Workshop on Diamond and Diamond-Like-Carbon Films for the Transportation Industry

Argonne National Laboratory
Argonne, IL

February 4–5, 1992

Sponsored by:

Tribology Program
Office of Transportation Materials
Office of Transportation Technologies
Conservation and Renewable Energy
U. S. Department of Energy

and

Argonne National Laboratory

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# Table of Contents

Abstract ......................................................................................................................... v  

1.0 Executive Summary ............................................................................................... 1  

2.0 Introduction ............................................................................................................ 4  
   2.1 History of the Tribology Program ........................................................................ 4  
   2.2 Office of Transportation Technology .................................................................. 4  
   2.3 Office of Transportation Materials ..................................................................... 7  
   2.4 Tribology Program .............................................................................................. 8  
   2.5 Current Task Areas ............................................................................................ 10  

3.0 Workshop Plenary Lectures ................................................................................... 11  
   Diamond and Diamond–Like Films for Transportation Applications —  
      Workshop Overview — Joseph M. Perez (DOE) ................................................... 12  
   Diamond Films: Historical Perspective —  
      Russell Messier (Pennsylvania State University) .............................................. 32  
   CVD Diamond – Fundamental Phenomena —  
      Walter A. Yarbrough (Pennsylvania State University) ..................................... 87  
   Comparative Evaluation of CVD Diamond Technologies —  
      Thomas R. Anthony (General Electric Corp. Res. & Develop. Center)............. 116  
   Ion–Beam Technologies —  
      George R. Fenske (Argonne National Laboratory) ......................................... 165  
   Characterization Methods —  
      J. T. Glass (North Carolina State University) .................................................. 184  
   Structure and Properties of Diamond and Diamond–Like Films —  
      R. E. Clausing (Oak Ridge National Laboratory) .............................................. 230  

4.0 Reports from Working Panels ................................................................................ 335  
   Panel 1 — Comparative Evaluation of Deposition Technologies —  
      Chairman — George R. Fenske (Argonne National Laboratory) .................... 335  
   Panel 2 — Properties of Diamond and Diamond–Like–Carbon Films —  
      Chairman — Peter J. Blau (Oak Ridge National Laboratory) ......................... 346  
   Panel 3 — Characterization —  
      Chairman — Robert A. Erck (Argonne National Laboratory) ......................... 350  
   Panel 4 — Applications to Transportation —  
      Chairman — Fred A. Nichols (Argonne National Laboratory) ......................... 357
ABSTRACT

Numerous applications exist in advanced transportation systems as well as in numerous manufacturing processes that would benefit from the superior tribological properties of diamond, diamond-like-carbon and cubic boron nitride coatings. The superior hardness of these coatings make them ideal candidates as protective coatings to reduce adhesive, abrasive and erosive wear in advanced diesel engines, gas turbines and spark-ignited engines and in machining and manufacturing tools as well. The high thermal conductivity of diamond also makes it desirable for thermal management not only in tribological applications but also in high-power electronic devices and possibly large braking systems.

A workshop has been recently held at Argonne National Laboratory entitled "Diamond and Diamond-Like-Carbon Films for Transportation Applications" which was attended by 85 scientists and engineers including top people involved in the basic technology of these films and also representatives from many US industrial companies. A working group on applications endorsed 18 different applications for these films in the transportation area alone. With this strong indication of industrial support, we envision a second workshop to address applications in the US manufacturing industry. It is anticipated that industrial expenditures will exceed $3000K per year and will result in numerous CRADAs between National Labs and US companies.
1.0 EXECUTIVE SUMMARY

Problem Definition: Numerous applications exist in advanced transportation systems as well as in numerous manufacturing processes that would benefit from the superior tribological properties of diamond, diamond-like-carbon and cubic boron nitride coatings. The superior hardness of these coatings make them ideal candidates as protective coatings to reduce adhesive, abrasive and erosive wear in advanced diesel engines, gas turbines and spark-ignited engines and in machining and manufacturing tools as well. The high thermal conductivity of diamond also makes it desirable for thermal management not only in tribological applications but also in high-power electronic devices and possibly large braking systems.

Objectives: The program envisioned to follow from this Workshop will focus on transferring technologies for depositing these films to advanced engine components (e.g. diesel injectors, piston rings, cylinder liners, bearings, valve stems, etc.). A critical issue in this process will be to establish the proper conditions for depositing smooth, adherent films on a number of substrates at low deposition temperatures, and to evaluate their performance under simulated and prototypical conditions.

Potential Industrial Participation: A workshop has been recently held at Argonne National Laboratory entitled "Diamond and Diamond-Like-Carbon Films for Transportation Applications" which was attended by 85 scientists and engineers including top people involved in the basic technology of these films and also representatives from many US industrial companies. A working group on applications endorsed 18 different applications for these films in the transportation area alone. With this strong indication of industrial support, we envision a second workshop to address applications in the US manufacturing industry. It is anticipated that industrial expenditures will exceed $3000K per year and will result in numerous CRADAs between National Labs and US companies. This initiative fits beautifully into the planning of the Presidential Initiative entitled "Advanced Materials and Processing Program" (AMPP) and some cooperative funding from that source is possible.

Technical Approach: Working with already-identified companies and further ones to result from the new workshop on manufacturing applications, cooperative programs will be established with industrial partners. Areas of application strongly endorsed by a working panel on applications to the transportation sector are:

1. Valve guide/stem wear at high temperatures in developmental low-heat-rejection engines.

2. Piston ring/bore tribosystem improvements to decrease wear, oil consumption and emissions for gasoline, diesel and alternative fuels.

3. Increased load-carrying capacity for gears and bearings (including journal bearings as temperatures rise in sump and loads increase due to higher cylinder and injection pressures) in spark-ignited/diesel engines and vehicular drive trains, including continuously variable transmissions (CVTs) as well as in manufacturing.
4. Electric fuel pumps and fuel-pump gears, to reduce wear and corrosion, especially when used with low-viscosity alternative fuels such as methanol.

5. Applications of diamond and DLC films require improved modeling of wear mechanisms as well as adhesion processes and improved analytical methods for extending the results of lab-bench tests to actual operating conditions.

6. Improved resistance to wear-in ("beat-in") and scuffing of fuel-injector plungers for diesel and especially for new alternative fuels in diesel and spark-ignited engines. Erosion-corrosion of injector spray holes must also be reduced to conserve fuel and decrease emissions.

7. Improvements in rolling-contact-fatigue (RCF) life of cams and cam-roller followers for both valves and injectors, which would also reduce emissions. Needs exist in both diesel, spark and gas-turbine engines.

8. Improvements in self-lubrication and scuffing resistance of new light-weight materials for automotive applications, e.g., Al block engine/cylinder bore surface, valve-train components, transmission case "hot spots" and air conditioning compressor hardware.


10. Diamond or DLC sensors for temperature, force and chemical conditions, along with associated packaging systems needed for harsh transportation-related environments, especially as temperatures continue to increase.

11. Improved abrasion/erosion resistance of compressor blades/stator vanes in gas turbines and turbochargers, where small amounts of wear result in drastic efficiency losses.

12. Improved abrasion resistance of windows on aircraft and automobiles.

13. Improved power-management capabilities for electric-powered vehicles and power transmissions, leading to extended vehicle range and improved safety/reliability/performance.

14. Improved thermal management to decrease thermal fatigue from hot spots in combustion chambers, especially in cylinder heads.

15. Improved machine/cutting tools for advanced materials, e.g., composites, ceramics.

16. Improved thermal management for heavy-duty trucks and aircraft braking systems, which is currently a critical problem area.
17. New lubricants may need to be developed for compatibility with diamond and/or DLC materials used in engines, transmissions, gears, etc.

18. Improved seals for many areas of application.

It must be strongly emphasized that if programs are undertaken with respect to any of these identified problem areas, applied work must be coupled with projects to improve our understanding and capabilities with respect to deposition techniques, film properties and characterization techniques. Working panels provided specific guidance for required parallel efforts in all three of these categories.
2.0 INTRODUCTION.

2.1 HISTORY OF THE TRIBOLOGY PROGRAM.

The Department of Energy (DOE) established the Energy Conversion and Utilization Technologies (ECUT) Program in FY 1980 with the mission of conducting generic, long-term, high-risk, applied research and exploratory development in energy conversion and utilization in areas pertaining to energy conservation, which private enterprise will not or cannot pursue. The Tribology Program of ECUT was formed in the fall of 1983. In April 1990, the Assistant Secretary for Conservation and Renewable Energy conducted a reorganization and placed the Tribology Program under the Office of Transportation Materials (OTM) in the Office of Transportation Technologies (OTT). The ECUT program was already heavily oriented to transportation needs and that emphasis continues and is further enhanced in the current program plans.

The current program is mainly intended to support researchers in industry, academia and government to explore ideas or concepts aimed at specific applications to bring them to a stage where private industry or other government programs can carry them into more advanced technology and engineering development. Its goals are to (1) establish feasibility of concepts that significantly reduce energy consumption in transportation systems, (2) carry out exploratory development on novel or innovative concepts for advanced transportation systems, (3) evaluate new concepts for improved efficiency or alternative-fuel use in advanced engines and (4) expand the technology base necessary for development of improvements in advanced transportation systems. The program attempts to be a bridge between basic research and large-scale technology and engineering development in the transportation sector.

2.2 OFFICE OF TRANSPORTATION TECHNOLOGY (OTT).

MISSION. The OTT is charged with long-term, high risk, and potentially high-payoff research and development of promising transportation technologies that are unlikely to be undertaken by the private sector alone. OTT activities are designed to develop an advanced technology base within the U.S. transportation industry for future manufacture of more energy-efficient, fuel-flexible and environmentally sound transportation systems. OTT operations are focused in three areas: advanced automotive propulsion systems including gas turbines, low-heat-rejection diesel, and electric-vehicle technologies; advanced-materials development and tribology research; and research, development, demonstration, test, and evaluation (including field testing in fleet operations) of alternative fuels.

OTT's research objectives focus on the two largest segments of the transportation sector: (1) automobiles and light-duty trucks and vans and (2) heavy-duty trucks and buses. Roughly, 64% of all the transportation petroleum consumed in the United States is pumped into automobiles and light-duty trucks and vans. Heavy-duty trucks and buses consume another 15%. By focusing research and development (R&D) efforts in these two areas, even small gains in efficiency can produce large payback for the taxpayers' funding dollar. A 10% reduction in gasoline consumption in the U.S. automobile and light-duty-truck fleet, attainable in the near term through increased efficiency, could accumulatively save the owners of new vehicles billions of dollars.
Current Program Structure of OTM

Office of Transportation Materials

- High Temperature Materials Laboratory
  - ORNL
- Tribology: Friction, Wear, and Lubrication Research
  - ANL
- Ceramics Technology
  - ORNL
OTT works closely with the Department of Transportation (DOT), the General Services Administration (GSA), and the Environmental Protection Agency (EPA) to ensure that legislatively mandated goals regarding alternative fuels, reduced emissions, and clean air are met.

OTT is structured to reflect the end-user orientation of DOE's Conservation and Renewable Energy organization and to effect timely technology transfer to industry. Three units comprise the office: (1) the Office of Alternative Fuels, which includes Bio-fuels Systems Division and the Fuel Utilization Data and Analysis Division; (2) the Office of Propulsion Systems, which includes the Electric and Hybrid Propulsion Division and the Advanced Propulsion Division; and (3) the Office of Transportation Materials. The synergism of the research conducted under the three units of OTT, as well as that carried out by investigators from other government agencies, industry and universities, holds promise for resolving our nation's transportation problems. A diagram of the organizational structure of OTT is found in Figure 1.

2.3 OFFICE OF TRANSPORTATION MATERIALS (OTM).

MISSION. The mission of the OTM is to develop an industrial base in advanced transportation-related materials and associated materials processing. The objective is to enable the development and engineering of energy-efficient transportation systems that will make possible the transition of the U.S. transportation sector from near-total dependence on petroleum to alternative fuels and electricity.

The current structure of the OTM, Figure 2, includes the Ceramics Technology for Advanced Heat Engines Program, the High Temperature Materials Laboratory and the Tribology Program which is the basis of this planning document.

In pursuit of its mission the OTM Program seeks to accomplish the following goals:

1. Understand and improve techniques, processes and materials necessary to the solution of specific problems associated with the efficiency limits and the multi-fuel-use capability of advanced transportation systems and components.

2. Monitor and evaluate advances in basic scientific research for applicability to transportation systems.

3. Conduct exploratory development of novel or innovative concepts.

4. Establish the feasibility of concepts having the potential to reduce energy consumption significantly.

5. Ensure a continual flow of information on conservation-related technical advances in the transportation sector to private industry.

Mainly, OTM supports research and exploratory development on a specific concept or idea at the laboratory or bench scale in order to bring it to a stage where it might be carried into more advanced technology and engineering development funded by private industry or
other government programs. The program encourages cooperative research between industry and government laboratories, with an emphasis on heavy industrial involvement and leadership.

2.4 TRIBOLOGY PROGRAM

MISSION. The mission of the OTM Tribology Program is to provide the base technology to enable savings in annual U.S. energy consumption through tribological advances in the transportation sector. These energy savings may be achieved directly or through savings of embodied energy or enhanced productivity. This mission is carried out in a manner so as to reduce the significant limitations in the operation of existing and advanced tribological systems which have to operate in severe environments such as high temperatures, high speeds, high loads, corrosive gases/liquids and combinations thereof. The program works closely with U.S. industry to determine current and future needs for advances of tribological systems for transportation applications and to facilitate the transfer of the new technologies which are developed in this program. Continual coordination and information interchange is maintained with the various other government-sponsored tribology programs.

The DOE-OTM Tribology Program Manager is Dr. Joseph M. Perez. The technical project direction is under the leadership of Argonne National Laboratory (ANL). The Tribology Project Manager at ANL is Dr. Fred A. Nichols. The organizational structure for the Tribology Project is shown in Figure 3.

The science and technology of tribology can play a critical role in raising the level of U.S. competitiveness in world markets. Research and engineering studies in tribology can help to decrease the estimated $100 billion annual energy and material losses in the manufacturing, metalworking, transportation and utility sectors by identifying the causes of friction and wear and devising and implementing methods to reduce these losses. Studies have shown that a major portion of these potential savings resides in the transportation sector where the emphasis of this program lies.

A major barrier to these advances in tribological technology, however, is the lack of effective communication of new research results and of the best state-of-the-art technologies. The complex, interdisciplinary research required to understand and eliminate tribological losses involves scientists and engineers from many very diverse areas of expertise who report their research results in journals and at meetings specialized to their individual discipline. Such compilations of results and techniques are being generated at ever-increasing rates. Nevertheless, progress in tribology is hindered by the relative inaccessibility of information on these advances. It has been estimated that a significant fraction of these tribological losses could be saved simply by better technology transfer.

Additional savings in energy, as well as significant increases in the efficiency and reliability of tribological components and systems, could be achieved if it were possible to optimize their performance and increase their operating lifetimes through the use of realistic design and analysis methods. The need for adequate models and codes becomes
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Advanced Lubrication

Argonne National Laboratory
George R. Fenske
Engineered Tribological Interfaces

Argonne National Laboratory
Fred A. Nichols
Advanced Tribomaterials and Components

Fig. 3.
even more urgent as the operating conditions become more severe (e.g., high temperature, high loads, corrosive atmospheres, etc.).

2.5 CURRENT TASK AREAS.

The current major task areas of the tribology program are Advanced Lubrication, Engineered Tribological Interfaces and Advanced Tribomaterials and Components:

The Advanced Lubrication task area includes experimental and theoretical investigations of lubrication phenomena and the development of improved or novel lubricants and lubricant-delivery systems for current and advanced transportation systems.

The Engineered Tribological Interfaces task area includes research and development on advanced coating processes to modify the microstructure and chemical composition of near-surface regions in order to improve their friction and wear properties for use in advanced transportation systems.

The Advanced Tribomaterials and Components task area encompasses two subtasks: tribomaterials evaluation, which assesses the potential of newly developed materials for transportation applications; and tribocomponents, which includes transportation-system component models, design-tool development, and the dissemination of tribology information to U.S. transportation industry.

Project Management encompasses the administrative and managerial duties of planning, including assessments of application areas with significant tribological energy losses and opportunities for tribological advances in the transportation sector; program implementation, including the review of proposals, organization and conduct of Requests for Proposals (RFP) and/or Research Opportunity Announcements (ROA), advice on selection of R&D projects and the issuing of subcontracts, grants and purchase orders; monitoring of project activities (site visits, phone contacts and review of reports); reporting (bi-monthly and semi-annual reports as well as special formal and information reports) and information interchange.
3.0 WORKSHOP PLENARY LECTURES
Diamond and Diamond–Like Films for Transportation Applications

Workshop Overview

Joseph M. Perez
Tribology Program Manager
Office of Transportation Materials Conservation and Renewable Energy

February 4 & 5, 1992

Argonne, Illinois
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OFFICE OF TECHNICAL AND FINANCIAL ASSISTANCE
F. M. Stewart
Office of Transportation Materials

Materials Development Program

Origin - DOE / CE  Reorganization April 1990

- Action

- The Office of Transportation Materials (OTM) was created to provide a centralized materials development support to the programs of the Office of Transportation Technologies
Office of Transportation Materials

Current Program Structure of OTM

- Ceramics Technology
  - ORNL
- Tribology: Friction, Wear, and Lubrication Research
  - ANL
- High Temperature Materials Laboratory
  - ORNL
Office of Transportation Materials

Mission

- Develop an industrial technology base in advanced transportation-related materials and associated materials processing

- Enable development and engineering of energy-efficient transportation systems that will make possible the transition of the U.S. transportation sector from near total dependence on petroleum to alternative fuels and electricity
Office of Transportation Materials

The Office of Transportation Materials is developing a comprehensive R&D program which seeks to extend throughout the transportation sector of the economy the benefits of modern materials science and engineering.

- Materials technology enables components and systems to achieve their design performance capabilities.

- Improved materials of all types (metals, metal matrix composites, intermetallics, polymers, polymer matrix composites and ceramics) can be exploited so that their inherently superior properties can make the largest contribution to:
  - improving energy efficiency;
  - reducing environmental degradation; and
  - utilizing alternative fuels all at the lowest cost possible.
Office of Transportation Materials
Materials R&D
Focus is on Materials Properties

Materials is a key "enabling technology"

Performance of a system or component depends on materials properties

Materials properties (high temperature strength, corrosion resistance, cycle fatigue, creep strength, fracture toughness, etc.) are determined by composition and microstructure of a material

Structure (microstructure and/or molecular in the case of polymers) is determined by how a material is processed

Processing is a major contributor to materials cost
Office of Transportation Materials

Tribology Program

Procurement Plan for FY 1992

Task Area: 1.0 Extreme Environment Lubrication

Task Area: 2.0 Engineered Tribology Interfaces

Task Area: 3.0 Tribology by design
### Office of Transportation Materials

#### Tribology Program

<table>
<thead>
<tr>
<th>DOE-ECUT Tribology Program:</th>
<th>Long-range, High risk, Basic research</th>
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<tr>
<td>DOE-OTM Tribology Program:</td>
<td>Shorter-term, Industry relevant</td>
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Office of Transportation Materials

Tribology Program

Purpose

To obtain industry input on program in Tribology / Advanced Lubricants areas of interest.
Office of Transportation Materials

Tribology Program

Approach

Input on possible areas for interaction
- One on one
- Surveys
- Workshops

Multi-Year Program Plan

Industry Input / Comments

Review

Implement
Office of Transportation Materials

Tribology Program

Objective

Identify opportunities for cost effective application of diamond and diamond-like carbon (DLC) in transportation systems.
Office of Transportation Materials

Tribology Program

Approach

• Current Status Overview (Speakers)

• Work Sessions - Panels
  - Define needs
  - Identify barriers
  - Potential benefits

• Panel Chairmen

• ANL Summary
Office of Transportation Materials

Tribology Program

Panels

Comparative Evaluation of Deposition Technologies
George Fenske, ANL

Properties of Diamond and Diamond-Like-Carbon Films
Peter Blau, ORNL

Characterization
Robert Erck, ANL

Applications to Transportation
Fred Nichols, ANL
Office of Transportation Materials

Tribology Program

Goals

• Improve competitiveness
• Reduce energy dependence
• Environmentally friendly
Acknowledgments

Fred Nichols and staff (ANL)
Ted Vojnovich and Jim Eberhardt (USDOE)
Denise Moores for outstanding arrangements
DIAMOND FILMS:
HISTORICAL PERSPECTIVE

Russell Messier
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Presentation at: Diamond Films Workshop
Department of Energy
Argonne National Laboratory
February 4-5, 1992
LOW PRESSURE CVD
PYROLYSIS OF CH₄
AND OTHER HYDROCARBONS
↓
DIAMOND FILMS
& MICROCRYSTALS

DIAMOND SYNTHESIS
ELECTRICAL ION BEAM
& DISCHARGE HYBRIDE
METHODS
PLASMA IN HYDROCARBON GAS IONS FROM
HYDROGENATED DIAMOND-LIKE FILMS DIAMOND-LIKE FILMS
VARIED \( \frac{sp^2}{sp^3} \) RATIO VARIED \( \frac{sp^2}{sp^3} \) RATIO

1911 BOLTON IN GERMANY
1954 HIGH PRESSURE & GE
1955 BRIDGEMAN
1958 EVERSOLE & U.C.
HOMOEPITAXY

1967 ANGUS DERTJAGUN
1973 at CWR
1976

1975 ATOMIC HYDROGEN
1975 H² SUPEREQ.
MICROCRYSTALS
1981 H² SUPEREQ.
MICROCRYSTALS

1976 HOLLAND
1976 SPENCER+

1979 WIESMANTAL

1983 KOIDL +

1982 MATSUMOTO & SETAKA
W FILAMENT & MICROWAVE PLASMA

1984

1985 MATSUMOTO
RF PLASMA IN MIXTURE 1% CH₄ IN H₂

1971 AISENBERG & CHABOT
1979 SOKOŁOWSKI P
1982 BANKS NASA
Synthetic Diamonds

Their recent production was the culmination of a hundred years of attempts, some of which were claimed to be successful. An account of these efforts and the thermodynamic laws defining the problem

by P. W. Bridgman

Now that the problem of synthesizing diamond has at last been solved, it is perhaps of interest to survey some of the highlights of the history of this long endeavor. The attempts to solve this glittering problem have revealed the whole human spectrum: those engaged in it have ranged from first-rate scientists to downright muckers and charlatans. There has been no little wishful thinking and self-deception, not unmixed with avarice. The project has generated an extensive literature in technical journals and many accounts in the popular press, based on rumors later proved unsubstantial. Many amateurs have done their own unpublished thinking about the subject. I suppose that over the last 25 years an average of two or three people a year have come into my office, offering to share the secret and the profit of making diamonds in return for my constructing the apparatus and reducing the idea to practice. The problem has got into the thriller literature, and I have often encountered the belief that the successful solver of this problem would be in danger of his life from the Diamond Syndicate.

