of metal borohydrides ($M[BH_4]_4$) and epitaxial growth of ZrN on silicon has recently been achieved.

- What are the factors that limit growth rates? Innovative ways of increasing the efficiency of deposition (grams of deposited material per watt-hour) and of coating three-dimensional objects (throwing power) must be sought.

PVD Growth

The PVD R&D issues such as deposition rate, throwing power, substrate thermal mismatch, deposition efficiency, and gas-phase chemistry studies related to epitaxy and formation of large-area single-crystal films and layered composites are similar to those discussed in the previous section. For PVD growth, the local or substrate-deposit interface temperature generally, should not exceed 500°C. This will require control of vapor chemistry and particle kinetic energies.

MATERIALS CHARACTERIZATION

There are voids in knowledge of the dielectric, mechanical (including hardness and friction), thermal, and optical properties of diamond and diamond-like films as a function of hydrogen content and alloy additions. In addition, since carbon can form double and triple bonds, it is important to clarify the nature of the bonding and structural network of the amorphous diamond-like hydrogenated films.

Crystal or material features on an atomic level, such as atomic location of hydrogen and impurity atoms, crystal defects (stacking faults, etc.), and electron energy levels for impurity atoms need to be characterized and understood. Furthermore, since Raman spectra are frequently obtained for these materials, much work needs to be done to understand features of the spectra.

Surface reconstruction or rearrangement of surface atoms is well known to occur for sp^3-bonded materials (silicon, for example), and (100)-(110) surface characterization is a research issue that should be examined so as to understand surface properties that are orientation- and composition- (hydrogen, for example) dependent.

Determination of electron affinity of diamond and diamond-like materials is a property of importance from the standpoint of their possible use as cold cathode materials.

APPLICATIONS

Diamond and diamond-like materials are already being developed for several electronic applications--e.g., as films for masks for fabrication of 1.3-μm distributed feedback lasers (Gozdz et al., 1988) and as coatings for magnetic disks and heads (Seki et al., 1987; Tsai and Bogy, 1987).

Smooth, defect-free single-crystal diamond films could find application as transistors for high-temperature, high-frequency applications, just as SiC is now being developed for remote elevated-temperature sensor applications. Issues associated with this application include obtaining dopant uniformity and epitaxial high-temperature-stable metal contacts. Perhaps the nitrides of the transition elements, such as ZrN, now being explored as a metallization for silicon, and other metallic nitrides, such as TiN, VN, HfN, and TiCN, are possibilities.

The possibility of making high-energy lasers, UV detectors, and optoelectronic devices from diamond needs to be explored. Diamond is an indirect-gap material, and for efficient laser operation direct electronic transitions are necessary. Perhaps by suitable alloying to form donor and acceptor bands within the gap or by forming a strained epitaxial layer that becomes a direct gap material, efficient lasers, very likely optically pumped, might be developed. Perhaps diamond can be used to fabricate photoconducting, PIN, and/or avalanche detectors.

Since the conduction band of diamond is above the vacuum level, it may be possible to form high-current cold cathodes with diamond. The use of such cathodes could be very important for future high-frequency development, not only for traveling-wave tubes but also for micrometer vacuum tubes, which could surpass the present state of the art of semiconductor devices even with the addition of diamond devices.

Increasing attention is being directed toward the use of diamond and diamond-like coatings as a packaging material (to minimize wear and abrasion and to protect against corrosion) for electronic items (magnetic disks and heads) and as heat sinks for semiconductor lasers used in optical communications. Application of films surely will increase as one learns how to optimize coating thickness for a given substrate (as well as developing nondiamond substrates), how to dope or alloy these films with nonionized impurities to increase microfracture toughness, and how to scale-up the deposition process. The use of diamond and diamond-like coatings for creating an impervious layer on optical fiber is another possible application.

Other diverse applications of diamond films are as x-ray lithography masks for manufacture of ultra-high-density integrated circuit chips and in prosthetic devices.

BEYOND DIAMOND: OTHER MATERIALS AND ISSUES

There should be increased activity concerned with the synthesis of diamond-like and nondiamond-like materials in bulk and thin-film form and with the control of microstructures, such as in composites and in modulated structures for enhanced properties.

Emphasis should be placed on spectroscopic studies directed toward understanding the chemistry and physics of plasmas used for plasma-enhanced deposition of films. This information is important for scaling-up plasma deposition processes.

The superlattice TiC-TiCN-TiN is now in commercial use (Quinto, 1988) for cutting tools, while the superlattice TiN-VN is receiving attention (Barnett et al., 1988). Thin-film ternary nitrides (Randhawa et al., 1988; Penttinen et al., 1988) such as (TiZr)N containing TiN and ZrN in the ratio of 25:75 exhibit a microhardness in excess of 3100 kg/mm^2 and excellent wear resistance.