The beginning of a foundation for scientific attack on the problem was laid in 1770 when the Englishman Smithson Tennant showed that diamond is a form of elementary carbon. This may be proved by burning a pure diamond in an atmosphere of pure oxygen; it burns to carbon dioxide without any residue.

The common crystalline form of carbon, of course, is graphite. Diamond has a density of 3.51 against 2.25 for graphite. Modern X-ray analysis has disclosed the structural differences between them. Diamond crystallizes in a cubic system with each atom symmetrically surrounded by four others, all at the same distance and arranged at the corners of a regular tetrahedron. Graphite crystallizes in the hexagonal system: the atoms are arranged in layers; within each layer the pattern is not greatly different, but the arrangement in diamond, but the layers are separated by comparatively large intervals. It is to this that graphite owes its lubricating properties, for the layers can slip over one another under the action of weak mechanical forces.

Paradoxically, although diamond is very dense and is the hardest substance known, its atoms are not packed in the closest possible geometrical arrangement. It would be much denser if each atom were surrounded by 12 other equidistant atoms instead of only 4.

Willard Gibbs's work in thermodynamics at the turn of the 19th century made it possible to say theoretically under what conditions carbon...
The thermodynamic potential of a substance is a measure of its stability. In the case of diamond, the thermodynamic potential is higher than graphite, making diamond the thermodynamically preferred form. However, this does not mean that graphite cannot transform into diamond under certain conditions. The transformation requires a large amount of energy, and the process is not spontaneous. The formation of diamond from graphite is a metastable state, meaning it is possible but unlikely.

One of the earliest attempts to create diamonds was by J. B. Hannay in 1880. He mixed hydrocarbons, bone oil, and lithium with a mixture of iron and graphite in a press. The mixture was compressed to about 20,000 atmospheres, but no diamonds were formed. The process was repeated several times, but no diamonds were ever produced.

However, Hannay's claim was met with skepticism. The Frenchman Henri Mousson, who was also working on the same problem, died in 1892 before he could publish his results. His assistant, Kathleen Lonsdale, continued the work and found that under certain conditions, diamonds could indeed be formed. Lonsdale's experiments confirmed Hannay's results and showed that diamonds could be formed under conditions of high pressure and temperature.

The process of diamond formation is complex and involves the melting of graphite and the nucleation of diamond crystals. The conditions required for diamond formation are very specific, and it is not a simple process to achieve.

In conclusion, the formation of diamond from graphite is possible under the right conditions, but it requires a significant amount of energy and is not a spontaneous process. The discovery of diamond formation from graphite has important implications for our understanding of the Earth's deep interior and the formation of diamonds in the Earth's mantle.
METHOD FOR PRODUCTION OF MAGNESIUM HYDRIDE

John F. Fong, Samuel L. Clark, E. C. Fair, Howard Pullin, and Theodore L. Haynes, assignors to Gilf Mahon Chemical Corporation

9 Claims. (Cl. 21-1099)

1. In the production of magnesium hydride by reacting magnesium metal and molecular hydrogen, the step of introducing into the reaction mixture consisting essentially of magnesium metal and hydrogen a catalytic amount of a component of the class BXX where B is an aliphatic hydrocarbon radical containing from 1 to 3 carbon atoms, X is selected from the group consisting of chlorine, bromine, and iodine and X is selected from the group consisting of chlorine, bromine, iodine and hydrogen.

PROCEDURE FOR PRODUCING BORON TRICHLORIDE

Sheldon L. Clark, Lewis T. Byers, and Theodore L. Haynes, assignors to Gilf Mahon Chemical Corporation, a corporation of Virginia

9 Claims. (Cl. 22-399)

1. A process for the production of boron trichloride which comprises pyrolyzing diborane in a first reaction zone under conditions providing products including a mixture of boron hydrides higher than decaborane, separating the mixture of boron hydrides higher than decaborane from the other pyrolysis products, especially removing the mixture of boron hydrides higher than decaborane in a second reaction zone at a temperature within the range from 50° to 150° C. with a gas stream consisting essentially of chlorine, and removing boron trichloride from the reaction products.

MANUFACTURE OF HYDROGEN PEROXIDE

Donald F. Krum, Buffalo, and Leonard E. Danzen, Grand Island, N.Y., assignors to PMC Corporation, a corporation of Delaware

No Drawing. Filed May 14, 1945. Ser. No. 733,673
9 Claims. (Cl. 23-397)

1. In the production of hydrogens peroxide by the alternate reduction and oxidation of an alkylated amorphous substance as the working material carried in solution and wherein the working material is hydrogenated by passage through a fixed particular catalyst bed of a noble metal catalyst deposited as a surface coating upon an inert solid carrier, the improvement comprising such inert carrier being within the range of 4 mesh to 60 mesh and having a surface area of less than five square meters per gram and a pore volume as to pores of less than 800° A. less than 0.03 cc. per gram.

SYNTHESIS OF CARBON BLACK

William G. Enslow, New York, N.Y., assignor to Union Carbide Corporation, a corporation of New York

No Drawing. Filed July 13, 1945. Ser. No. 736,299
9 Claims. (Cl. 25-1099)

1. A solid-gas contacting process for growing diamond on diamond seed crystal which comprises providing diamond seed crystal; contacting said diamond seed crystal solely with a gas stream from the group consisting of carbon monoxide and mixtures of carbon dioxide and carbon monoxide at temperatures between about 682° C. and about 1600° C. and pressures above about 20 atmospheres.

METHODS OF CHEMICAL TREATING OF ORES

Walter P. Baume, New York, N.Y., assignor to Union Carbide Corporation, New York, N.Y., a corporation of New York

No Drawing. Filed Apr. 30, 1945. Ser. No. 74,282
9 Claims. (Cl. 23-396)

1. A method of determining the recoverable number of mineral oxides which are subject to contamination with...
Growth of Diamond Seed Crystals by Vapor Deposition

JOHN C. ANGUS, HERBERT A. WILL,* AND WAYNE S. STANKO
Case Western Reserve University, Cleveland, Ohio
(Received 30 November 1967)

Carbon was deposited on virgin, natural diamond powder from methane gas at 1050°C and 0.3 Torr. The deposits were identified as new diamond by chemical analysis, chemical etching, density measurements, x-ray and electron diffraction, microwave absorption, electron spin resonance, and visual observations. The crystalline quality of the new diamond layers has not been established; it could range from polycrystalline material with a large number of defects to true epitaxial layers.

I. INTRODUCTION

The history of diamond synthesis is long and colorful and relatively familiar.1 Most efforts were directed at transforming carbonaceous material to diamonds at high pressures where diamond is the thermodynamically stable phase. These efforts were successful in 1955.2 It is less well known that there have been a number of serious, independent proposals for growing diamond at low pressures. Among those discussing the possibility were Bridgman,1 Ubbelohde and Lewis,1' Suits,1 Lander and Morrison,1 and Angus.4 In addition, claims of successful low-pressure syntheses were made by Brinkman1 and Everdell,5 the latter being the more relevant for the present work. All of the proposed processes involve deposition of carbon onto a diamond seed crystal at pressures where diamond is thermodynamically unstable with respect to graphite.

In the light of this history it is remarkable that the question has received so little serious attention. In this paper we present evidence conclusively demonstrating that diamond crystals can be grown at subatmospheric pressures.

II. DISCUSSION OF METHOD

The tendency to discuss diamond synthesis in terms of equilibrium thermodynamics can obscure the fact that kinetic factors may provide the possibility of diamond synthesis in a temperature-pressure regime where diamond is actually thermodynamically unstable with respect to graphite. For example, there is a significant activation barrier impeding the spontaneous transformation of diamond to graphite. In fact, the rate of spontaneous transformation does not become significant until 1300°C. Also the mobility of carbon atoms on clean diamond surfaces at 1000°C is quite high.4

These considerations show that a diamond seed crystal might be expected to grow if placed in an environment supersaturated with respect to carbon at temperatures ranging from 1000°C to 1300°C. A competing process will, of course, be the spontaneous nucleation of new graphite crystals from the super-saturated vapor phase. (This is not to be confused with the spontaneous transformation of the diamond substrate into graphite.) It can be expected that the rate of homogeneous nucleation of graphite in the vapor phase will be small because of the surface free-energy barrier to nucleation predicted by conventional nucleation theory. Heterogeneous nucleation of graphite on the diamond seed crystals cannot be avoided, but the mobile carbon atoms on the diamond surface may be more likely to attach themselves to the diamond crystal rather than to form new graphite nuclei.

Graphite has a lower Gibbs free energy (chemical potential) than diamond. Therefore, if the atmosphere above the crystal is supersaturated with respect to diamond, then it will be even more supersaturated with respect to graphite. This means that the possibility of nucleating graphite can never be eliminated but it is expected that the probability will be low because of the factors listed above.

In this paper we report on the growth of natural, virgin diamond powder by vapor deposition at subatmospheric pressures. Our experiments show that new diamond is formed. The crystalline quality of the new diamond has not been established, however.

III. EXPERIMENTAL METHOD

A. Deposition and Cleaning Procedures

A gas phase supersaturated with carbon was provided by the thermal decomposition of methane gas at pressures ranging from 0.15 to 458 Torr and tem-
ОГЛАВЛЕНИЕ

Предисловие

PRINCIPLES OF NUCLEATION THEORY
ОСНОВНЫЕ ЗАКОНОМЕРНОСТИ НУКЛЕАЦИИ
1. Теория гомогенной нуклеации
2. Влияние поверхностных сил на образование и
   свойства новой фазы
3. Теория гетерогенной нуклеации

GROWTH OF DIAMOND
РОСТ АЛМАЗА
И ГРАФИТА GRAPHITE
ИЗ ГАЗОВОЙ ФАЗЫ
из GAS PHASE

GROWTH OF GRAPHITE FROM GAS PHASE
2. Рост графита из газовой фазы
1. Физико-химическая теория роста графита
2. Экспериментальная проверка предложенной
   теории роста графита
3. Рост графита в мезокристаллических условиях
4. Нитевидные кристаллы графита

KINETICS OF PHYSICO-CHEMICAL SYNTHESIS OF
3. КИНЕТИКА
ФИЗИКО-ХИМИЧЕСКОГО СИНЕЗА АЛМАЗА
1. Из истории синтеза алмаза
2. Кинетика роста алмаза на алмазных порошках
3. Циклический метод наращивания алмазных
   порошков
4. Механизм роста алмаза
5. Синтез алмаза из смесей углеводородов (не-
   аддитивность скоростей реакций)
6. Фракционирование стабильных изотопов угле-
   рода
7. Определение удельной поверхности порошков
8. ЭПИТАКСИАЛЬНЫЕ АЛМАЗНЫЕ ПЛЕНИКИ

4. ЭПИТАКСИАЛЬНЫЕ АЛМАЗНЫЕ ПЛЕНИКИ
   И НИТЕВИДНЫЕ КРИСТАЛЛЫ
1. Синтез и свойства алмазных пленок
2. Потенциальный способ наращивания алмаза
3. Нитевидные и изометрические кристаллы алмаза

Приложение

Издательство «Наука»
Москва
SELECTIVE CASSIFICATION OF DATA

2. ELECTRICAL DISCHARGE
3. W FILAMENT

4.生態學的細胞和動物的免疫系統

HYPOTHETICAL SOLVENT

...
VAPOUR GROWTH OF DIAMOND ON DIAMOND AND OTHER SURFACES

B.V. SPITSYN, L.L. BOUILOV and B.V. DERJAGUIN
Institute of Physical Chemistry, Academy of Sciences of the USSR, Moscow, USSR

It is shown that diamond crystallization by chemical vapor deposition should preferably be carried out at reduced pressures. Selective growth of diamond is ensured by introducing atomic hydrogen into the crystallization zone; this suppresses crystallization of graphite. The growth rate of homoepitaxial diamond films reaches 1 μm/h at 1000°C; film properties were identical to those of bulk crystals. The lattice parameter in boron-doped films (~0.1 at.%) decreased by 0.009 Å, the film and substrate parameters coincide at dopant concentrations of ~1 at.%, and the semiconductor diamond film intergrows with the substrate without stress. Diamond crystals up to several tens of microns in thickness were grown also on non-diamond substrates. At large supersaturation, the crystal habit is octahedral and at low supersaturation, it is cubic. The linear growth rate is constant at the early stages of crystal growth but then it diminishes to a level typical for the homoepitaxial growth of diamond films.

1. Introduction

The unique combination of excellent mechanical, physical, and chemical properties of diamond has been the driving force for the development of new and cheaper methods of synthesis. Different fields of diamond applications both in research and industry can be satisfied only by essentially different techniques of crystallization. For instance, the unique electrical and thermal properties of diamond, as a high-temperature semiconductor, can be fully developed only under the following strictly controlled conditions of synthesis: layered structures are grown, consisting of alternating dielectric and semiconducting single crystals; diamond films with thickness of the order of one micron each. Such conditions can be obtained by means of vapor growth techniques at reduced pressure, that is in the region of metastability of diamond. Research in this direction [1, 2] began almost at the same time as the well-known work on diamond synthesis at ultrahigh pressures.

2. Physical and chemical crystallization

The simplest process of diamond crystallization is the sublimation of graphite and subsequent condensation of the carbon vapor on the surface of the diamond seed crystal. The material is transferred to the growing crystal due to the temperature gradient between the source and the substrate [3]. Although this process is, in principle, possible, in practice it is inhibited by a number of factors:

1. According to LEED data [4], the diamond surface retains the bulk structure up to temperatures ~1300°C (in vacuum). At such temperatures the equilibrium carbon vapor pressure over the diamond phase is almost twice [3] that over graphite [5], and reaches ~1 × 10^-13 Torr. An acceptable growth rate (about 1 μm/h) requires that the carbon vapor pressure over diamond phase exceed 10^-8 Torr. Hence, the sublimation growth of diamond at such rates requires supersaturation ~10^7 which obviously entails high defect density in the overgrowth. In addition, the probability of nucleation and growth of the graphite phase which is stable at low pressures, will also be considerable at such high supersaturations [6].

2. The composition of carbon vapor over graphite shows a predominance of C-type molecules [5] with multiple bonds between carbon atoms; this factor inhibits incorporation of carbon units into the diamond lattice.

3. Finally, even single carbon atoms in the ground (non-excited) state are bivalent, so that about 96 kcal/g-atom has to be expended to...
when the crystallization temperature decreases and the partial pressure of the component comprising the crystallized material increases. In the synthesis techniques that we have chosen, the supersaturation is a function of both the pressure of hydrocarbons, and of the partial pressure of atomic hydrogen. The latter changes the concentration of the hydrocarbon complexes adsorbed on the substrate, by interacting with hydrocarbons in the gas phase and on the surface. Hence, the atomic hydrogen not only maintains selectivity of the process but also affects the growth rate, thus having the role of an active participant in the diamond crystallization.

3. Diamond growth on diamond surfaces

Substrate temperature is one of the factors which determine the rate of the process and the structure of the deposit. Diamond layers grown on single crystals at 600°C are polycrystalline with grain size of 15 to 20 Å [15]. However, high-perfection single-crystalline layers were obtained on the (110) face of natural diamond at 750°C; this is confirmed by electron diffraction (fig. 1) which shows a well-pronounced system of Kikuchi lines. As the temperature is increased further, the growth rate of homoepitaxial film increases (activation energy of the order of 25 kcal/mole) and reaches a maximum at ~1000°C. Further increase in temperature results in reduction of the growth rate and in deterioration of the structure of the diamond layers, so that HEED analysis reveals graphite inclusions.

Cathodoluminescence [17] and X-ray topography [16] have demonstrated that void-type growth defects produce stresses in homoepitaxial diamond films. As the crystallization temperature is lowered from 1100 to 800°C, the stress in the film increases by a factor of approximately three. When the stresses in the substrate-film system exceed a certain threshold, lattice discontinuities and microtwins lamellae are formed in the film [18]. At the same time, ESR studies show that the film contains broken C–C bonds. Stresses produced during growth and high rates of crystallization may result in deterioration in the morphology of the diamond deposit (fig. 2) and in a gradual transformation from a single-crystalline film into a polycrystalline one. The diamond layers were characterized (using SIMS) by a comparatively high purity [19]; the impurity content was found to be approximately the same as in natural single crystals. One exception is

**Fig. 1**: Electron diffraction pattern \((E = 65\text{ keV})\) of a diamond film 0.8 μm thick, grown on (110) face of a natural diamond crystal at a growth rate ~0.4 μm/hour.

**Fig. 2**: Diamond layer ~4 μm thick, grown at a rate of ~2 μm/hour on (111) face of a natural crystal.

**DIAMOND ON DIAMOND**
at cubic crystals, which are at considerable units on the side at the intersection of a number on the side to be [20]; a growth of crystals at least up to 50 µm takes

of crystals at least 10 and 0.9 and Crystal usually anodic to the crystal. The adjacent by twin forms. The growth of the and of the crystals, or the high-pressed polycrystalline copper specimen annealed in hydrogen (fig. 5a). After a certain growth time the specimens were extracted from the reactor, photographed in a scanning electron microscope, and then returned to the reactor. A conducting gold layer was not found necessary to obtain an image when applying a scanning electron microscope to photograph diamond crystals, having sizes up to 50 µm. that were grown on a conducting substrate.

Figs. 5b and 5c show the same area of the copper substrate as that in fig. 5a, after 15 and 30 min of growth. Crystals spontaneously nucleated on the substrate surface are seen to

Fig. 4. Growth twinning on (a) {111}, and (b) {100}, faces.

Fig. 5. Growth of diamond crystals on copper substrate: (a) area of substrate with two rounded-shape diamond seed crystals, (b) and (c) same area after 15 and 30 min of crystallization, respectively.
Vapor Deposition of Diamond Particles from Methane

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and Nobuo SETAKA

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(Received February 9, 1982; accepted for publication March 20, 1982)

Microcrystalline diamond has been formed on silicon or molybdenum substrates by vacuum deposition from a gaseous mixture of methane and hydrogen. Cubo-octahedral or multiply-twinned crystals were obtained. The structure of the deposits was identified by electron diffraction and Raman spectroscopy.

The considerable effort that has been devoted to the synthesis of diamond has been motivated by the unique combination of properties exhibited by this material. These properties include great hardness, high thermal conductivity, high electrical resistivity, optical transparency and semiconductivity induced by impurity doping. Besides high pressure techniques, currently used for commercial production of diamond, attempts have been made to make diamond by chemical vapor deposition (CVD), ion-beam techniques, and plasma-induced vapor deposition. The carbon films obtained by these techniques are often termed diamond-like, since they show, to some extent, properties similar to those of diamond. Unambiguous identification of the structure of these films, however, is difficult owing to the amorphous nature of the films or the appearance of forbidden reflections and of reflections from structures other than diamond in electron diffraction.

On the other hand, Deryagin et al. reported that octahedral or cubo-octahedral diamond crystals can be grown on non-diamond substrates such as copper and gold by chemical transport in a closed system. Recently, a more detailed account of the growth features, characterization and possible growth mechanisms has been given by Spergan et al. Diamond crystals were grown on silicon, tungsten and molybdenum at growth rates of up to 5 μm/h. The importance of the role played by atomic hydrogen was pointed out, but the details of the deposition technique were not given. In this paper, we report that diamond crystals can also be grown on non-diamond substrates by CVD in a flow-system.

Deposition was carried out by passing a mixture of gaseous methane and hydrogen through a depositing chamber, in which a tungsten filament was mounted near the substrates, as shown in Fig. 1. Silicon wafers or molybdenum plates were used as the substrates. Observations by SEM were made with the deposits obtained under the following conditions: methane concentration, ca. 1 vol %; total gas pressure, 10–100 Torr; flow rate, ca. 10 ml/min; temperature of deposition chamber, 800–1000°C; filament temperature, ca. 2600°C. The temperature of the deposition chamber was measured by a thermocouple in contact with the silicon substrate holder, as shown in Fig. 1. The positions of the substrate surface may be higher than the temperature measured by the thermocouple as a result of radiation from the filament. After deposition runs of 3 hours' duration, diamond particles up to 3 μm were formed as shown in Fig. 2(a). There appeared to be little difference in the growth characteristics between silicon and molybdenum substrates. Multiply-twinned crystals as well as cubo-octahedral crystals were observed. The microphotographs resemble those observed with crystals deposited by chemical transport in a closed system. Film-like regions are also formed by the contact of crystals, as shown in Fig. 2(c). The density of nucleation appears to depend strongly on the substrate conditions, and preferential growth along scratches or edges was often noted.

The structures of the deposits were identified by reflection electron diffraction. As Fig. 3 shows, spotted rings were observed; the pattern consists of diffraction spots from more than a hundred particles. As Table I shows, the d-values obtained from the diffraction rings are in good agreement with the reported values for cubic diamond except that the 222 double diffraction ring appears in the diffraction pattern.

Raman scattering of the deposits was also observed as support for the structural identification. The spectra were recorded at room temperature using a Spex Raman
Fig. 2. Scanning electron micrographs of diamond deposited on silicon. (a) Diamond particles deposited at 790 °C (micrograph taken by tilting substrate). (b) Film-like region formed at 880 °C.

Table 1. Comparison of observed interlayer spacings with reported values.

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<tr>
<th>Observed</th>
<th>Reported (ASTM 6-675, Diamond)</th>
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<td>( d (\text{Å}) )</td>
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<tr>
<td>( 2.06 )</td>
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<td>( 1.26 )</td>
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<td>( 1.08 )</td>
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<td>( 1.03 )</td>
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<td>( 0.99 )</td>
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<td>( 0.81 )</td>
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<td>( 0.72 )</td>
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<td>( 0.68 )</td>
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<td>( 0.63 )</td>
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<tr>
<td>( 0.60 )</td>
<td>( m )</td>
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\* Calculated from the reported value of \( \alpha = 3.5667 \text{ Å} \).

The Raman spectrum of the 1401 spectrometer with a back-scattering geometry. The 488.0 or 514.5 nm lines of an argon ion laser or the 441.6 nm line of an He–Cd laser were used for excitation. In the Raman shift range of 300–2500 cm\(^{-1}\), the spectra consist of Raman peaks due to diamond as well as the substrate, and background due to weak luminescence as Fig. 4 shows. Raman scattering from amorphous

Fig. 3. Reflection electron diffraction of diamond particles deposited on silicon.

Fig. 4. Raman spectrum of as-grown specimen silicon substrate. 441.6 nm line of He–Cd laser was used for excitation.
G.O.P. MAY DO WELL IN VOTE FOR HOUSE, EXPERTS FORECAST

They See Democratic Gains as Being Much Smaller Than History Would Suggest

By E. J. DABOSSO JN. JR.
WASHINGTON, Sept. 13 — White House analysts have forecast on the basis of a new poll that will determine the size of the Democratic gains in the House — and that their chances for dramatic gains are minuscule.

The polls are based on a survey of Democratic Party voters in the 1972 election. The pollsters are confident of their accuracy, and believe that their findings will have a major impact on the outcome of the election.

The pollsters believe that the Democratic gains will be much smaller than expected, and that the Republicans have a good chance of maintaining their majority in the House.

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Soviet Says a C.I.A. Station Chief Passed On Instructions to Daniloff

By PHILIP TALBANK

MOSCOW, Sept. 13 — The Soviet Union has accused the United States of providing information to its intelligence services that was used to implant a Soviet agent in the U.S. government.

The U.S. government has denied the charges, and has called for a probe into the incident.

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Today's Sections:

Why Stocks Feel Anxiety, With

By LINDA

The prospects seemed dimmed on the New York stock exchange.

45
Diamanter av sumpgas!

Att tillverka diamanter vedlade sig tidigt som ett tillfället till att använda sumpgas som materia. Sumpgas, som kommer från ekonomiska branscher som underhåll och miljöförråd, innehåller mycket små mängder av diamanter som kan användas i industriella fält. Detta innebär att det finns möjligheter att producera diamanter med hjälp av sumpgas. Detta har lett till att det finns flertalet projekt som har avancerat i detta område.

En av de mest framgångsrika projektet är den så kallade "Diamantprojektet" i USA, Japan, Västtyskland och Sverige. Denna teknologin utvecklats på grund av det stora behovet av diamanter inom industriella fält. En av de största förmåner i projektet är att det kan leda till att produktionen av diamanter kan öka betydligt.

I dagligt levande verklighet har det skapats ett nytt område för diamanter, och detta har lett till att diamanter har uppmuntrat att användas i olika områden. Genom att använda sumpgas som en tillvägagångssätt kan det bli möjligt att producera diamanter med hög kvalitet.

Detta projekt har också lett till att det finns möjligheter att producera diamanter med hög kvalitet. Detta har lett till att det finns flertalet projekt som har avancerat i detta område. Detta har lett till att det finns möjligheter att producera diamanter med hög kvalitet. Förutom att det finns möjligheter att producera diamanter med hög kvalitet finns det också möjligheter att producera diamanter med låg kvalitet. Detta har lett till att det finns flertalet projekt som har avancerat i detta område.

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<td>1987</td>
<td>We're Behind! ⇒ START!</td>
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<td>1988</td>
<td>We're all in for the long-haul.</td>
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Soviets On Cutting Edge Of Earth's Diamond Age

By MICHAEL DOHERY

MOSCOW — Historians who chronicle human progress in terms of new materials that change society will never here who fashioned the first stone tools that ushered in the Stone Age, or exactly which inspired individuals deserve credit for the Bronze Age or the Iron Age.

But if scientists’ expectations prove correct, the founders of the next such era — the Diamond Age — will be easily identifiable.

They are working in a modest laboratory at the Base Institute for Physical Chemistry here, trying to perfect a process for coating materials with a thin film of gem-quality diamond, the hardest material known to man.

“A diamond age,” Dr. Boris Der- yagin said. His thumbs and forefingers circumcised a small wafer of material coated with diamond in the process that he and Dmitri Fedoseyev invented a decade ago.

“Yes, maybe so,”

Although they published a detailed report on the process in 1977, scientists around the world ignored it — for reasons that are unclear.

Shrug Of Bemusement

Dr. Victor Spitsyn, director of the institute and a member of the prestigious Academy of Sciences of the USSR, shrugged his shoulders in bemusement when asked why it has taken the scientific community so long to recognize the implications of the process. Dr. Spitsyn also has participated in the diamond-film research.

During the last year, Drs. Spitsyn, Deryagin, and Fedoseyev have become folk heroes of materials science, the effort to develop stronger and more economical materials for use in industrial and consumer products. Their names are becoming widely known in a number of other fields where diamond films can be used. Scientists believe that the three are prime candidates for a Nobel Prize.

Indeed, some predict that thin-film diamond technology will have a broader impact on society than any other technological achievement since 1900 — the year of the invention of the process that made aluminum widely available.

That process, developed by Charles Hall and Paul Hersee, transformed aluminum from a semiprecious metal that sold for more than $7 an ounce into a common metal that cost less than 2 cents a pound by 1910.

Dr. Deryagin questions whether diamond films will be used as extensively in consumer products as aluminum is. But he predicted “a great expansion” in mankind’s exploitation of the unique properties of diamond. It is the hardest and most chemically inert material on earth, giving it the ability to cut all other materials and resist attack by chemicals.

It also conducts heat better than silver, copper, and other metals. Unlike those metals, it does not conduct electricity, but acts as an excellent electrical insulator. Those properties give diamond numerous potential applications in electronics, where heat dissipation is a major factor limiting how tightly transistors can be packed together on printed circuit boards.

Dr. Deryagin said that diamond films could be used on everything from knives and industrial cutting tools that remain sharp indefinitely to a new generation of computers and other electronics products.

Fils Extremely Thin

The films are extremely thin, perhaps only 0.00001 inch thick.

Scores of industrial firms are trying to develop products that would use diamond coatings. Dr. Deryagin pointed out that the Japanese have taken the lead in transforming the Soviet Union's basic research on diamond films into technology with the potential for producing "enormous profit."

The Japanese reportedly are developing numerous products, including diamond-coated stove speakers, scratch-proof airplane windows and camera lenses, and diamond-coated computer chips that dissipate heat very rapidly.

Dr. Spitsyn suggested that cooperation between U.S. and Soviet scientists might be one way of preventing the Japanese from dominating diamond-film technology, just as they have dominated other forms of advanced technology.

Turn to Page 4, Col. 2
Soviets On Cutting Edge

Continued from First Page

He and his associates acknowledged that diamond-film technology has military applications. The American Star Wars program, for example, has become a major financier of diamond-film research because of its potential for improving the performance of lasers and other optical devices.

U.S.-Soviet Cooperation

But Dr. Spitzer indicated that there could be U.S.-Soviet cooperation on nonmilitary aspects of thin-film diamond technology. American scientists speculate that the initial 1977 Soviet report on diamond films was ignored because the technology for depositing the films appeared so simple that it was barely believable.

Scientists knew that manufacture of synthetic diamonds, first achieved in the United States in 1954, required extremely high temperatures and pressures. Synthetic diamonds are made from carbon that has been subjected to enormous pressures and ultra-high temperatures.

The Soviet process, in contrast, is simple, inexpensive, and uses lower temperatures and pressures. It uses methane, a common gas that is the major component of natural gas, and microwaves similar to those used in ovens.

Electrically Charged Gas

Each molecule of methane consists of one atom of carbon and four atoms of hydrogen. In the diamond-film process, microwaves are used to heat methane, separating the carbon from the hydrogen atoms and forming an electrically charged gas known as a plasma.

When the plasma comes into contact with an object, carbon atoms accumulate on its surface in the specific crystalline form of diamond.

The Soviet apparatus now is able to deposit about 4 micrometers of diamond an hour, Dr. Fedoseyev said. That rate should be adequate for most purposes, he added. One micrometer is about 0.000039 inch.

Dr. Fedoseyev said the Soviets are capable of depositing two distinct kinds of films, one consisting of ordinary diamond, and another of a diamond-like material that a translator termed "diamond slag."

All three of the Soviet scientists visited many pleasant encounters with American scientists. Dr. Spitzer expressed the hope that political differences would not hinder scientific cooperation between the United States and the USSR.
ALL HYDROCARBON GASES MAKE DIAMOND ≈ SAME

Fig. 1. Schematic diagram of thermal CVD apparatus.

Table 1. Organic compounds for diamond synthesis in this study.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl alcohol</td>
<td>CH₃OH</td>
</tr>
<tr>
<td>ethyl alcohol</td>
<td>C₂H₅OH</td>
</tr>
<tr>
<td>isopropyl alcohol</td>
<td>(C₃H₇)CH₂OH</td>
</tr>
<tr>
<td>2-methyl-2-propanol</td>
<td>(C₃H₇)COH</td>
</tr>
<tr>
<td>acetone</td>
<td>CH₃C(OH)₂</td>
</tr>
<tr>
<td>isopropyl ether</td>
<td>[(C₃H₇)CH₂]O</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>C₆H₁₂OC₂H₆</td>
</tr>
<tr>
<td>methyl acetate</td>
<td>CH₃C(OH)₂</td>
</tr>
<tr>
<td>acetaldehyde</td>
<td>CH₃CHO</td>
</tr>
<tr>
<td>trimethylamine</td>
<td>(C₃H₇)₃N</td>
</tr>
</tbody>
</table>

From Y. Hirose and Y. Terasawa
Jpn. JAP 25, L519 (1986)
2回以上売買16％

陸上部の民間企業同士が67％

61年、都白書

大阪市民の申請を受理

新幹線公害

調整委が初の調停へ
You can make diamond easily!
(The Yomiuri Shimbun* March 29, 88, P2)

Dr. Hirose, an associate professor of Nippon Kagyo University, developed a much easier way to synthesize diamond than ever reported. This method works in the air, so it doesn't need a vacuum pump or vessel. As shown in the below figure, the flame ejected from the burner deposits diamond particles on a silicon substrate which temperature is held between 600°C and 900°C. The key point is to use a reducing flame which temperature is above 1500°C. XRD and Raman spectrum identify the particles as diamond. So far, the biggest particle grown for an hour has 200 micron diameter size. This new process seems to be suitable for coating on cutting tools or curved surfaces rather than for making diamond semiconductor.

Dr. Hirose will give a presentation about this work at 35th Applied Physics Seminar today.

![Diagram of the new process](attachment:diagram.jpg)

SI substrate
(600°C < temp. < 900°C)

A Schematic Image of the New Process

--

*The Yomiuri Shimbun is one of three big Japanese newspapers.*
Gas Temperature vs. Diamond Deposition Rate

Deposition Rate vs. gas temperature [°C]

- flames
- conventional microwave & filament techniques
- low pressure DC or RF discharges

从 Bachmann and Lydian
MRS Symp Proc 165 (1989)
GE Process!
1986
DIAMOND ←→ DIAMOND-LIKE

HOMOEPITAXY →

HETEROEPITAXY →

ORIENTED POLYCRYSTALLINE

POLYCRYSTALLINE

POLYCRYSTALLINE

AMORPHOUS

Acheived:

Indications: β-SiC, c-BN

By controlling deposition conditions and seeding

Typical: 800-1050°C

Near optimum: 0.5%CH₄-H₂

Chemistry controlled

Non-optimum: low Ts (< 500°C)

Conditions: high %CH

Oxygen additions

High nucleation density

Bombardment (some)

Low Ts

does a-C (sp³) exist?
dense hydrocarbons

Bombardment controlled
HOMOEPITAXIAL DIAMOND

TOP

(110) Plane

A. RADZIAN & T. BADZIAN
Diamond on Silicon

980°C
80 Torr
0.4% C_H_4/ H_2

18 μm

A.R. Badzian and T. Badzian
MCVD
Diamond on Si

MPACVD

different substrate position

different substrate position

lower actual T

A. Badzian & T. Badzian
CH$_4$ 3.0\%; t = 44 \mu m
from Y. Sato (NIRIM)
NUCLEATION
[Specific sites/buffer layers]

FREE GROWTH OF DIAMOND

INTERGROWTH OF DIAMOND

RENUCLEATION

SECONDARY EFFECTS
[twinning/impurities]

EVOUTIONARY SELECTION OF CRYSTALLITES
[relative growth rates of crystal planes]
<table>
<thead>
<tr>
<th>Author</th>
<th>Orientation</th>
<th>Temperature</th>
<th>Methane Content</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Windischmann</td>
<td>[110]</td>
<td>800°C</td>
<td>~1% CH₄</td>
<td>low growth rate at high T and % CH₄</td>
</tr>
<tr>
<td>Zarker</td>
<td>[110]</td>
<td>~650°C</td>
<td>~1 mm/arc</td>
<td></td>
</tr>
<tr>
<td>Wild</td>
<td>[110]</td>
<td>~900°C</td>
<td>1.5% CH₄</td>
<td>twinning on [111]</td>
</tr>
<tr>
<td>Narayam (ICP-MS)</td>
<td>[110]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Khure (MPCVD)</td>
<td>[110]</td>
<td>at lower Tₙ (~600°C)</td>
<td></td>
<td>low defects</td>
</tr>
<tr>
<td>Var. (MPCVD)</td>
<td>[110]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gatto (MPCVD)</td>
<td>[100]</td>
<td>850°C</td>
<td>3-4% CH₄</td>
<td></td>
</tr>
<tr>
<td>Feng</td>
<td>[110]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clasing (HFCVD)</td>
<td>[100]</td>
<td>950°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kae (HFCVD biased)</td>
<td>[110]</td>
<td>900°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[100]</td>
<td></td>
<td></td>
<td>similar Conditions</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SF and MT near Grain boundaries</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SF and MT distributed throughout</td>
</tr>
</tbody>
</table>
• High Quality
• Large Area Heteroepitaxy
• Adhesion
• Nucleation $\Rightarrow$ Nucleation Density $\Rightarrow$ Morphology
• Crystallite Size $\Rightarrow$ Surface Roughness
  (Polishing required $\Rightarrow$ mechanical & chemical)
• Post-Deposition Processing
  (Surface Polishing, Laser Cutting, Defect Annealing)
• n-type dopant
UNIQUE ASPECTS OF DIAMOND S&T

• C is Smallest Group IV Element
  \[ \Downarrow \]
  Diamond has largest atom number density
  \[ \Downarrow \]
  Large # of Unique Properties

• Diamond Technology \[ \Rightarrow \] Metastable Material
  - can defects be reduced during prep\textsuperscript{1} post-dep\textsuperscript{2}
  - stable to high T's

• New Approach to Materials Synthesis
  - can it be generalized (e.g. CBN) or
    is it unique to carbon chemistry?