More work on the synthesis of cubic BN must be undertaken. It has been suggested that the electronic energy gap of this material is greater than that of diamond.

The nature of the bonding and arrangement of atoms in a solid determines its mechanical properties, and quantum-chemical calculations should be undertaken to shed light, in parallel with experiment, on the bonding in superhard materials. Theoretical results suggest that C-N bonds within an appropriate host crystal structure might yield harder materials than pure diamond. Boron-oxygen and boron-carbon-nitrogen materials need to be synthesized.

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Appendix

BIOGRAPHICAL SKETCHES OF COMMITTEE MEMBERS

John D. Venables, the committee chairman, received his B.S. degree in physics from Case Institute of Technology and his Ph.D. in Physics from the University of Warwick, England, in 1971. He currently holds the position of Corporate Scientist at Martin Marietta Laboratories and is responsible for long-range R&D planning and technical interactions between the laboratories and the corporation's operating divisions. Much of his prior work has been concerned with structure-property relationships in high-temperature materials, including transition metal carbides and ceramics.

Jack H. Wernick, vicechairman of the committee, received his B.S. and Ph.D. degrees from the University of Minnesota and Pennsylvania State University respectively. He conducted research at Los Alamos Scientific Laboratory, taught metallurgy at Penn State for 5 years, and then joined Bell Labs in 1954, where he rose to managerial research positions that included head of the Solid State Chemical Research Department and head of the Device Materials Research Department. He was elected to the National Academy of Engineering in 1979. Since divestiture of the operating telephone companies from AT&T, he has managed Materials Science Research for Bell Communications Research, Inc.

John C. Angus, a chemical engineer, received his B.S., M.S., and Ph.D. degrees at the University of Michigan. Since 1963 he has been at Case Western Reserve University and became professor there in 1970. His research on low-pressure growth of diamond dates back to 1965.

Peter M. Bell is Vice President for Corporate Technology at Norton Company in Worcester, Massachusetts, and is associated with the Geophysical Laboratory in Washington, D.C. He began his scientific career as solid state physicist at the Air Force Cambridge Research Laboratory after receiving his B.S. degree at St. Lawrence University, his M.S. at the University of Cincinnati, and A.M. and Ph.D. degrees at Harvard University. Since then he has been at the Geophysical Laboratory, with occasional periods of teaching at Harvard, Johns Hopkins, SUNY, and the California Institute of Technology.

Jerome J. Cuomo received his B.S. degree from Manhattan College and his M.S. degree from St. Johns University in physical chemistry. He later attained a Ph.D. in physics from Odense University in Denmark. He is currently manager of the Materials Laboratory in Central Scientific Services at the IBM T. J. Watson Research Center, where for the past 25 years he has been working in the science and technology of materials and materials processing. In particular, he has developed ion beam processing for material deposition, modification, and synthesis. He has also been recognized for his work in magnetic semiconductor and superconducting materials.

Robert C. DeVries' background in mineralogy (the field in which he received his Ph.D. from Pennsylvania State University) led to work at General Electric R&D Center on phase equilibria at high temperatures and pressures. He worked on high-pressure, high-temperature synthesis of diamond and cubic BN for more than 20 years and on CVD diamond for more than 2 years before retiring after 34 years at G.E. He taught at Rensselaer Polytechnic Institute from 1961 to 1965. In 1981 his position at the R&D Center was designated as a Coolidge Fellow.

Albert Feldman received degrees in physics from City College of New York (B.S.) and the University of Chicago (M.S. and Ph.D.). He has been conducting research at the National Institute of Standards and Technology (formerly the National Bureau of Standards) over the past 22 years principally in the area of optical materials research. He is currently leader of the Optical Materials Group.

Michael W. Geis received his degrees from Rice University and stayed on for post-graduate work. For the past 10 years he has been at Massachusetts Institute of Technology's Lincoln Laboratories. He has worked on thin-film silicon, on submicrometer technology, and on diamond device development.

David S. Hoover was educated at Juniata College (B.S.) and Pennsylvania State University, where he obtained his Ph.D. degree in earth and mineral sciences. He has been employed by Air Products and Chemicals, Inc., since 1980, currently as manager for inorganic materials. His expertise is in carbon and carbon-containing materials and composites.

Russell Messier teaches and conducts research at the Pennsylvania State University, where he received his doctorate in 1973. His B.S. was from Northeastern University, and his industrial experience was with GTE Sylvania. His membership in IEEE, American Vacuum Society, and MRS reflect his interests in thin-film preparation and characterization (including diamond) by high-frequency sputtering.