• New Deposition Methods
  - MPACVD
  - HFCVD
  - Combustion Flames
  - Thermal Plasmas
ニューダイヤモンドフォーラムの
活動状況

佐藤 原一

1. はじめに——ニューダイヤモンドとは

ダイヤモンドが、古くから古代エジプトの時代からその豪華な装飾をもって人類の装飾品として最高の地位を獲得し現在にまで継続していることは周知のとおりである。

一方、ダイヤモンドが最高の硬さを有することを古くから知られていたわけではない。創書にも石材をダイヤモンドで加工したことが記されており、加工道具としての利用においても装飾に劣らず古い歴史をもっていることも驚くべきことである。

これにより、ダイヤモンドそのものを始めて各種の石工、特に磨削技術における高精度を要する加工にダイヤモンドが工具材として用いられてきたが、いずれも天然のダイヤモンドであって、資源的制約から利用面が制限されたものに限られざるを得なかった。

ダイヤモンドの成因は、従来より地球物理学の興味を引くテーマとして研究されているが、一方、これを人工的に製造して工業の重要な支を務めるための努力が携われる技術の専門家達によって行われてきたのも周知のとおりである。

ダイヤモンドが工業材料として広く利用される道を開いたのは、

1955年米国ゼネラルエレクトリック（GE）社の静水圧法によるダイヤモンド合成の成功である。これ以後、ダイヤモンド石を中心とした利用が飛躍的に増大し、現在、ダイヤモンド工具は生産額で年間700億円以上、伸び率で年15～20％になっている。

更にこの技術、ダイヤモンドの静水圧法による製造、気相法による製造ダイヤモンドの製造が可能になり、硬さを生かした切削・研磨工具、耐摩耗工具への応用のみならず、ダイヤモンドの化学的、熱的、光学的、電子的な特性に注目したより広い機能材料としての応用の可能
the "diamond technology" tree
<table>
<thead>
<tr>
<th>Property</th>
<th>Material</th>
<th>Silicon</th>
<th>GaAs</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>optical band gap [eV]</td>
<td></td>
<td>1.1</td>
<td>1.4</td>
<td>5.5</td>
</tr>
<tr>
<td>hole mobility [cm$^2$/V sec]</td>
<td></td>
<td>600</td>
<td>400</td>
<td>1500</td>
</tr>
<tr>
<td>electron mobility [cm$^3$/V sec]</td>
<td></td>
<td>1500</td>
<td>8500</td>
<td>1900</td>
</tr>
<tr>
<td>breakdown voltage [V/cm]</td>
<td></td>
<td>$5 \times 10^6$</td>
<td>$6 \times 10^6$</td>
<td>$1 \times 10^7$</td>
</tr>
<tr>
<td>electron velocity at high fields [V/sec]</td>
<td></td>
<td>$1 \times 10^7$</td>
<td>$1 \times 10^7$</td>
<td>$2.7 \times 10^7$</td>
</tr>
<tr>
<td>dielectric constant</td>
<td></td>
<td>11</td>
<td>12.5</td>
<td>5.5</td>
</tr>
<tr>
<td>resistivity [Ω cm]</td>
<td></td>
<td>$10^3$</td>
<td>$10^8$</td>
<td>$&gt;10^{12}$</td>
</tr>
<tr>
<td>thermal conductivity [W/cm$^2$K]</td>
<td></td>
<td>1.45</td>
<td>0.46</td>
<td>20</td>
</tr>
<tr>
<td>thermal expansion coefficient [1/K]</td>
<td></td>
<td>$2.6 \times 10^{-6}$</td>
<td>$5.9 \times 10^{-6}$</td>
<td>$1.1 \times 10^{-6}$</td>
</tr>
<tr>
<td>refractive index</td>
<td></td>
<td>3.4</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>Vickers hardness [kg/mm$^2$]</td>
<td></td>
<td>1000</td>
<td>600</td>
<td>10000</td>
</tr>
<tr>
<td>sound propagation velocity [m/sec]</td>
<td></td>
<td></td>
<td></td>
<td>18500</td>
</tr>
<tr>
<td>elasticity [N/m$^2$]</td>
<td></td>
<td></td>
<td></td>
<td>$1.2 \times 10^{12}$</td>
</tr>
<tr>
<td>density [g/cm$^3$]</td>
<td></td>
<td></td>
<td></td>
<td>3.5</td>
</tr>
<tr>
<td>melting point [°C]</td>
<td></td>
<td>1420</td>
<td>1238</td>
<td>N/A</td>
</tr>
</tbody>
</table>
### Unique Properties

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td><strong>Hardest material known, 9000 kg/mm²</strong></td>
</tr>
<tr>
<td>2.</td>
<td><strong>Highest velocity (long 18000 m/sec)</strong></td>
</tr>
<tr>
<td>3.</td>
<td><strong>Highest thermal conductivity, 20 W/cm°C</strong></td>
</tr>
<tr>
<td>4.</td>
<td><strong>Most transparent in I-R, 225 nm-Far IR</strong></td>
</tr>
<tr>
<td>5.</td>
<td><strong>Highest hole mobility 1600 cm²/V-sec, highest keyes figure of merit</strong></td>
</tr>
<tr>
<td>6.</td>
<td><strong>Lowest friction among low-wear</strong></td>
</tr>
<tr>
<td>7.</td>
<td><strong>Extreme chemical stability</strong></td>
</tr>
</tbody>
</table>

### Applications

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td><strong>Abrasives, cutting tools, surgical knives</strong></td>
</tr>
<tr>
<td>2.</td>
<td><strong>Acoustics, speakers to saw devices</strong></td>
</tr>
<tr>
<td>3.</td>
<td><strong>Thermal management, dense IC</strong></td>
</tr>
<tr>
<td>4.</td>
<td><strong>Optics (IR, visible)</strong></td>
</tr>
<tr>
<td>5.</td>
<td><strong>New electronics</strong></td>
</tr>
<tr>
<td>6.</td>
<td><strong>Tribology (ball bearings to diesels)</strong></td>
</tr>
<tr>
<td>7.</td>
<td><strong>Corrosion protection</strong></td>
</tr>
</tbody>
</table>
APPLICATIONS

• MECHANICAL
  • Cutting tools
  • Knives (wood cutting)
  • Bearings
  • Optical scanners
  • Noggles
  • Eyelets
  • High T, sliding seals
  • Abrasives

• CHEMICAL

• BIOCOMPATIBILITY

• OPTICAL
  • X-ray windows
  • X-ray litho masks
  • High Power Laser Mirrors
  • UV windows
  • IR windows

• THERMAL
  • Dense IC packaging
  • TAB Bonding
  • Laser Diodes
  • High Power electronics

• PASSIVE ELECTRONICS
  • Thermistors

• ACTIVE ELECTRONICS / OPTOELECTRONICS
  • Schottky Diodes
  • MESFET and MOSFET Transistors
  • Electro luminescent Light Emitters
図8 直径25mmビュア・ダイヤモンド・セラミックドームスピーカーの特性

"Component of the year of 1987"
Stereo Sound
Japanese audio magazine
THERMAL CONDUCTIVITY

from Mike Geis
THERMAL CONDUCTIVITY

Raman spectra of diamond films for different methane concentrations.

CVD Diamond Coating

Thermal conductivity of diamond films for different methane concentrations.

Ono, Baba, Funamoto, and Nishikawa
Jpn. JAP (1986)
MPACVD
FIG. 3. Thermal conductivity of two diamond films (open circles: DT-13; full circles: DT-15). Bold lines are fits using different crystallite sizes $L$. Dashed line indicates data of Berman, Foster, and Ziman (Ref. 3) on a single crystal of lateral dimension of 1.1 mm.
DIAMOND COATINGS ON SIHON CERAMIC CUTTING TOOLS

Blank wear

\approx 5 \mu m \text{ diamond coating}

AL-390 (16.18% Si)

1500 rpm min. 5x10
0.005"/rev end
0.030" depth

from Bill Durlin
HEAT DIFFUSERS

10 mm  20

1 um

DC plasma torch deposition

Koshino (1988)
[Fujitsu]
- Metal Build-up

- Some Center Wear

- Adhesion Failure

(from Bill Drawl)
### Materials for X-Ray Mask Substrates

<table>
<thead>
<tr>
<th>Material</th>
<th>$\tau_{0.5}$</th>
<th>$k$</th>
<th>$\alpha$</th>
<th>Kn.H</th>
<th>UTS</th>
<th>Y.M.</th>
<th>O.T.</th>
<th>FM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>5.5</td>
<td>1.6</td>
<td>2.3</td>
<td>800</td>
<td>.007</td>
<td>1.3</td>
<td>Poor</td>
<td>1</td>
</tr>
<tr>
<td>$Si_3N_4$</td>
<td>2.3</td>
<td>0.2</td>
<td>1.8</td>
<td>2200</td>
<td>.05</td>
<td>3.36</td>
<td>Good</td>
<td>0.54</td>
</tr>
<tr>
<td>$BaC$</td>
<td>6</td>
<td>4.9</td>
<td>2.9</td>
<td>2750</td>
<td>.0015</td>
<td>3.9</td>
<td>Unk.</td>
<td>2.7</td>
</tr>
<tr>
<td>BN</td>
<td>3.3</td>
<td>0.8</td>
<td>2.9</td>
<td>2500</td>
<td>.10</td>
<td>1.8</td>
<td>Good</td>
<td>5.42</td>
</tr>
<tr>
<td>B</td>
<td>7.5</td>
<td>0.65</td>
<td>4.2</td>
<td>2900</td>
<td>.023</td>
<td>4.5</td>
<td>Unk.</td>
<td>7.6</td>
</tr>
<tr>
<td>SiC</td>
<td>3.6</td>
<td>0.41</td>
<td>2.3</td>
<td>2540</td>
<td>.20</td>
<td>3.8</td>
<td>Good</td>
<td>10.6</td>
</tr>
<tr>
<td>C(Diam.)</td>
<td>3.0</td>
<td>6.55</td>
<td>1.2</td>
<td>8000</td>
<td>.02</td>
<td>11.2</td>
<td>Good</td>
<td>37</td>
</tr>
</tbody>
</table>

* Maximum measured value

$$FM_{max} = \tau_{0.5} \times (k \times \alpha) \times UTS \times Y.M.$$  

$$FM = \frac{FM_{max}}{FM_{Si}}$$

- $\tau_{0.5}$: Thickness for 50% x-ray transmission at 3.33 Å
- $k$: Thermal Conductivity
- $\alpha$: Thermal Expansion
- Kn.H: Knoop Hardness
- UTS: Ultimate Tensile Strength
- Y.M.: Young's Modulus
- O.T.: Relative Optical Transparency
- FM: Figure of Merit

---

From J.R. Maldonado  

---

77
Table I

Comparison of X-Ray Mask Materials Based on Optical Transparency and Mechanical Stiffness Factor

<table>
<thead>
<tr>
<th>Material</th>
<th>$t_0$, thickness</th>
<th>Stiffness Factor $S = t_0E/(1-v)$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[μm]</td>
<td>[GPa-μm]</td>
</tr>
<tr>
<td>Polyimide</td>
<td>&gt; 5</td>
<td>43</td>
</tr>
<tr>
<td>Mylar</td>
<td>&gt; 5</td>
<td>42</td>
</tr>
<tr>
<td>Ti</td>
<td>Opaque</td>
<td>---</td>
</tr>
<tr>
<td>Be</td>
<td>Opaque</td>
<td>---</td>
</tr>
<tr>
<td>Si</td>
<td>1</td>
<td>181</td>
</tr>
<tr>
<td>BN</td>
<td>3</td>
<td>330</td>
</tr>
<tr>
<td>SiO₂</td>
<td>5</td>
<td>444</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>1</td>
<td>448</td>
</tr>
<tr>
<td>Si₃N₄</td>
<td>6</td>
<td>728</td>
</tr>
<tr>
<td>SiC</td>
<td>3</td>
<td>1,590</td>
</tr>
<tr>
<td>Diamond</td>
<td>2</td>
<td>2,340</td>
</tr>
</tbody>
</table>

$t_0$ is the thickness required for 50% transmission at 632.8 nm.

From H. Windischmann (1991)
# Properties of Semiconductive Materials

<table>
<thead>
<tr>
<th>Properties</th>
<th>Diamond</th>
<th>Si</th>
<th>GaAs</th>
<th>SiC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap (eV)</td>
<td>5.5</td>
<td>1.1</td>
<td>1.4</td>
<td>3.0</td>
</tr>
<tr>
<td>Carrier mobility (cm²/V.sec)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electron</td>
<td>1,800</td>
<td>1,500</td>
<td>8,500</td>
<td>400</td>
</tr>
<tr>
<td>Hole</td>
<td>1,600</td>
<td>600</td>
<td>400</td>
<td>50</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>5.5</td>
<td>11.8</td>
<td>10.9</td>
<td>10</td>
</tr>
<tr>
<td>Thermal conductivity (W/cm K)</td>
<td>20</td>
<td>1.5</td>
<td>0.5</td>
<td>5</td>
</tr>
<tr>
<td>Absorption edge (µm)</td>
<td>0.2</td>
<td>1.4</td>
<td>1.1</td>
<td>0.4</td>
</tr>
</tbody>
</table>
Products are beginning to appear which take advantage of diamond's excellent:

- mechanical properties
- thermal properties
- optical properties

Electronic properties/applications seem to be the least developed and have the most commercial potential ⇒ New Japan MITI Program $45M

Companies are continuing to make commitments to manufacturing

Most hard coating companies have significant efforts:
- Sandvik Coromant
- Norton
- Kennametal
- GE
- Mitsubishi Metal
- Sumitomo Electric
- GTE Valenite
- Toshiba Tungaloy
- Asahi Diamond

Joint Ventures:
- GE/Asahi Diamond
- Norton/Sandvik, etc.
- Kennametal/Idemitsu Petrochemical
- Diamonex/Seiko
DIAMOND S&T
PUSH

- Replace HPHT Diamond Powder Manufacture
- Replace PDC's (Polycrystalline Diamond Compacts)
- Replace other Coatings
Diamond S&T
PULL

- **Enabling Technology**
  - Unique Aspects/Properties of CVD Diamond
  - New Specific Applications
  - New Generic Technology Impacts

  *for example:
  Transportation
  - advanced heat engines
  - higher reliability
  - lower friction $\rightarrow$ lower energy
  - decrease pollution
  - economical machining of non-ferrous metals
  - sensors in hostile locations

  Manufacturing
  - low wear
  - low friction
  - higher system reliability
  - better performance
  - better quality

  Energy Production
  etc.

- **Creating New Interest in New/Old Related Materials**
DIAMOND IS AN ENABLING TECHNOLOGY

- X-RAY MASKS MADE OF DIAMOND WILL ENABLE THE PRODUCTION OF LARGER SCALE INTEGRATED CIRCUITS.

- LUBRICATION-FREE DIAMOND BEARING/JOURNAL SURFACES WILL ENABLE USE IN DEMAND ENVIRONMENTS WHERE LUBRICANTS EVAPORATE.

- SOLID STATE MICROWAVE AND MILLIMETER WAVE DIAMOND AMPLIFIERS WILL REPLACE VACUUM TUBE DEVICES (AND THEIR BUILT-IN WEAR-OUT MECHANISMS).

- DIAMOND THERMAL SPREADERS WILL ENABLE COMPUTER CHIPS TO BE PACKAGED 6 TIMES CLOSER TOGETHER WITH COMMENSURATE SPEED, VOLUME AND WEIGHT IMPROVEMENTS.

- DIAMOND AND ITS HIGH ACOUSTIC "Q" WILL ENABLE FAR MORE COMMUNICATIONS/DATA CHANNELS PER UNIT SPECTRUM.

- DIAMOND CUTTING TOOLS WILL ENABLE A MUCH MORE AGGRESSIVE USE OF ALUMINUM IN THE AUTOMOBILE AND RELATED INDUSTRIES.

- DIAMOND OPTICS WILL ENABLE PORTABILITY OF FELs.
STATUS OF PRODUCT DEVELOPMENT

1. ACOUSTIC IN SONY SPEAKERS.

2. DIAMOND COATED CUTTING TOOLS.

3. FUJITSU HEAT SINKS.

4. X-RAY LITHOGRAPHY MASKS.  

5. X-RAY WINDOWS.  

6. GRIT FOR GRINDING WHEELS.  

7. ELECTRONIC PACKAGING.  

8. CORROSION PROTECTION.  

9. FRICTION REDUCTION.  

10. OPTICAL COATINGS AND WINDOWS.
Electronic Devices for Severe Environments such as in Space or in Nuclear Reactors
- Electro-optical devices
- LED
- Microwave Power Devices
- Sensors
- High Speed Electronic Devices

- Sensors for Severe Environments such as in Space and in Nuclear Reactors
  - Thermistor for Automobile Engines
  - X-ray and UV Sensors
  - Heat-resistive Sensors

- High Hole Mobility
- Transparent

- Single-crystalline Films
- Formation of p-n Junction

- Acid Resistant
- Radiation Resistant
- Heat Resistant
- Large Band Gap

- B-doping for p-type Semiconductor
- Formation of n-type Semiconductor

- High Thermal Conductivity
- Electric Insulator

- Uniform Deposition on a large area

- High-rate Deposition

Thin Film Technology
Microfabrication Technology
Microwave Technology

Heat Sinks

Abrasive Coatings

from K. Kobashi
Kobe Steel
CURRENT STATUS
OF
CVD DIAMOND

SCIENCE
- Progress is being made
- Basic and Applied Science needed
  (the more questions answered, the more posed)

TECHNOLOGY
- Companies are beginning to make major and long term commitments
- Products are beginning to appear

GENERAL
- We're in for the long-haul!
CVD Diamond - Fundamental Phenomena

WALTER A. YARBROUGH
Materials Research Laboratory
The Pennsylvania State University
University Park, PA 16802

Department of Energy Workshop
Argonne National Laboratory
4-5 February 1992
Graphite/Diamond Equilibrium

\[ dG = Vdp - SdT \]

\[ \left( \frac{\partial(\Delta G)}{\partial p} \right)_T = \Delta V \]

\[ \left( \frac{\partial(\Delta G)}{\partial T} \right)_p = -\Delta S \]

For diamond:
\[ \bar{V} = 3.42 \text{ cm}^3 \text{ mol}^{-1} \]
\[ \bar{S} = 2.38 \text{ J mol}^{-1} \text{ K}^{-1} \]

For graphite:
\[ \bar{V} = 5.34 \text{ cm}^3 \text{ mol}^{-1} \]
\[ \bar{S} = 5.74 \text{ J mol}^{-1} \text{ K}^{-1} \]

Hot Filament Assisted CVD

~ 1% CH\textsubscript{4} in H\textsubscript{2}
~25 Torr

~2,000° C refractory metal (Ta, W, Re) wire(s)

Mounting and power supply

Substrate
~700 to 1000° C
Combustion Synthesis of Diamond

Various "zones" in an oxyacetylene brazing torch (~1:1 O/C or less)

1. Transparent, colorless. Preheat zone. Premixed gas at high velocity is heated to combustion.

2. Bright incandescent white. Primary combustion. Premixed acetylene and oxygen burns to produce primarily CO and H₂. Adiabatic combustion temperature (1:1 C₂H₂ - O₂) 3300 K. Much H₂ expected to be atomic. Diamond growth observed here.


Substrate, ~700 to 1100 K
Deposition of Diamond from Fluorocarbons

tube furnace

long substrate (copper, nickel, monel, etc.)

850°C

~250°C

Diamond

Diamond

SOOT
Observations

* Diamond can be grown without hydrogen

\[ \text{CS}_2 + 6 \text{F}_2 \rightarrow \text{C}_{(\text{dia})} + 2\text{SF}_6 \]

* Methane, fluorine, hydrogen mixtures work.

* Some oxygen important - best results with alcohols, ketones, etc.

* Carbon furnace best - less metal halide.

* Temperature control in hot zone important

* Temperature gradient may be important
Why Diamond?
(and not graphite, or lonsdaleite, or glassy carbon, or cliftonite, etc.)

Critical Observations

Diamond can be grown on diamond by simple hydrocarbon decomposition, i.e. without atomic hydrogen.

BUT only in small amounts - graphite nucleates eventually - then graphite growth dominates.


if diamond and graphite both are present in "excess" atomic hydrogen: graphite decreases - diamond increases. Diamond is nucleated and grown on graphite.

**Competitive Growth Model**

Graphite is "etched" or gasified faster than diamond, hence diamond persists.


If equilibrium calculations are modified to include an enhanced etching of graphite by atomic hydrogen then the first solid obtained is diamond.

What is the synthetic Paradigm?

Reacting gas phase

--- DLC ---
Diamond Graphite

Bridgman, Eversole, etc.

$C_xH_y \rightarrow xC + H_y/2$ \hspace{1cm} $\Delta G < 0$

$\Delta G \ll 0$

$C_d \rightarrow C_g$

$G_2$

$G_1$

$G_0$

Simultaneous gasification of graphite and deposition of diamond appears to violate second law.
Growth Surface Stabilization:

**Stabilization by Hydrogen -**

Hydrogenated diamond surface is stable relative to hydrogenated graphite.

Atomic hydrogen maintains surface hydrogenation at high temperature and low pressure.


At thermostatic equilibrium: For filament at 2000°C (50 Torr):
\[
\log [H^0] = -6.78 \quad \text{Graphite is predicted}
\]
\[
\log [H^0] = -2.68 \quad \text{Diamond is predicted}
\]

Graphitic defects and twinning/stacking faults (polytypes or diamond - lonsdaleite crystalline solutions) possible.

Surface temperature:
\(~1000^\circ\text{C}\)
Hydrogenated, Unreconstructed (111) Surface of Diamond
Hydrogenated, Unreconstructed (110) Surface of Diamond
Hydrogenated, Unreconstructed (100) Surface

Using Lennard-Jones Potentials with \( A = 31.4 \, \text{Å}^6 \) and \( B = 2.97 \times 10^3 \, \text{Å}^{12} \) kcal/mole, \( \Delta H \approx 0.7 \times 10^4 \) kcal/mole!

Simple hydrocarbon (cyclooctane) model, \( \Delta H \approx 2.5 \) kcal/mole

Molecular mechanical modeling, \( \Delta H \approx 40 \) kcal/mole

(Yang and D'Evelyn, 1991)

Hydrogenated, Reconstructed (100) Surface of Diamond

\[
\begin{align*}
H\cdot C\cdot C^\cdot H + H &\rightarrow H\cdot C\cdot C^\cdot + H_2 \\
H\cdot C\cdot C + CH_3 &\rightarrow H\cdot C\cdot C^\cdot CH_3 \\
H\cdot C\cdot C^\cdot CH_3 + H &\rightarrow H\cdot C\cdot C^\cdot CH_2^\cdot + H_2 \\
H\cdot C\cdot C^\cdot CH_2 &\rightarrow H\cdot C\cdot C^\cdot CH_2 \\
\end{align*}
\]

B. Garrison (Penn State) \\
& D. Brenner (NRL) 1991
A Methyl Radical Mechanism

Gas Phase Activation

\[ \text{H}_2 \rightarrow \text{H}^\circ \+ \text{H}^\circ \]  \hspace{2cm} (1)

\[ \text{CH}_4 \+ \text{H}^\circ \rightarrow \text{CH}_3^\circ \+ \text{H}_2 \]  \hspace{2cm} (2)

Surface Activation

\[ \text{C}_{(s)} \text{H} \+ \text{H}^\circ \rightarrow \text{C}_{(s)}^\circ \+ \text{H}_2 \]  \hspace{2cm} (3a)

\[ 2 \text{C}_{(s)} \text{H} \rightarrow 2 \text{C}_{(s)}^\circ \+ \text{H}_2 \]  \hspace{2cm} (3b)

Addition

\[ \text{C}_{(s)}^\circ \+ \text{CH}_3^\circ \rightarrow \text{C}_{(s)} \text{CH}_3 \]  \hspace{2cm} (4)

Incorporation

\[ \text{C}_{(s)} \text{CH}_2^\circ \+ \text{C}_{(s)} \text{CH}_2^\circ \rightarrow \text{C}_{(s)} \text{CH}_2 \text{CH}_2 \text{C}_{(s)} \]  \hspace{2cm} (5)

\[ \text{C}_{(s)} \text{CH}_2^\circ \+ \text{C}_{(s)}^\circ \rightarrow \text{C}_{(s)} \text{CH}_2 \text{C}_{(s)} \]  \hspace{2cm} (6)
Unresolved Questions

Kinetic modeling, to date, treats diamond surface as large hydrocarbon. How good is this assumption?

\[ 2 \text{C}_{(s)}\text{H} \leftrightarrow 2 \text{C}_{(s)}\cdot + \text{H}_2 \]

Is it possible? important?

For simple hydrocarbons - not likely - forbidden by orbital symmetry rules, hence

\[ \text{C}_2\text{H}_4 + \text{H}_2 \leftrightarrow \text{C}_2\text{H}_6 \]

does not happen.

Do reactive sites (radicals?) diffuse on the diamond surface?

Can carbon species (\(\text{R-CH}_3\), \(\text{R=CH}_2\), etc.) diffuse on diamond?
Dissociative chemisorption of $\text{H}_2$ on diamond is known at low temperature.


(111) diamond surface loses hydrogen at low pressure and high temperature.

If associative desorption does not happen - what is the mechanism?
Polishing to enhance diamond nucleation

Post polished with c-BN

Light diamond nucleation

Polished with diamond

Heavy diamond nucleation

Image 10KU 22.7X 1000U 0117 8-4
Nucleation of Diamond on Graphite

[Diagram showing crystallographic planes and orientations related to diamond and graphite phases, including [111], [100], and [110] planes.]
Y. SATO, C. HATA and M. KAMO, "Formation and Structural Features of Needle-like Diamond"

from Y. Sato (NIRIM)

1st International Symp. New Diamond Science & Technology
Tokyo, Japan Oct. 24-26, 1988
Modeling of Texture Development in Polycrystalline Films

A schematic illustrating the uniaxial growth of polycrystalline layers. Nucleation occurs at discrete sites on the substrate and these nuclei may be randomly oriented with respect to their crystallographic axes as illustrated in (b) above. As growth continues, those crystals which are favorably oriented, i.e. have their dominant growth axis aligned more or less normal to the substrate, will begin to dominate and upon continued growth the film or layer will begin to exhibit this crystallographic texture. Impurities and voids may be intergranularly entrained, the shaded regions in (a), leading to greater perfection with continued growth.
Possibility for a vicinal <100> Texture

axis orthogonal to the plane of the coating.

For vicinal <100> texture see:
E.D. Sprecht, R.E. C'Causing and L. Heatherly
Requirement for Elastic Isotropy in Cubic Materials

\[
\frac{2c_{44}}{c_{11} - c_{12}} = 1
\]

*Values for diamond*


\[c_{11} = 10.76, \ c_{12} = 1.25, \ c_{44} = 5.77 \times 10^{11} \text{ Nm}^{-2}\]

or

\[
\frac{2c_{44}}{c_{11} - c_{12}} = 1.21 \text{ for diamond}
\]

Conclusion: Diamond is elastically anisotropic.
Table 1 Deposition condition of diamond films.

<table>
<thead>
<tr>
<th>Method</th>
<th>Microwave Plasma CVD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction gas</td>
<td>CH₄ + H₂</td>
</tr>
<tr>
<td>CH₄ concentration(CH₄/H₂)</td>
<td>0.1~3.0 vol%</td>
</tr>
<tr>
<td>Total gas pressure</td>
<td>4 kPa</td>
</tr>
<tr>
<td>Flow rate</td>
<td>3000 SCCM</td>
</tr>
<tr>
<td>Microwave power(2.45GHz)</td>
<td>500W</td>
</tr>
<tr>
<td>Temperature(on sub.)</td>
<td>~600°C</td>
</tr>
<tr>
<td>Substrate</td>
<td>Si(100)</td>
</tr>
<tr>
<td>Substrate dimensions</td>
<td>30 X 5 X 0.6mm</td>
</tr>
<tr>
<td>Thickness of diamond films</td>
<td>7~30 μm</td>
</tr>
</tbody>
</table>

Fig. 4 Schematic diagram for synthesis equipment of microwave plasma CVD method. ① magnetron (2.45 GHz), ② wave guide, ③ plunger, ④ quartz tube, ⑤ sleeve, ⑥ substrate.

Fig. 5 Thermal conductivity of diamond films for different methane concentrations.

Fig. 6 Raman spectra of diamond films for different methane concentrations.

Chip Carrier Possibilities

CVD diamond layer

Signal and Power plane structure

Flip chip solder bump structure

Pin Grid Array

Free standing, patterned CVD diamond slab

Hermetically sealed chip carriers with diamond lids

Notes:

1. Thermal "grease" at chip and carrier or carrier and board levels - expansion mismatch no problem.

2. Signal/power plane structure/materials optimized for expansion and permittivity at carrier and board levels. No need to consider $\kappa_T$.

3. Uniform operating temperature - reduced connection fatigue.
Brazed Diamond Cutting Tool and its performance

Asahi Industrial Diamond Co., Ltd.
Osaka, Japan

Future Possibilities

- Composite designs, e.g. consider cubic boron nitride under compressive stress.

- Passivation of diamond surface.
  - Oxidation resistance
  - Graphitization/reaction/dissolution

- "Classical" CVD a possibility
  - Methyl fluoride work confirmed
Comparative Evaluation  
of CVD Diamond Technologies

Thomas R. Anthony  
General Electric Corporate Research & Development Center  
River Road, Schenectady, New York, 12309, USA

Abstract  

Chemical vapor deposition (CVD) of diamonds occurs from hydrogen-hydrocarbon gas mixtures in the presence of atomic hydrogen at subatmospheric pressures. Most CVD methods are based on different means of generating and transporting atomic hydrogen in a particular system. Evaluation of these different techniques involves their capital costs, material costs, energy costs, labor costs and the type and quality of diamond that they produce. Currently, there is no universal agreement on which is the best technique and technique selection has been largely driven by the professional background of the user as well as the particular application of interest.
Comparative Evaluation of CVD Diamond Technologies

Thomas R. Anthony
General Electric Corporate Research & Development Center
River Road, Schenectady, New York, 12309, USA

Ia CRITERIA FOR EVALUATION

Four different factors should be considered in evaluating a process for the low-pressure deposition of diamond. The first factor is the basic process potential. This potential includes the maximum rate of diamond growth, the ability to deposit on flat surfaces as well as three-dimensional surfaces, the maximum area or volume of deposition, the maximum diamond thickness achievable, the uniformity of the deposition and the adaptability of the process to manufacturing. The latter criterion includes the process "ruggedness", its reproducibility from run to run and its technical sophistication.

Once a process satisfies the basic process potential, the costs of the process must be calculated. These costs include the capital cost based either on the physical life of the equipment or, more realistically at this point in diamond research, on the time to technological obsolescence. A second cost is the energy costs to run the process. Energy costs put most CVD processes above a dollar per carat and eliminate many of the applications described in the popular press. Another cost is labor. This cost tends to be low with simple processes and high with technically sophisticated processes. Cost for consumable materials such as gases, electrodes and filaments vary considerably from process to process. Some high-rate diamond deposition processes fail this criterion. Finally, the research and development costs must be amortized in the product costs or the organization spending these startup costs will fail. Certain processes
that require large amounts of R&D spending to launch are really uneconomical. However, if these costs are covered by a third party, ie the government, who is not subject to the discipline of the market place, these costs can be ignored.

The third general set of criteria that must be considered are application dependent criteria. These include: 1) the deposition temperature, eg, coating plastic with diamond requires a very low deposition temperature; 2) the required substrate composition, eg, coating stellite valves that contain cobalt that catalyzes the conversion of diamond to graphite necessitates operating under special conditions that not every process is capable of; 3) substrate cooling, eg, most high-deposition rate processes require forced water cooling of the substrate which is not possible with some applications; 4) substrate size and shape, eg, this may not be compatible with a particular process; 5) high adhesive bonding strength of diamond to substrate, eg, some processes are better at making a good bond with the substrate than others; 6) low adhesive bonding strength of diamond to the substrate, eg, some applications require free-standing diamond films where a low adhesive bonding strength to the substrate is needed to remove the diamond from the substrate without damaging it.

The last set of general criteria is the diamond quality produced by a particular process. Diamond quality includes its toughness, wear resistance, electrical breakdown strength, electrical resistivity, transparency to IR and visible light, thermal conductivity, grain size, grain size distribution, preferred grain orientation and the intrinsic stress grown into the film. End users may have demanding specifications that were not anticipated when a process was being developed and that are not achievable by the process. Diamond quality will gradually emerge as the principal arbiter of the "best process" in the coming years.

The selection of the best deposition method is a difficult, time-consuming, expensive and semi-empirical process. Currently, many of the questions arising from the above criteria are unanswerable from information in the public literature and choices must be based on intuition and best guesses. In the following discussion, we can only begin to examine the selection problem.
Ib. BRIEF HISTORY OF LOW-PRESSURE DIAMOND SYNTHESIS

For many years the metastable growth rate of diamond at low pressures was very small and diamond substrates were required to obtain any diamond at all. These processes were of scientific interest only because the cost of diamond produced by them greatly exceeded the cost of either natural diamond or synthetic diamond formed at high pressures. Most low-pressure methods stemmed from the work of Eversole[1] who alternatively exposed diamond substrates to a hydrocarbon gas and then hydrogen at high temperatures and low pressures[1-3]. Under these conditions, the hydrocarbon was pyrolyzed to form a mixture of diamond and graphite and then hydrogen was used to etch the graphite away. This cycle (Reactions 1 and 2) was repeated over and over again until the diamond deposit grew to the desired thickness.

\[
\text{Heat} \\
\text{CH}_4 \rightarrow \text{Deposit (Diamond & Graphite)} + 2\text{H}_2 \quad (1)
\]

\[
\text{Heat} \\
\text{H}_2 + \text{Deposit} \rightarrow \text{Diamond} + \text{CH}_4 \quad (2).
\]

In the late 1970's, an important invention changed this cyclic CVD (Chemical Vapor Deposition) process to a continuous one., increased the diamond growth rate by orders of magnitude, eliminated the need for diamond substrates and made the process technologically significant[4]. This new process[5] is shown in Reaction 3.

\[
\text{Heat & Atomic Hydrogen} \\
\text{CH}_4 \rightarrow \text{Diamond} + 2\text{H}_2 \quad (3)
\]

The key idea was the addition of atomic hydrogen to the reaction by Boris Spitsyn and his coworkers[5] following a suggestion by Prof John Angus of Case Western Reserve. Atomic hydrogen has many important roles in CVD diamond growth. These roles have been recently summarized and will not be covered here[6]. A large number of CVD methods based on the process of Reaction 3 have been developed over the last decade. Most methods are basically
just different ways of generating[7] the atomic hydrogen required in Reaction 3.

II CVD DIAMOND DEPOSITION PROCESSES

IIA HOT FILAMENT PROCESS

Langmuir first reported the dissociation of molecular hydrogen on a hot tungsten filament in the early 1900's [8-11]. This method has also been used to make atomic hydrogen in CVD diamond growth. Typically, a hot filament is heated to a temperature range of 1950-2300 Centigrade in the presence of molecular hydrogen and 1-2% hydrocarbon [11-13] as shown in Fig 1. The molecular hydrogen adsorbs on the surface of the metal filament and dissociates into two atomic hydrogens that subsequently pass back into the surrounding gas (Fig 2).

\[ \text{H}_2 \rightarrow 2 \text{H} ; \quad \Delta H = +104,000 \text{ kcal/mole} \quad (4) \]

In addition, many other reactions[14,15] take place on the filament involving the hydrocarbon. The concentration of atomic hydrogen and other hydrocarbon species around the filament have been directly measured[16,17]. A general conclusion of these experiments is that thermodynamic equilibrium calculations give a reasonable guide to the type and number of species that are actually present. The rate of deposition is dependent only on the carbon concentration in the gas and is independent of the type of hydrocarbon gas used.

There are some constraints on the electrically conductive refractory materials that can be used for atomic-hydrogen filaments. First, the melting point of the material must be higher than the operating temperature of the filament. Secondly, the binary eutectic temperature of carbon and the filament material must exceed the filament operating temperature to prevent the melting and breakage of the filament. This later requirement makes molybdenum filaments marginal since a hot spot on a Mo filament may take it above the Mo-C eutectic temperature of 2200 C and cause the filament to melt and fail before the Mo filament is fully carburized.

While a carbon filament satisfies the melting-point and eutectic-point requirements, it does not produce CVD diamond
because atomic hydrogen that forms on a carbon filament reacts with the carbon and releases a hydrocarbon species into the gas rather than atomic hydrogen. Without atomic hydrogen at the substrate, graphite is deposited instead of diamond. The failure of carbon filaments to produce diamond[18] suggests that the atomic hydrogen does not form in the hot gas surrounding the filament but actually forms on the filament surface[9-11] where it can react with the filament material.

Of the remaining electrically conductive refractory materials, tungsten, tantalum and rhenium have been used to produce CVD diamond. Rhenium is usually not considered because it is 100 times as expensive as tantalum or tungsten. Both tantalum and tungsten react with the hydrocarbon in the gas to form carbides. Thus, the tungsten and tantalum filaments quoted in the literature are really tungsten carbide and tantalum carbide filaments. It is interesting to note that W₂C is a commonly used catalyst material in gaseous hydrocarbon chemistry. However, experiments that have compared the difference in diamond growth rates between tungsten or tantalum carbide filaments show no special catalytic effect for tungsten carbide[19]. Of course, the rate of diamond growth may not be controlled by the production of atomic hydrogen or carbon radicals on the filament surface but may instead be limited by some other process. Filament carburization can have a catalytic effect on the diamond nucleation rate by increasing the electron emission from the filament because of the lower work function of the carbide[20]. Electron bombardment of the substrate is known to increase the diamond nucleation rate.

Carburization is a two stage process with M₂C forming first followed by MC where M is one of the refractory metals(Fig 3). Under typical hot-filament CVD diamond growth, M₂C forms in all cases. However, MC does not always form because the activity coefficient of carbon is too small[21] under some conditions of CVD diamond growth. Since the carbides of tantalum and tungsten have a molar volume that is 40-70% larger than the molar volume of the metal from which they were formed, the filaments swell, crack, bend, distort and embrittle as inward radial carburization proceeds. Because carburization occurs most rapidly along grain boundaries where carbon mobility is the highest, cracking usually follows the grain boundary patterns of the original metal filament. Carburization significantly decreases the grain size of the wire. This reduction in grain size can lead to superplastic deformation under some some
conditions. Carburization and cracking increase the electrical resistance of the filament[20] so the current and voltage must be monitored and changed to keep a constant filament temperature. To avoid filament carburization, Aikyo and Kondo introduced the hydrocarbon downstream from the hot filament[22]. Diamond was successfully deposited and the filament life and the quality of the diamond film was improved. Unfortunately, the diamond deposition rate was decreased.

A disadvantage of the filament process is that a filament is a remote source of atomic hydrogen. During the transport of atomic hydrogen from the filament to the substrate, a considerable fraction is lost through trimolecular collision between two atomic hydrogens and a third gas molecule[23]:

\[ \text{H + H + M } \rightarrow \text{H}_2 + \text{M} \]  

(5)

where \( \text{H} \) is atomic hydrogen and \( \text{M} \) represents a gas molecule or the walls of the reactor.

Associated with Reaction (5) is a recombination length, \( L_r \), which gives the average distance that an atomic hydrogen travels before it recombines in a trimolecular collision. For typical filament-method process conditions of \( T = 1500 \text{ K} \) and \( P = 10 \text{ torr} \), the recombination length \( L_r \) is 13 cm[24]. Matsumoto and coworkers[12] in the original filament paper found that the filament-substrate separation must be less than 3 centimeters to get diamond growth.

The loss of hydrogen by recombination can be decreased by reducing the filament-substrate separation distance. Hirose used tiny filaments that were very close (<1 mm) to the substrate as well as oxygen additions to attain growth rates of 10 microns/hr which is 10 times the usual diamond growth rate for the filament process[25]. Presumably, the small separation between filament and substrate decreased the loss of atomic hydrogen and other active hydrocarbon species.

The quality of diamond produced by the filament technique can vary widely. Problems with contamination of the diamond films by filament material can affect electronic and thermal properties[26]. Also, filaments as discussed above are in effect point sources of atomic hydrogen and heat and the diamond films produced under a
filament or filaments will reflect this nonuniformity. The thickness, grain size and quality of a diamond film produced by a filament system will vary from place to place. Finally, because of a finite filament life, the maximum thickness of a diamond film that can be produced by the filament technique is limited. The construction costs of a filament system are relatively low as it can be built with readily available simple equipment. However, because of the low diamond growth rate with a filament system, the capital costs per unit of diamond produced are in the midrange of the various CVD techniques. Because of the simplicity of a filament system, its labor costs are relatively low as it does not require highly-trained personnel to operate it. Its operating costs as far as gas consumption and energy consumption are moderate.

IIB HOT FILAMENT EACVD

The hot filament process has been modified by some investigators to include a positive or negative bias between the hot filament and the substrate[27] (Fig 4). The process has been named hot-filament EACVD (electron-assisted chemical vapor deposition). The applied bias has been reported to cause changes in the nucleation rate, the growth rate and the crystal quality of the deposited CVD diamond. A general remark that must be made here is that all filament processes have an EACVD character. Consider a filament with a current passing through it. One end of the filament is at ground potential and the other end is at some applied voltage that is needed to drive the current through the filament. If the substrate is at ground potential, then the entire filament is biased with respect to the substrate except for the very end of the filament at ground potential. If EACVD had a large effect on CVD diamond growth, one would see a change in diamond growth along the substrate parallel to the filament. The lack of such reports in the literature imply that EACVD effects are not striking.

Generally, an increase in the nucleation and growth rate of the deposited diamond has been reported if the filament is held at a negative bias with respect to the substrate. Alternatively, if the filament is held at a positive bias with respect to the substrate, the diamond nucleation and growth rate decrease while the diamond crystal quality increases [28,29] In both cases, the bias potential must be kept below the breakdown point of the gases since the formation of a plasma seems to erase these favorable effects. There
has been some confusion in the literature because some researchers heat their filaments with AC and others heat their filaments with DC. Identical filament-substrate biases with AC and DC heated filaments, respectively, can cause very different results on CVD diamond growth. Six separate cases should be documented: 1) AC heating, positive DC bias; 2) AC heating, negative DC bias; 3) DC heating, positive DC bias; 4) DC heating, negative DC bias; 5) AC heating, AC bias; 6) DC heating, AC bias.

The negative effects[28] of plasma formation in hot-filament EACVD is somewhat surprising since the next section will show that plasmas have been effectively used for CVD diamond deposition. This contradictory evidence is not uncommon in CVD diamond deposition. Generally, it is not the result of erroneous experiments. Rather there are dozens of independent parameters in an experiment and changing one parameter unavoidably changes other parameters and makes a clear interpretation of the data difficult. As an example, let us list some of the important parameters in a simple process such as hot-filament EACVD: 1). Filament composition; 2). Filament temperature; 3). Filament size and geometry, ie, wire, strip, mesh, etc; 4). Substrate composition; 5). Substrate temperature; 6). Substrate geometry; 7). Filament-to-substrate distance; 8). Gas pressure; 9). Gas temperature; 10) Gas flow rate; 11). Gas flow geometry; 12). Gas temperature gradient above substrate; 13). Gas temperature gradient near filament; 14. Hydrocarbon concentration in gas; 16). Impurity concentration in gas, ie, oxygen, water, nitrogen; 17). Filament-to-Substrate bias: positive, negative, AC; 18). Filament-to-Substrate current;19) Filament Heating: AC or DC

If an experimenter changes the filament-to-substrate bias, he will also change the gas temperature, the substrate temperature, the temperature gradient in the gas, the filament temperature and the filament-to-substrate current. He may then report an increase of growth rate with increasing bias that may be just an increase in growth rate arising from an increase in substrate temperature rather than a new filament-to-substrate bias effect. Banholzer has, in fact, recently carried out a very careful study investigating reports that EACVD increases the CVD diamond growth rate[30]. He finds that there is no such effect when he keeps the filament and substrate temperature constant as he applies a filament-substrate bias. What previous investigators were seeing were effects caused by an increased filament temperature and/or an increased substrate temperature when the EACVD bias was turned on. Banholzer,
however, did see an increased nucleation density of diamond with a negative bias applied to a DC heated filament.

Much of what was said about the cost of a filament system could be repeated here for a hot-filament EACVD system. A hot-filament EACVD system will cost more than a filament system. In most cases, a more costly DC power supply must be substituted for an AC power supply. Also a separate DC bias supply must also be provided. Biasing can decrease filament life by causing unwanted electric arcs or plasma discharges which physically erode the filament. Contamination of the growing diamond film is more of a problem because of the chance of bias sputtering of the filament, reactor wall or substrate material into the diamond film. Finally, the added complication of biasing inevitably reduces the percentage of successful runs.

IIIC. PLASMAS

Another popular method to generate atomic hydrogen is with gas plasmas. Plasmas can be formed by many methods. Typically, a gas is ionized by exposure to high temperatures or high electric fields to form a neutral mixture of electrons, negative ions and positive ions. In plasmas exposed to high AC electric fields, hydrogen dissociation occurs by electron impact. Although the dissociation energy of hydrogen is only 4.5 ev, the electron impact dissociation of hydrogen requires electrons with energies above 9.5 ev because of the large mass difference between the electron and a hydrogen molecule (Fig 5). Such hydrogen dissociation by electrons reaches a peak at electron energies of 25 ev. Atomic hydrogen with a very high kinetic energy is consequently produced in plasmas since the difference between the dissociation energy and the electron impact energy must be taken up by the kinetic energy of the atomic hydrogen. This situation contrasts with thermal methods of generating atomic hydrogen where low kinetic energy atomic hydrogen is formed since a direct transfer of thermal energy breaks the hydrogen molecule apart without imparting additional excess energy that would appear as the kinetic energy of the atomic hydrogen product.

The typical charge density in a plasma is very low(Fig 6). Most molecules remain as molecules which are not reactive and do not take part in CVD diamond deposition. About 1% of the molecules in a plasma are converted to neutral radicals that are chemically reactive
molecules with a dangling unsatisfied bond. These radicals are the main component of the gas that is active in CVD deposition. Finally, about 0.01% of the molecules in a plasma are ions. Like radicals, these ions are chemically reactive and can take part in CVD diamond deposition. However, the extremely small concentration of ions indicates that they are not the important depositing species in diamond deposition. Although charged ions have a very low concentration and are not the principal depositing species during CVD deposition, it is possible that they may have some catalytic effects.

Plasmas can be conveniently divided into low-pressure and high-pressure plasmas (Fig 5). At low pressures in a gas excited by an alternating electric field, the electrons and molecules are not in thermal equilibrium. Although electrons and molecular ions have the same charge, the mass of the molecular ion is typically 40,000 times that of an electron. Hence, the electron can accelerate rapidly in an alternating electric field and gain energy while the ion is too massive to accelerate quickly and lags behind the electron in energy gain from the alternating electric field. If the mean-free path for collisions between electrons and molecules is large as in a low pressure gas, there will not be a redistribution of energy between the high energy electrons and the slowly moving molecules and they will have different temperatures. As a result, a low-pressure plasma typically has a relatively cool gas temperature. Generation of atomic hydrogen and reactive molecular radicals will be accomplished principally by collisions with high energy electrons. As a consequence of the scarcity of electrons in the plasma and the large mean free path path for collision with gas molecules, the absolute concentration of atomic hydrogen and molecular radicals will be low in a low pressure plasma.

In high pressure plasmas on the other hand, the mean free path for collisions between electrons and molecules will be small and any excess energy absorbed by the electrons from the electric field will be quickly redistributed to the more massive molecules by electron-molecule collisions. Hence, the temperature of the gas molecules and electrons will equilibrate at a relatively high temperature. Generation of atomic hydrogen and molecular radicals can now occur as the result of either high-energy molecular or electron collisions in the plasma. Thus, the absolute concentration of atomic hydrogen and molecular radicals will be high in a high-pressure plasma.
Because of the higher concentration of atomic hydrogen and hydrocarbon radicals in a high-pressure plasma, the CVD diamond growth rate will be greater in a high-pressure plasma than in a low-pressure plasma. Such a correlation is observed experimentally where CVD diamond deposition rates in a high-pressure plasma are typically 500 microns/hour whereas the deposition rate in low-pressure plasmas are 0.2 microns/hour.

If the growth rate was the only parameter of interest in diamond deposition, low-pressure plasmas would be ignored. However, high-pressure plasmas have a very high energy content which necessitates elaborate cooling schemes for the substrate to prevent substrate melting. Furthermore, high pressure plasmas tend to be unstable and difficult to control. For many applications, these problems rule out the use of high-pressure plasmas.

IIC1. Low-Pressure Glow Discharge

A common low-pressure plasma method of atomic hydrogen generation is based on the Wood's Tube method[31] where a stream of low-pressure molecular hydrogen is passed through a glow discharge between two metal electrodes (Fig 7). Over a pressure range of 0.1 to 20 torr, up to 25% atomic hydrogen can be generated by this method. The substrate is placed in this glow discharge or one electrode serves as the substrate so that atomic hydrogen is generated close to the substrate surface. Although AC or DC can be used to form the discharge, DC is advantageous if an electrode is used as a substrate since diamond growth rates are higher on the positive electrode. This method has been used to produce very fine-grain CVD diamond films by Crystallume of Palo Alto, California for such applications as diamond windows. Disadvantages of this process include the limited pressure range of operation, the erosion of and contamination from the electrodes and the generally high film stress, the high hydrogen content in the resulting diamond films and the low rate of diamond film growth. Construction costs for a low-pressure glow-discharge system are moderate. However, because of the very low diamond growth rates, the capital costs are relatively high per unit of diamond produced. Labor costs are low as it is a simple stable system that can be run for long periods without operator intervention. Material costs such as gas and electricity are also low.
IIC2. Low-Pressure Microwave Discharge

Low-pressure microwave discharges have been used more than any other method to generate atomic hydrogen for CVD diamond synthesis (Fig 8) [32-52]. Since microwave discharges are electrodeless, electrode erosion problems are avoided. Microwave discharges are also very stable and provide up to 25% H atoms under typical CVD diamond growth conditions[7]. Moreover, microwave sources are very economical because of the mass production of microwave sources for microwave ovens. During CVD diamond deposition, the plasma must not contact the walls of the reactor since diamond and/or graphite can deposit on the walls. This carbon deposit will couple with the microwaves and heat up causing more deposition and the walls of the reactor (usually quartz) will gradually become opaque to microwaves. Under other operating conditions, the plasma can seriously erode the reactor walls by atomic-hydrogen reduction of the quartz. These problems can be avoided by magnetic confinement of the plasma.

A common magnetic confinement method uses an axial magnetic field in a cylindrical cavity with a microwave window and substrate, respectively, on opposite ends of the cylindrical cavity[32,36,50]. A gradient in the axial field is adjusted so electron-cyclotron-resonance (ECR) conditions exist near the substrate end of the cavity but not near the microwave window (Fig 9). Circularly polarized microwave electric fields drive free electrons in circular orbits around the axial field lines. Near the substrate, the ECR resonance conditions allow the electrons to receive resonance impulses during each orbit so these electrons acquire a higher energy than electrons elsewhere in the cavity. Thus, the plasma forms preferentially in the region of these high energy electrons adjacent to the substrate. No plasma forms at the microwave window at the opposite end of the cavity where ECR conditions do not exist and electrons do not receive the added boost in energy. Hence, the microwave window is kept free of carbon deposits or erosion. An interesting observation in ECR experiments is that as the chamber pressure is lowered, the substrate temperature for diamond formation tends to decrease[32].

Similar to the work of Aikyo and Kondo for hot filaments[22], Martin and Hill have introduced the hydrocarbon downstream from a microwave plasma hydrogen discharge and successfully grown
These experiments again demonstrate that the only necessary condition for CVD diamond growth is a source of atomic hydrogen. Much work has been done on the morphology of films grown in microwave discharges under varying conditions[41-43,46,48]. Low substrate temperatures and low hydrocarbon concentrations favor the development of (111) facets on the diamond crystals, indicating that the <111> direction is the slowest growth direction under these conditions. High substrate temperatures and high hydrocarbon concentrations favor the development of (100) faces showing the <100> direction is the slow growth direction. At intermediate hydrocarbon concentrations and temperatures, (110) facets will develop.

The lowest temperatures (365-500 C) for CVD diamond deposition have been reported for microwave plasma deposition techniques[40,51]. Additions of oxygen carrying species such as alcohols, water, etc can increase the diamond film growth rate or lower the pressure necessary for diamond growth[33,40,44,45,49]. Lower gas pressures are particularly important as they allow the plasma to spread and make a more uniform deposit over a wider area[33,50]. The electromagnetic waves used in microwave discharges are launched into the deposition chamber from outside sources. The penetration length of these waves into a low pressure chamber varies inversely with the intrinsic plasma frequency of the gas[53]. The plasma frequency, in turn, is directly proportional to the square root of the gas pressure. Consequently, lowering the gas pressure will result in a greater penetration length and a more uniform discharge. For a pressure of about 10 torr, the penetration length of microwaves in a plasma discharge is only a few centimeters[54].

The quality of diamond produced by the microwave technique can vary widely. If the plasma is in contact with the walls or substrate of the reactor, the diamond film can become contaminated with this material. Because of the exponential decay of microwaves into a plasma, nonuniformities can develop in plasmas larger than the microwave plasma penetration length and the diamond films produced under such a nonuniform plasma will reflect this nonuniformity with the thickness, grain size and quality of a diamond film varying from place to place. The microwave penetration length also puts a limit on the maximum size of a diamond film that can be grown under a microwave discharge. The maximum thickness of a diamond film that can be produced by the
microwave technique is limited by the surprisingly low (in view of the high atomic hydrogen concentration) diamond growth rate of microwave reactors. The construction costs of a microwave system are moderate because of the widespread availability of microwave magnetrons. However, because of the low diamond growth rate with a microwave system, the capital costs per unit of diamond produced is in the higher range of the various CVD techniques. The microwave system has a low energy consumption because most of its energy goes into producing atomic hydrogen rather than heat or radiation. Its operating costs as far as gas consumption are also low. Finally, microwave discharges are easy to use and are very stable and can be run for long periods without much attention. Therefore, labor costs for a microwave system are expected to be low.

IIC2. Remote Low-Pressure Microwave Discharge

One way to avoid the microwave penetration length limit on the size of the microwave reactor is to generate atomic hydrogen by a microwave discharge in a small volume with dimensions less than the microwave penetration length and then to quickly distribute this atomic hydrogen to a much larger-area substrate by convective gas flow. This method requires very high gas velocities on the order of 10,000 cm/sec in order to transfer the atomic hydrogen from its remote source to the substrate before the atomic hydrogen can recombine[ 55]. As a result, the process uses such a large quantity of gases that the process is uneconomical unless the gases are recirculated. Gases must not only be recirculated but their composition must be constantly adjusted. In addition, it may be necessary to remove some gas products produced in the microwave discharge if they build up in a recirculating system and tend to poison the diamond growth process. Currently, Astec Corp of Woburn, Mass is designing and building a CVD diamond machine of this type complete with a gas recirculating system, all of which should be commercially available in 1992-93 time frame. The advantages of a remote discharge system with its larger area of deposition will have to be balanced against the complications and costs of the required gas recirculating system. Labor costs and energy costs are both expected to be higher than with a simple microwave discharge system. The cost per unit area of diamond films will probably be higher with this reactor but the films will be
more uniform, possibly of higher quality and much larger in area than they could be with a simple microwave system. Consequently, this machine may fill a market need where uniform large-area diamond films are necessary in a particular application.
IIC3. Low-Pressure RF Discharge

There has been much less work\[56-62\] done with low pressure RF discharges than with microwave discharges for CVD diamond growth (Fig 10). At first glance, this is somewhat surprising as RF is easier to scale to large volume and high power. Moreover, large RF plasma discharge units have been used in the semiconductor industry for some time. The scarcity of reported work in the RF area in CVD diamond growth may be the result of many unreported failures to achieve good quality diamond films rather than the result of not trying RF sources. The deposition rate of CVD diamond is closely correlated with the generation of atomic hydrogen and hydrocarbon radicals. The generation of such radicals seems to be more efficient in a microwave plasma than in an RF plasma. This is probably caused by both the higher energy and higher density of electrons in a microwave plasma. Average electron energies in a microwave plasma at 2450 MHz and 1 torr pressure average about 10 ev \[63,64\] which is enough energy (8.5ev) to dissociate hydrogen. On the other hand, average electron energies in an RF discharge at 13.56 MHz at 1 torr are about 4 ev \[65\] which is insufficient to dissociate hydrogen. In addition, electron densities are higher in microwave discharges\[66\].

Nevertheless, low-pressure electrodeless radiofrequency discharges have also been used to grow CVD diamond \[56-62\]. Depending on the pressure, atomic hydrogen concentrations of 10 to 65% can be produced in a RF discharge\[7\]. These discharges are less stable than microwave discharges and Ar sometimes has to be added to the hydrogen-hydrocarbon mixture to stabilize the discharge. Similar to the microwave discharge, deposits of carbon on the walls of the reactor can be a problem with an RF discharge. In addition, the RF can electromagnetically couple with any electrically conductive body in the reactor chamber and heat it. Finally, RF power sources are more expensive than microwave sources per watt of delivered power.

Diamond made by RF discharges has been of poorer quality than diamond made by microwave discharge\[56\]. In addition, large well faceted diamond crystals are usually not obtained.

RF generators are more expensive and less efficient in generating atomic hydrogen than microwave generators. The quality
of diamond produced by the RF technique has been generally poor. Because of the RF has a much lower frequency than microwaves, the penetration length problem discussed above with microwaves is absent with an RF discharge. Thus, larger areas of diamond could be made with an RF discharge than with a microwave discharge. Attempts to make remote RF discharges (where the atomic hydrogen is generated at one place and transported by gas flow to the substrate) work have been unsuccessful although they were one of the first techniques tried. The maximum thickness of a diamond film that can be produced by an RF discharge is low because of the very low diamond growth rate in RF reactors. The low diamond growth rate puts the capital costs per unit of diamond in the higher range of the various CVD techniques. RF system operating costs as far as gas consumption and energy are relatively low. Finally, labor costs for a RF system not expected to be as low as for a microwave system because the RF discharge is not as stable as a microwave discharge.

IIC4. High-Pressure DC Discharge

High-pressure DC discharges between fixed electrodes at atmospheric pressure have been used to grow CVD diamond from hydrogen-hydrocarbon mixtures at very high rates of up to 200 microns/hour and thickness greater than 1 mm (Fig 11) [67-71]. Because of technology developments over the years to make plasma torches, these DC discharges are now very stable. The substrate is biased positively in all cases. One disadvantage of this process is that the substrate must be directly cooled with running water to prevent it from melting because large amounts of power per unit of substrate area are used. Other disadvantages include the high power consumption, the erosion of the electrodes, the nonuniformity of the discharge and the small deposition area and the need for constant attention because of the large amount of power being used. Because of electrode erosion and the consequential contamination of the diamond film, it is expected that the diamond may not be suitable for applications in electronics. Also, with such high energy processes, overheating and degradation of the diamond film is a constant concern. Finally, all high intensity energy processes tend to be less reproducible from run to run. Because of the high rates of diamond growth, the capital cost per unit of diamond are expected to be moderate. Labor and operating costs for gases and energy will be relatively high.
IIC5. High-Pressure Microwave Discharge Jets

A high-pressure microwave discharge jet has also been used to grow CVD diamond at moderately high rates of 30 microns/hour at atmospheric pressure over a square inch of area[72]. A gas mixture of Ar-H$_2$-CH$_4$ is used with a CH$_4$/H$_2$ ratio as high as 10%. Sustained operation is difficult because of plasma instabilities and the need to vigorously cool the substrate. The plasma is initially ignited by electric breakdown around the central electrode and then sustained by microwave electromagnetic waves generated between the central electrode and chamber walls. One advantage of low-pressure microwave discharges is that they are electrodeless. However, with high-pressure microwave jets, this advantage has been lost by using electrodes that are immersed in the plasma and that therefore can erode. Operating costs tend to be very high with this process because of the large amounts and types of gases, particularly, argon that are required. Labor costs also are large as skilled personnel must keep a constant watch over the process.

IIC6. High-Pressure RF Discharge

High-pressure radiofrequency discharges have also been used to grow CVD diamond (Fig 12) [73]. These discharges are very unstable and large amounts of Ar are routinely added to the hydrogen-hydrocarbon mixture to increase the stability of the discharge. Nevertheless, the discharge must be monitored continuously and is typically only run for short periods of time. The danger associated with this arc instability has restricted high-pressure RF discharge growth of diamonds to a few scientific laboratories. High rates of diamond deposition are possible during these short runs. As with other high-pressure discharges, the high power input requires that the substrates be cooled directly with running water.

IIC7. High and Low-Pressure Flames

Hydrogen atoms are created during the burning of hydrogen or hydrocarbons in an oxygen flame (Fig 13) [74-76]. With a suitable ratio of carbon, hydrogen and oxygen, Hirose[77] discovered that CVD diamonds can be grown with a simple plumbers torch at atmospheric pressures in the "feather" of the flame just downstream of the flame front [77-86]. High temperatures (2800-3400 °C) in common flames
cause a plasma to form and atomic species to be generated at the flame front[87]. The flames are operated under fuel-rich conditions so atomic hydrogen and hydrocarbon radicals are abundant in the feather of the flame where the substrate is placed. Growth rates of 30 microns/hr are attained.

Hydrogen atoms can also be generated in low-pressure hydrogen and hydrocarbon flames.[75,76] Advantages of low-pressure flames may be a higher carbon-to-diamond conversion rate, a wider spatial zone in the flame where diamond will grow and a much lower heat input to the substrate. Although work is underway at several laboratories, no successful CVD diamond growth has been reported yet in a low-pressure flame.

So far, work has been limited to hydrogen-hydrocarbon-oxygen flames. Flames with other chemical reactants may also generate CVD diamond growth. For example, hydrogen-hydrocarbon-fluorine, hydrogen-hydrocarbon-chlorine, hydrocarbon-fluorine, hydrocarbon-chlorine, halocarbon-fluorine and halocarbon-chlorine flames are promising candidates among many possibilities.

The capital cost of a flame system, particularly at atmospheric pressure, are very low. Its simplicity would also allow low labor costs. Furthermore, diamond is produced at high rates. However, deposition is only successful over a relatively small area. The restriction in area is a result of the structure of the flame. There is only a limited zone in the flame where conditions are favorable for diamond formation. Outside of this zone, diamond either will not be formed or will burn in the flame. These restrictions combined with the gas flow required to flow around the substrate produces an uneven and inhomogeneous diamond deposit on the substrate unless the substrate is very small in area. Scanning the flame may help but it also may smear out the problem and produce diamond of a uniformly poor quality. The high energy intensity of the flame method requires vigorous cooling of the substrate. The principal problem with the flame technique is its very low conversion rates of carbon to diamond (of the order of 0.01%). The very low conversion rate is not surprising as most of the carbon must be burned in the flame to produce the high temperatures necessary to generate a plasma and atomic hydrogen. At these low carbon-to-diamond conversion rates, the flame technique is the most expensive way to make diamond of the popular CVD diamond methods because of gas costs. If these low conversion rates can not be increased, the torch
method will only be economical in producing gem stones for the jewelry trade.

III OTHER LOW-PRESSURE DIAMOND PROCESSES

IIIA COMBINATION PROCESSES

Some investigators have used combinations of processes to see if any advantages would ensue. For example, a direct-current spiral hollow cathode combines features of the hot filament, electron beam and plasma process. Such a hollow cathode was used to grow CVD diamond in an Ar-H₂-CH₄ gas at a disappointing rate of one micron/hour[19,88,89]. The results of these experiments indicate that this particular combination of processes has no technical or economic advantage over a simple hot filament process.

IIIB THERMAL PROCESSES-SUBSTRATE ONLY

The thermal activated[90-92] growth of CVD diamond in various halogen-hydrocarbon or fluorchlorohydrocarbon-hydrogen-helium mixtures without the assistance of any external excitation such as a plasma or hot filament has been reported. In one case[92], only heating of the diamond substrate was required. In the other case[91,92], the gases at atmospheric pressure were preheated in a furnace tube at about 800-900 C and passed over a substrate at a temperature between 250-750 C (Fig 14). Diamond formed on the substrate at rates of 0.5-2 microns/hour.

Although halogens such as fluorine can stabilize the diamond surface in the same way that hydrogen does, the carbon-fluorine bond (108 kcal/mol) is much stronger than the fluorine-fluorine bond (38 kcal/mol). Thus, molecular or atomic fluorine can not produce vacant sites on a diamond surface covered with fluorine in the same manner[93,94] that atomic hydrogen produces vacant sites on a diamond surface covered with hydrogen. Without vacant sites, carbon deposition would cease. However, all of the gas mixtures used successfully contain hydrogen whose bond strength with fluorine (136 kcal/mol) exceeds the carbon-fluorine bond strength (108 kcal/mol). Thus atomic hydrogen can react with a monolayer of fluorine on the surface of diamond to form HF, thereby forming the vacant sites needed for additional carbon deposition and diamond
growth. This is an exothermic reaction with an energy release 28 kcal/mol and there would be no shortage of vacant sites. Starting from molecular hydrogen with a bond strength of 104 kcal/mol, a net expenditure of 24 kcal/mol must be spent to produce a mole of vacant surface sites on a surface of diamond covered with fluorine. Generation of vacant sites by molecular hydrogen would give a relatively low concentration of vacant sites but they may be sufficient to allow diamond growth if the kinetics of vacant site formation were rapid, i.e., as vacant sites were filled, new ones would form rapidly to maintain their equilibrium concentration.

There are potentially many chemical systems like the halogen based one discussed above that may produce diamond.[90,93,94]. Generally, one looks for a reaction scheme where carbon can be deposited in a series of exothermic reactions in the presence of chemical species that can form a single sp³ bond to the diamond surface. The exothermic chemistry drives the reaction while the sp³ bonding species stabilizes the diamond surface and prevents its reconstruction to a graphite-like surface.

There may also be reactions that are not quite exothermic but require a slight boost from an external energy source. Recently, Rudder and his coworkers at RTI have recently reported making diamond from a mixture of alcohol:acetic acid: water mixture of 20:20:60 in the presence of a graphite body. This gas mixture was subjected to RF excitation at a power level of 1/8 that required in conventional RF methane:hydrogen CVD system.[95]. Diamond was deposited on a silicon substrate at 300 Centigrade.

Most of capital costs of a thermally-activated process would be very modest, particularly for the systems[90] running at atmospheric pressure. For a fluorine-based system as discussed above, the reactivity of fluorine would require monel piping and tubing for the apparatus. For the other halogens, quartz or vicor would suffice. Expensive gas cabinets and safety systems are also be required with any system using the elemental halogens. In addition, because of environmental concerns about the ozone layer, the exhaust from this system could not be vented directly to the atmosphere as is now done for hydrogen-hydrocarbon systems but would have to be inactivated. Labor costs would be very low for a thermally activated
process as it is simple and does not require much attention once it is running. Energy costs would be the lowest of any current CVD diamond process. Depending on the halogen or fluorochlorohydrocarbon chosen, gas costs would range from low to high. Some fluorochlorohydrocarbons are expensive with prices ranging from $10 to $130 per kilogram. Halogens are even more expensive with fluorine costing almost $1000 per kilogram. However, the more common dichlorodifluorocarbon with which some of the best experimental results were obtained[90] sells for only $2 per kilogram. These prices compare with hydrogen at less than $1 per kilogram and methane from a natural gas tap. With current synthetic diamond prices of a few dollars/carat or $10,000/kilogram, the conversion efficiency of nutrient gas to diamond could be very small before high gas costs would be a problem.

IIIC LASER EXCITATION

There have been some reports[96,97] of the deposition of CVD diamond using laser excitation. One of these reports was later withdrawn[97]. More recently, a group in India has been reported that diamond was made by subjecting an organic fluid to a laser pulse. Also, diamond has been made by directing a laser pulse onto a graphite layer on a copper slab[98]. Although these reports have generated widespread scientific interest, laser excitation does not seem to be a technologically viable method of diamond growth. Economically, lasers would be a poor choice for diamond production because of their high capital cost, their low rate of conversion of electrical power to laser light (typically, 3-10%) and low efficiency in converting nutrient carbon to diamond.
IIID. ALTERNATING CHEMICAL REACTIONS

Recently, reports have circulated that diamond can be grown layer by layer by alternating exposures of diamond to different gases. No details are available about these experiments. However, the type of paired reactions that should work are shown in Equations 6 and Figs 15a and 15b for CF₄ and CH₄:

\[
\begin{align*}
\text{CH}_4 + \text{Diamond-F} &\rightarrow \text{Diamond-C-H} + \text{HF} \\
\text{CF}_4 + \text{Diamond-H} &\rightarrow \text{Diamond-C-F} + \text{HF}
\end{align*}
\]

(6a) (6b)

where Diamond-F and Diamond-H represent, respectively, diamond covered with a monolayer of fluorine and hydrogen. This idea is an extension of the alternating reaction work of Eversole[5] shown in Equations 1 and 2. This reaction works because the bond strength of H-F exceeds the bond strengths of C-F and C-H. Both reactions are exothermic with an enthalpy of reaction of about 8 kcal/mole.

One can generalize this type of reaction in a number of ways. One way is to use compounds of the type CNXM and CLZP:

\[
\begin{align*}
\text{CNXM} + \text{Diamond-Z} &\rightarrow \text{Diamond-C-X} + \text{ZX} \\
\text{CLZP} + \text{Diamond-X} &\rightarrow \text{Diamond-C-Z} + \text{ZX}
\end{align*}
\]

(7 a) (7b)

where Diamond-Z and Diamond-X represent, respectively, diamond covered with a monolayer of Z and X. If the Z-X bond is stronger than the C-X and C-Z bonds, then alternate exposures of diamond to the respective gases will cause alternate exothermic chemical reactions where carbon is placed down during each exposure. These types of reactions inherently prevent the generation of double or sp2 carbon bonds and thus stop graphite formation. Examples of gases that can be used in such reactions pairs are all of the fluorochlorocarbons, fluorochlorohydrocarbons, alcohols, halogens and hydrogen.

If CNXM and CLZP do not react in the gas phase, then a gas mixture of them can be used to grow diamond instead of the alternating exposure of one and then the other depicted in Reactions
7. In this latter case, the reactions still alternate between (a) and (b)
on a microscale but not on a macroscopic scale:

\[ C_{n}X_{M} + C_{l}Z_{P} + X\text{-}Diamond\text{-}Z \rightarrow Diamond + ZX \quad (8) \]

where X-Diamond-Z is diamond covered with a monolayer of a
mixture of X and Z. A process like this may be what is actually
taking place in the thermally activated diamond deposition
experiments discussed above[90-92].

III. DEPOSITION FROM LIQUID SALT BATHS

Patel and Cherian [99,100] reported evidence of diamond
growth on a diamond crystal that was placed in a small amount of
liquid sodium hydroxide contained in a nickel crucible at 600 C.
When the NaOH which is volatile and unstable at this temperature
evaporated[101], a small deposit less than 1/2 micron thick was left
on portions of the diamond crystals. Independent analysis of this
deposit has not disproven that the deposit is diamond[101]. All
of the test that can be performed with such a small volume of
material are consistent with the deposition of very thin and small
particles of diamond. If this experiment is valid, we can speculate
as to why it may have worked by using a NaOH bath as an example.
There is an analogy between conventional CVD diamond growth from
an acetyline-hydrogen gas mixture in the presence of atomic
hydrogen and diamond growth from a NaOH salt bath containing
sodium acetylide. Atomic hydrogen, sodium and hydroxyl form
single bonds with carbon and prevent the formation of carbon double
bonds which might lead to graphite growth. The stabilization of the
diamond surface by atomic hydrogen is analogous to the
stabilization by either sodium or hydroxyl ion in a liquid salt solution.
The main difference between the two cases is that the bonding with
diamond is predominantly covalent in the case of hydrogen and
predominantly ionic in the case of sodium and hydroxyl ions. A
simple extension of this method of diamond growth would involve a
temperature gradient in a molten alkali salt bath containing graphite
and a diamond seed. Alternatively, the graphite could be replaced
with an alkali acetylide.

The amount of diamond produced by this process was
extremely small and at present is not economically viable. Until the
process is modified and improved, it will remain a scientific curiosity somewhat like the early work of Eversole with CVD diamond.

III. DEPOSITION FROM LIQUID METAL SOLUTIONS

Over the years, a number of patents have been issued claiming to have grown diamond from a liquid metal solution at low pressures. Many of these patents stemmed from the success of using metal catalysts in high-pressure, high-temperature diamond synthesis. Some of these patents are undoubtedly "paper" patents which were never really tried but which sounded logical and reasonable to a patent examiner. The success of using atomic hydrogen to stabilize diamond, however, reintroduces the question of whether a liquid metal bath can be used to grow diamond at low pressures. Diamond in a liquid metal bath may have its surface stabilized by metal atoms reacting with the diamond to form a carbide monolayer. If a metal with a metal-carbide bond energy equal to the hydrogen-carbon bond energy were used, one can argue that a low-pressure liquid-metal processes analogous to conventional CVD diamond deposition should be possible.

IV SUMMARY

Many innovative means of making diamond at low pressures have been developed in recent years. A number of these methods are only of scientific interest at the present time because of their high costs or impracticality. Even after these processes are eliminated from consideration, there remains a number of processes that are currently being used to make diamonds and which appear to be economically viable. Some applications are most easily addressed by a particular process and this is the reason for the choice of the process in such cases. In other cases, the previous background and experience of an individual or group of workers has dictated what diamond process was selected. People with no applicable experience have tended to select the filament process because of its simplicity or the microwave process because commercial equipment was available for purchase. After gaining experience with these techniques, they have graduated to other techniques which they find more suitable for their particular uses and applications. Currently, there are over 30 companies in the world actively pursuing CVD diamond research and trying to develop a diamond business from their research. Many
different methods of diamond making are being used by these companies which will be eventually sorted out by the marketplace. Currently, the advantages, disadvantages and economics of these various processes are closely guarded proprietary secrets. The determination of the "best" CVD diamond process, if one really exists, is not possible at this time from information available in the literature. Much more process research and development must be done before this determination will be possible.

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78. S.Yazu, S.Sato and N.Fujimori, SPIE Proceedings (San Diego, August 16-20, 1988)
95. M. Yoder, personal communication
101. R.Chrenko, personal communication
LIST OF FIGURES

Figure 1. Filament-Assisted CVD Growth of Diamond from a Hydrogen-Hydrocarbon Mixture

Figure 2. Reactions of Leading to the Formation of Atomic Hydrogen and Carbon Radicals on a Hot Filament

Figure 3. Carburization of a Tungsten Filament During CVD Diamond Growth

Figure 4. Electron-Assisted Hot Filament CVD Growth of Diamond. The filament is usually biased negatively to cause electron bombardment of the substrate

Figure 5. Electron and Gas Temperatures versus Pressure in a Hydrogen-Hydrocarbon Plasma Used for CVD Diamond Growth

Figure 6. Molecular, Neutral Radical and Ion Densities in a Gas Plasma. Condensable Species that can contribute to CVD Diamond Growth are Noted.

Figure 7. Low-Pressure Glow Discharge Method of Making CVD Diamond

Figure 8. Low-Pressure Microwave Discharge Method of Making CVD Diamond.

Figure 9. ECR Microwave Low-Pressure Discharge Method of Making CVD Diamond.

Figure 10. RF Low-Pressure Discharge Method of Making CVD Diamond.

Figure 11. High-Pressure DC Discharge Method of Making CVD Diamond.

Figure 12. High-Pressure RF Discharge Method of Making CVD Diamond.

Figure 13. The Combustion Flame Method of Making CVD Diamond.
Figure 14. Atmospheric-Pressure Thermal Halogen Method of Making CVD Diamond.


Figure 15b. Addition of Carbon onto a Hydronated Diamond Surface by Carbon Tetrafluoride. Figs 15a and 15b are the Two Steps of a Cyclic Method of CVD Diamond Growth.
FILAMENT-ASSISTED DIAMOND CVD

H₂ + CH₄

1800–2400°C

450–1150°C

SUBSTRATE

DIAMONDS
DISSOCIATION OF GAS MOLECULES ON FILAMENT
CARBURIZATION OF TUNGSTEN WIRE
ELECTRON ASSISTED CVD

GAS

SUBSTRATE

~
ELECTRON AND GAS TEMPERATURE VS PRESSURE IN A PLASMA

- H → H⁺ + e
- C → C⁺ + e
- H₂ → 2H, CHn → CHn⁻¹ + H

TEMPERATURE (eV)

ELECTRONS

GAS

PRESSURE (TORR)

METASTABLE DIAMOND GROWTH
<table>
<thead>
<tr>
<th>SPECIES</th>
<th>RELATIVE CONCENTRATION</th>
<th>CONDENSABLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOLECULES ((\text{H}_2, \text{CH}_4))</td>
<td>10,000</td>
<td>NO</td>
</tr>
<tr>
<td>NEUTRAL RADICALS ((\text{H}, \text{CH}_3, \text{CH}_2, \text{CH}, \ldots))</td>
<td>100</td>
<td>YES</td>
</tr>
<tr>
<td>IONS ((\text{H}^+, \text{CH}_4^+, \text{H}_2^+, \ldots))</td>
<td>1</td>
<td>YES</td>
</tr>
</tbody>
</table>
ARC DISCHARGE

GAS

SUBSTRATE
ECR PCVD DIAMOND GROWTH

MICROWAVE GENERATOR

RECTANGULAR MICROWAVE GUIDE
QUARTZ WINDOW
HEMHOLTZ COILS
CIRCULAR MICROWAVE GUIDE
PLASMA

SUBSTRATE
VACUUM SYSTEM
RF - ASSISTED DIAMOND CVD

H₂ + CH₄ →

RF COILS

PLASMA

DIAMONDS

SUBSTRATE
DC PLASMA CVD

1KV

ANODE

SUBSTRATE

PLASMA

GAS

GAS

CATHODE
RF THERMAL PLASMA

SUBSTRATE

PLASMA

RF COIL

GAS
FLAME DIAMONDS

\[ C_xH_y + O_2 \rightarrow C_xH_yO_2 \]

**FLAME FRONT**
- **HYDROCARBON FEATHER**

**OUTSIDE FLAME**

**TORCH**

**DIAMONDS**

**WATER-COOLED SUBSTRATE**

**FLAME FRONT:** \( C + \frac{1}{2} O_2 \rightarrow CO \) (3000°C)

**HYDROCARBON:** \( C + \frac{1}{2} O_2 \) (EXTERNAL) \( \rightarrow CO \)

**OUTSIDE FLAME:** \( CO + \frac{1}{2} O_2 \) (EXTERNAL) \( \rightarrow CO_2 \)
HALOGEN-ASSISTED THERMAL GROWTH OF CVD DIAMOND

GAS TUBE

F$_2$Cl$_2$C, H$_2$, He

900 C

Furnace 1

700 C

Furnace 2

CVD DIAMONDS

SUBSTRATE

ATMOSPHERIC PRESSURE
ALTERNATING REACTION ONE DURING DIAMOND GROWTH
ALTERNATING REACTION TWO DURING DIAMOND GROWTH
Ion-Beam Technologies

by

George R. Fenske

Materials and Components Technology Division

Argonne National Laboratory

Presented at the DOE Tribology Program Workshop on Diamond and Diamond-Like-Carbon Films, Argonne National Laboratory, Argonne, IL, Feb. 4–5, 1992
Diamond/DLC Films

Why?

• High hardness
• High thermal conductivity
• Low thermal expansion coefficient
• Chemical stability (<500–1300°C)
• Low friction coefficient
Outline

- Review/description of deposition processes
  - CVD
  - PVD
  - IBD/IAD
- Properties of IBD/IAD
- Tribological performance of IBD/IAD Coatings
- Issues
Deposition Techniques

- CVD (e.g., HFCVD, PACVD, etc.)
- PVD (plasma sputtering, ion beam sputtering, evaporation, etc.)
- IBD (low-energy ion implantation)
- Hybrid processes (biased sputtering, IBAD, biased HFCVD, etc.)
PVD Deposition Processes

- Evaporation (e.g., electron beam evaporation)
- Cathodic arc discharge
- Sputtering
- Ion beam sputtering
- Laser evaporation
Hybrid Process

- **Simultaneous**
  - Ion Beam Assisted Deposition
    - e–beam evaporation
    - ion–beam sputtering
  - Biased Sputtering
  - Biased PECVD (Chang)
  - Ion Plating (hollow cathode, laser)

- **Sequential**
  - Laser/HFCVD
  - IBS/IBD
## Comparison of Typical Deposition Conditions

<table>
<thead>
<tr>
<th>Process</th>
<th>Carbon Source</th>
<th>Particle Energy (eV)</th>
<th>Substrate Temperature °C</th>
<th>Film Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>CVD</td>
<td>Dilute hydro-carbon gas in hydrogen</td>
<td>0.1–1 eV</td>
<td>Typical 800–1100°C (&lt;500°C possible)</td>
<td>Poly-crystalline diamond &amp; DLC/DLHC</td>
</tr>
<tr>
<td>PVD</td>
<td>Solid carbon</td>
<td>0.1–10 eV</td>
<td>R.T. and higher</td>
<td>DLC/DLHC</td>
</tr>
<tr>
<td>IBD</td>
<td>Gas (CH₄, H₂, etc.) (solid carbon)</td>
<td>0.1–100 keV</td>
<td>R.T. and higher</td>
<td>DLC/DLHC</td>
</tr>
<tr>
<td>Hybrid</td>
<td>Gas solid</td>
<td>0.1–10 keV</td>
<td>R.T. and higher</td>
<td>DLC/DLHC</td>
</tr>
</tbody>
</table>
Process Deposition Parameters

Chemical Bonding Structure Hydrogen Content

Thermo-Mechanical Properties ($\rho$, $H_v$, $k_t$, etc.)

Tribological Performance

DOE OTM Tribology Program
Effect of Process Process Parameters on DLHC Properties

![Graph 1: Vickers Hardness vs. Substrate Potential](image)

![Graph 2: Hydrogen Content vs. Substrate Temperature](image)

Okada et al.

DOE OTM Tribology Program
IBD/IAD processes typically produce amorphous carbon films with <1% hydrogen (denoted as a–c or DLC), or, amorphous hydrogenated carbon films with 20–60% hydrogen

- amorphous (small crystallites)
- hydrogen content – \( \rho \), \( \text{sp}^3 \) bonding

DOE OTM Tribology Program
Structure of Amorphous Carbon Films (Angus et al.)

- Short range $sp^2/sp^3$ bonding
- No long-range order
Friction Coefficient of DLHC Films on Ceramics (Erdemir, Wei, and Wilbur)
Friction Coefficient of DLHC Films on Ceramics (Erdemir, Wei, and Wilbur)

Friction Coefficient

- Nitrogen
- Argon
- Dry Air
- Normal Air
- Humid Air

Materials:
- Si3N4/DLC-Si3N4
- Sapphire/DLC-ZrO2
- Diamond/Si3N4

DOE OTM Tribology Program
Friction and Wear of DLHC Films on Ceramics (Erdemir, Wei, and Wilbur)

(a)

Friction Coefficient

(b)

Wear Rate ($10^{-8} \text{mm}^3/\text{N.m}$)

DOE OTM Tribology Program
Rolling Contact Fatigue Tests of Thin DLC Films on M50 Steel (Wilbur, et al.)

---

DOE OTM Tribology Program
Issues

- Film Stability
  - environment
  - temperature
  - mechanical loading
- Surface Finish
- Film Adhesion
- Deposition Rates
- Geometries
- Competing Processes
  - mature processes – TiN
  - emerging processes – c–BN
    - superlattices
- Cost
CHARACTERIZATION METHODS

for

DOE workshop on Diamond and Diamond-like Carbon Films

February 4th & 5th
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* Current Employer: GE Superabrasives
Outline

Introduction
Raman Spectroscopy
SEM
TEM
Surface Analysis
Comparison of Techniques
In-vacuo Analysis
In-situ Analysis
Summary
Carbon Bonding

\[ \text{C - C} \quad (\text{sp}^3) \]

(1\,\text{e}^2) \quad 2\text{sp}^3 \quad (4\text{π}^2)

Diamond
Tetrahedral

\[ \text{C = C} \quad (\text{sp}^2) \]

(1\,\text{e}^2) \quad 2\text{p}^1 \quad 2\text{sp}^2
1\text{π} \quad 3\text{π}^2
Graphitic
Planar

\[ \text{C ≡ C} \quad (\text{sp}^1) \]

(1\,\text{e}^2) \quad 2\text{p}^2 \quad 2\text{sp}^1
2\text{π} \quad 2\text{π}^2
Carbyne
Linear
I. Identification of the Diamond Phase

A. Composition (Carbon)

Auger Electron Spectroscopy
X-ray Photoelectron Spectroscopy
Secondary Ion Mass Spectrometry
Rutherford Backscattering
Infrared Spectroscopy

B. Structure (Diamond, Fd3m space group)

X-ray Diffraction
Electron Diffraction

C. Bonding (sp³, tetrahedral)

Raman Spectroscopy
Auger Electron Spectroscopy
Electron Energy Loss Spectroscopy
X-ray Photoelectron Spectroscopy

II. Defects in Diamond Films

A. Scanning Electron Microscopy

Grain Boundaries
Particle Morphology
Secondary Nucleation

B. Transmission Electron Microscopy

Dislocations
Stacking Faults
Twins
Grain Boundaries

C. Electrical Measurements

Impurities
Electrically Active Defects
1332 cm\(^{-1}\) - primary 1\(^{st}\) order diamond peak
1580 cm\(^{-1}\) - primary 1\(^{st}\) order graphite peak
1355 cm\(^{-1}\) and 1590 cm\(^{-1}\) - primary, 1\(^{st}\) order
microcrystalline graphite peaks
\(\alpha_2\) - amorphous graphite peaks
\(\alpha_1\) - amorphous Si spectrum scaled to the diamond frequency to represent amorphous dia.

Note:
Amorphous "graphite" \(\rightarrow\) 3-fold coordinated, \(sp^2\) bonded carbon with no long range order
Amorphous "diamond" \(\rightarrow\) 4-fold coord, \(sp^3\) bonded C
First-order Raman spectra of diamond thin films. (a) "diamond-like" film with features similar to microcrystalline graphite (b),(c) the sharp feature at 1322 cm\(^{-1}\) is indicative of crystalline diamond while features between 1350 and 1600 cm\(^{-1}\) are attributed to sp\(^2\) bonded carbon. (Shroder (1988)).

- 1332 cm\(^{-1}\) - Diamond
- 1355 \& 1580 cm\(^{-1}\) - Microcrystalline Graphite
- 1490 cm\(^{-1}\) - Disordered (amorphous) Graphite
- 1550 cm\(^{-1}\) - Downshifted Microcrystalline Graphite
- 1140 cm\(^{-1}\) - Amorphous Diamond (?)

Note: \(I_G \approx 50I_D\)
Electron Spectroscopies

A. Auger Electron Spectroscopy

B. X-ray Photoelectron Spectroscopy

C. Electron Energy Loss Spectroscopy
Lower curve: distribution of energies of secondary electrons ejected from a graphite surface by incident electrons of energy 1000 eV. Upper curve: differential distribution over the energy range containing the carbon KLL Auger peaks. In the differential distribution the peak 'position' is taken to be that of the high energy minimum, by convention

*contains diffraction information
Narrow window AES scan about the C (KVV) peak showing fine structure

CVD Diamond

<table>
<thead>
<tr>
<th>Peak energy</th>
<th>268</th>
<th>256</th>
<th>240</th>
<th>230</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak position relative to A₀</td>
<td>12</td>
<td>28</td>
<td>38</td>
<td></td>
</tr>
<tr>
<td>Calculated energies (B.S.)</td>
<td>269</td>
<td>256</td>
<td>245</td>
<td>235</td>
</tr>
</tbody>
</table>

Identification (KV₁V₁) (KV₂V₂) (A₀ - ℏω₄) (A₀ - ℏω₃)

| Calculated energies [19] (I.C.) | 266 | 252 | 243 |
| Identification | (¹P₂) | (¹S₀) |

Graphite

<table>
<thead>
<tr>
<th>Peak energy</th>
<th>268</th>
<th>255</th>
<th>241</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak position relative to A₀</td>
<td>14</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>Other [11]</td>
<td>270</td>
<td>253</td>
<td>239</td>
</tr>
</tbody>
</table>

Amorphous-carbon

<table>
<thead>
<tr>
<th>Peak energy</th>
<th>268</th>
<th>243</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak position relative to A₀</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

(Lurie and Wilson (1977))

Diamond density of states (theoretical) (Painter, et al.)

KINETIC ENERGY, ev
(Williams and Glass (1988))

 Peak position relative to A₀ 12 28 38 270 253 239

Other [11] 270 253 239

Amorphous-carbon

<table>
<thead>
<tr>
<th>Peak energy</th>
<th>268</th>
<th>243</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak position relative to A₀</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

(Lurie and Wilson (1977))

194
Wide energy range XPS scan of a diamond film grown at 1% CH$_4$ in H$_2$.

Note the x-ray excited Auger peaks for the O and C. Oxygen and Silicon impurities were generally confined to the surface, probably due to Quartz reaction chamber in the microwave plasma CVD system. (Glass, Williams and Davis (1988)).
XPS, C1s peak - Natural Diamond and Graphite

Unprocessed photoemission spectra showing the peak positions for a clean diamond surface, a hydrogen-covered surface, and a graphite single crystal. The difference in binding energy between the hydrogen-covered and clean diamond bulk peak results from a shift in the Fermi-level pinning position when the hydrogen is removed from the surface. (Moran, et al. (1986)).

Note the relatively small binding energy shift between diamond and graphite. For detection, a monochromated X-ray source is necessary. Thus, for conventional, multi-technique surface analysis systems, the fine structure (AES or XPS) should be utilized to distinguish these phases, or electron energy loss spectroscopy, rather than Ef shift.
Electron Energy Loss Spectra from Carbon - plasmon loss region near zero loss peak

(1) $\vec{e}^-$ excitation
(2) Surface plasmon or interband trans.
(3) Bulk plasmon

EELS of Diamond films grown by EACVD;
a) $\text{CH}_4 = 2.0\%$, $T_3 = 1073 \text{ K}$
b) $\text{CH}_4 = 2.0\%$, $T_3 = 823 \text{ K}$
c) Specimen (b) after acid wash
d) $\text{CH}_4 = 0.5\%$, $T_3 = 823 \text{ K}$
(Sawabe and Inuzuka (1986))

Definition - A Plasmon is a collective excitation of conduction electrons. Frequency is determined by oscillation of the conduction electrons with respect to the positive core.
K-shell ionization spectra from EELS in a Transmission Electron Microscope (note similarity between Diamond Film, natural diamond - edge and shape)

Advantage of transmission EELS in a TEM is the spatial resolution. Using a 200Å spot size in this study grain boundaries and defects were examined for an sp³ component. However, only sp³ bonding was observed throughout the film.

(Williams and Glass (1988))
Electron Microscopies

A. Scanning Electron Microscopy

B. Transmission Electron Microscopy

C. Scanning Tunnelling Microscopy
Schematic of Diamond Nuclei on $\beta$-SiC
Sample preparation for transmission electron microscopy (TEM): (a) Preparation of standard planar samples involves polishing and a final etch or ion mill to thin the sample; (b) samples for cross section TEM involve (1) and (2) slicing sections about 1 mm thick; (3) using epoxy to hold two sections together and then polishing to about 50 μm thickness, and then (4) ion milling to produce the final sample thickness of about 500 Å.
Comparison of Different Methods

- SEM
- TEM
- Raman
- XPS
- AES
- Raman
Plan-view TEM micrographs of a single diamond grain grown under forward bias of 150 V, and corresponding scanning electron micrographs and Raman spectra of diamond films.
Plan-view TEM micrographs of a single diamond grain grown under zero bias, and corresponding scanning electron micrographs and Raman spectra of diamond films.
Comparative Sensitivities of AES, XPS-EELS, and Raman to sp2:sp3

Goal: Provide a comparison between techniques used by different researchers to evaluate the quality of diamond films.

Approach:

- Vary the methane concentration in the feedgas (1 to 50% in hydrogen) to increase/decrease the sp2 component in the deposited films.
- Apply known correction factors (in the case of Raman) and qualitatively determine the amounts of phases.
SEM micrograph of diamond film grown with 1% methane in hydrogen.

SEM micrograph of diamond film grown with 50% methane in hydrogen.
AES Spectra from Diamond Films

Auger spectra of diamond films grown with CH4 concentrations of a) 1%, b) 3%, c) 5%, d) 10%, e) 20%, f) 50%.
XPS-EELS from Series of Diamond Films
Raman Spectra of Diamond Films Grown with Different Methane Concentrations in the Feedgas
Fraction of Diamond (sp3) Determined by Deconvolution of AES, XPS-EELS, and Raman

![Graph showing the fraction of diamond versus CH₄ content.](image-url)

- AES
- XPS-EELS
- Raman
In Vacuo Analysis
IN-VACUO CVD/ANALYTICAL CHAMBER

A CVD Chamber
B Analytical
C Transfer Tube
D Load Lock
Nucl. Density vs. Bias Time

![Graph showing the relationship between nucleation density and bias time. The x-axis represents bias time in hours (0.0 to 2.0) and the y-axis represents nucleation density in cm$^{-2}$. The graph shows a logarithmic increase in nucleation density with increasing bias time.]
Surface Analysis During Biasing

![Graph showing C1s and Si 2p binding energy spectra during biasing]
Calculated Film Thicknesses From XPS Peak Area Ratios

A: During Biasing Pretreatment

B: During Growth, After 1 hr. Bias
High magnification HRTEM showing an amorphous interfacial layer between the diamond and the silicon substrate.
Adsorbed oxygen and amorphous hydrocarbons on the substrate prior to biasing.

- Adsorbed carbon is either etched away or converted to Si-C.
- Physisorbed oxygen is converted into Si-O.
- C-C bonding is found on the surface of the Si-C.

As biasing continues the oxide is etched away.
-Si-C islands continue to grow.

As local carbide islands reach critical thickness, excess carbon forms stable clusters.
-Some of the cluster become favorable for diamond nucleation.

As the rest of the carbide reaches critical thickness, more carbon becomes available to form diamond nucleation sites.

As biasing continues, etching occurs, which allows diamond to nucleate closer to the Si surface.
In Situ Analysis

- LRI
- Microbalance
- Ellipsometry
- IR absorption
MICROWAVE PLASMA CVD SYSTEM
LRI Theory

Growth Rate = \((\lambda/2\eta)/T\)

Where \(\lambda\) = laser wavelength

\(\eta\) = film refractive index

\(T\) = Period between interference cycles
LRI Scan

Reflected Intensity

Time (sec.)
Growth Rate vs CH₄ Concentration

- Growth Rate (µm/hr.)
- Methane Concentration (%)
- 740 °C
- 585 °C
SUMMARY

- SEM & Raman Spectroscopy are the minimum techniques necessary (easy sample prep and relatively inexpensive)

- Strong correlations between surface morphology, defect density and Raman signal exist

- Various surface analysis techniques can be utilized and allow in-vacuo characterization of the growth process

- Quantification of nondiamond component is currently very difficult and needs further development

- True in-situ techniques are limited due to growth environment but are currently under development (LRI, Ellipsometry, ATR...)
STRUCTURE AND PROPERTIES
OF DIAMOND AND DIAMOND-LIKE FILMS

R. E. Clausing
Metals and Ceramics Division,
Oak Ridge National Laboratory

Workshop
on
DIAMOND FILMS FOR TRANSPORTATION APPLICATIONS
Sponsored by: DOE, Office of Transportation Technologies
and Argonne National Laboratory (ANL)
February 4-5, 1992

ornl
Structure and Properties of Diamond and Diamond-Like Films

- Introduction
- Natural Ila Diamond (The Standard)
- Importance of Structure and Composition
- Control of Structure and Properties
SUMMARY

• Properties of CVD diamond films can compare favorably with natural diamond

• Properties are anisotropic, a strong function of structure and crystal perfection (including composition)

• Crystal perfection and morphology are functions of growth conditions and can be controlled.

• The manipulation of texture and thereby surface morphology and internal crystal perfection is an important step in optimizing CVD diamond films for applications.

ornl
• The properties of DLC and CVD Diamond Films can be superlative

• The properties of DLC and CVD Diamond Films are strong functions of structure
Why Use Diamond?

- Hardness
- Strength
- Friction and Wear
- Thermal Conductivity
- Corrosion Resistance
- Optical Properties
- Electronic Properties
- Combinations of the Above
PROPERTIES OF DIAMONDS

- Hardest Material: Indentation Hardness of $14.2 \times 10^6$ psi
  Scratch Hardness 10 on Mohs' scale

- At Room Temperature Diamond is a Brittle, Elastic Solid
  Young's Modulus is $160 \times 10^6$ psi
  (compared to Steels with $30 \times 10^6$ psi)
  Theoretical Tensile Strength is $\sim 425,000$ psi

- Low Coefficient of Friction of $\sim 0.1$, Comparable to Many Lubricants

- Best Room Temperature Thermal Conductivity (20 W/(cm-K)) of Any Material

- Coefficient of Thermal Expansion is Low - $0.8 \times 10^{-6}$ K$^{-1}$ (Room Temperature)

- Resistant to corrosion by All Acids, Even at High Temperatures.

- Transparent to Both Visible and IR Radiation
# SELECTED MECHANICAL PROPERTIES OF DIAMOND

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Units</th>
<th>Note</th>
<th>Table Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic (Young's) modulus</td>
<td>1050.</td>
<td>GPa</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>965.</td>
<td>GPa</td>
<td>Type la (nat.)</td>
<td>2</td>
</tr>
<tr>
<td>Bulk modulus</td>
<td>440.</td>
<td>GPa</td>
<td></td>
<td>1 (p. 8)</td>
</tr>
<tr>
<td></td>
<td>440-590.</td>
<td>GPa</td>
<td>Type IIa</td>
<td>3</td>
</tr>
<tr>
<td>Poisson's ratio</td>
<td>0.2</td>
<td>-</td>
<td>Type la (nat.)</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>-</td>
<td>synth. polyytl.</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>0.1-0.29</td>
<td>-</td>
<td>dep. on orient.</td>
<td>1</td>
</tr>
<tr>
<td>Tensile strength (theoretical)</td>
<td>190.</td>
<td>GPa</td>
<td>(&lt;111&gt; dir.)</td>
<td>1 (p. 285)</td>
</tr>
<tr>
<td></td>
<td>2.94</td>
<td>GPa</td>
<td>(best value)</td>
<td>1</td>
</tr>
<tr>
<td>Shear strength (theor., &lt;110&gt; [111] system)</td>
<td>121.</td>
<td>GPa</td>
<td></td>
<td>1 (p. 285)</td>
</tr>
<tr>
<td>Compressibility</td>
<td>1.7x10^-7</td>
<td>cm^2/kg</td>
<td>Type IIa</td>
<td>3</td>
</tr>
<tr>
<td>Cleavage velocity</td>
<td>7.2</td>
<td>km/s</td>
<td></td>
<td>1 (p. 289)</td>
</tr>
</tbody>
</table>

References:

### A COMPARISON OF THE ELASTIC MODULUS OF DIAMOND TO THAT OF OTHER MATERIALS

<table>
<thead>
<tr>
<th>Material</th>
<th>E (GPa)*</th>
<th>(\frac{E_{\text{diamond}}}{E})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrex™ glass</td>
<td>70.</td>
<td>15.4</td>
</tr>
<tr>
<td>mild steel</td>
<td>206.</td>
<td>5.1</td>
</tr>
<tr>
<td>partially-stabilized zirconia</td>
<td>205.</td>
<td>5.1</td>
</tr>
<tr>
<td>titanium nitride</td>
<td>251.</td>
<td>4.2</td>
</tr>
<tr>
<td>(\alpha) - silicon nitride</td>
<td>304.</td>
<td>3.5</td>
</tr>
<tr>
<td>(\alpha) - silicon carbide</td>
<td>400.</td>
<td>2.6</td>
</tr>
<tr>
<td>titanium carbide</td>
<td>430.</td>
<td>2.4</td>
</tr>
<tr>
<td>(\alpha) - alumina</td>
<td>380.</td>
<td>2.4</td>
</tr>
</tbody>
</table>

* Oak Ridge National Laboratory Datasheet on the Properties of Ceramics.
ELECTRICAL PROPERTIES OF DIAMOND EXCEED THOSE OF OTHER SEMICONDUCTORS

Excepting for electron velocity, the electrical properties of diamond exceed those of virtually all other semiconductors. Table I below provides the details.

Table I. Electrical Comparisons

<table>
<thead>
<tr>
<th>Property</th>
<th>diamond</th>
<th>GaAs</th>
<th>silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap (meV)</td>
<td>5450</td>
<td>1430</td>
<td>1100</td>
</tr>
<tr>
<td>Hole mobility#</td>
<td>1800</td>
<td>400</td>
<td>600</td>
</tr>
<tr>
<td>Electron mobility#</td>
<td>2000</td>
<td>8500</td>
<td>1500</td>
</tr>
<tr>
<td>Resistivity (ohm-cm)</td>
<td>$10^{16}$</td>
<td>$10^9$</td>
<td>$10^3$</td>
</tr>
<tr>
<td>Breakdown (V/cm x $10^6$)</td>
<td>10</td>
<td>6</td>
<td>5</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>5.7</td>
<td>12.5</td>
<td>11</td>
</tr>
<tr>
<td>Work function (eV)</td>
<td>*</td>
<td>4.7</td>
<td>4.8</td>
</tr>
<tr>
<td>High field electron</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>velocity (cm/sec x $10^7$)</td>
<td>2.7</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

# cm$^2$/volt-sec
* 4.8 eV (p-type). Diamond is thought to exhibit a negative electron affinity on its (111) surface.
LISTING/UNDERSTANDING THE PROPERTIES OF BULK IIA DIAMOND IS NOT ENOUGH.

- Natural Diamond Properties Are Quite Variable
- Properties Vary With Crystal Direction
- Polycrystalline Diamond Behaves Still Differently
  - Sintered Compacts
  - Bonded Aggregates/Composites
  - CVD Films
- DLC Has Very Different Properties
  - a-C:H
  - a-C
### Diamond Films and Diamond-Like, Hard Carbon Films Differ Substantially

<table>
<thead>
<tr>
<th>Diamond</th>
<th>Hard Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystalline</td>
<td>Amorphous</td>
</tr>
<tr>
<td>Hardness Material Known</td>
<td>0.1 Hardness of Diamond</td>
</tr>
<tr>
<td>Limited size (few cm²)</td>
<td>Large Areas Possible</td>
</tr>
<tr>
<td>Thickness typically limited to &lt;1mm</td>
<td>Thickness Limited to few μm</td>
</tr>
<tr>
<td>Growth Rate typically 1 μm/hr</td>
<td>Growth Rates of 10's μm/hr</td>
</tr>
<tr>
<td>Grown by Activated CVD</td>
<td>Grown by Plasma and Ion Techniques</td>
</tr>
<tr>
<td>Uniform Properties Possible</td>
<td>Variable Properties/Composition</td>
</tr>
<tr>
<td>Rapidly Moving Technology</td>
<td>Commercial Process</td>
</tr>
</tbody>
</table>
DEFINITIONS

- Natural Diamond
  - Type I - Impurity Absorption edge at 330 nm
    - Ia - Up to 0.3% Nitrogen Aggregated
    - Ib - Up to 0.05% Nitrogen in Single Substitutional Sites
  - Type II - Intrinsic Absorption Edge at 220 nm
    - IIa - Very Low Nitrogen, Insulator
    - IIb - Very Low Nitrogen, Semi-conductor
      - Contains Boron
  - Mixed
    - A Single Crystal May Contain Regions of Several Types
DEFINITIONS

- **CVD Films**
  - Long Range Order (Crystalline)
    - Crystalline Morphology
      - Faceted
      - Diffraction - Single Phase Diamond Structure
    - Raman - Narrow 1332 cm$^{-1}$ Line
      - sp$^3$ Bonding
  - Currently Mostly Polycrystalline
    - Can Contain DLC Phase

- **DLC Films**
  - No Long Range Order
    - Mixed sp$^2$/sp$^3$ Bonding
      - a-C Films Contain Little Hydrogen
      - a-C:H Films Contain 16 a% to 60 a% Hydrogen
        - sp$^3$ Bonding Increases With Hydrogen Content
    - Reportedly Can Contain Crystalline Diamond Phase
HYDROGEN PROMOTES $sp^3$ BONDING

Figure 5

The ratio of $sp^3$ to $sp^2$ sites in a-C:H; The points labeled $\Delta$ are from reference (23), the point labeled $\circ$ from reference (24) and the point labeled $+$ from reference (22). The first two were obtained from NMR measurements, the last one from analysis of the electron energy loss spectrum. The lines are the theoretical expressions for fully constrained, random hydrocarbon networks, i.e., equations (6) and (22). The right hand curve was derived assuming all $sp^2$ carbon atoms are present in single six-membered aromatic rings. The left hand was derived assuming the aromatic clusters contained 76 rings.
HYDROGEN PROMOTES $sp^3$ BONDING

Figure 6

Fraction of carbon atoms with $sp^3$ hybridization versus atomic fraction hydrogen. Conventional underconstrained (floppy) polymers are to the right of the lines. Overconstrained, crystalline or ordered solids are to the left. The data points are for hydrogenated diamondlike hydrocarbons ($a$−C:H). The points $\Delta$ and $\circ$ were obtained by nuclear magnetic resonance$^{23,24}$ and the points $+$ by electron energy loss spectroscopy$^{22}$. $a$−C refers to diamondlike carbons and PAH for polycyclic aromatic hydrocarbons. The point $\Theta$ is for an $a$−C sample reported by Cuomo.$^8$
CHARACTERISTICS OF DLC FILMS

- Tetrahedral bonding, sp³, increases with hydrogen content

- Band gap and optical transmission increase with sp³ bonding/hydrogen content

- Hardness decreases with hydrogen content

- Hardest most dense films have least tetrahedral bonding
  - Hydrogenated (a-C:H) - 16-60 Atom % H
    - Density 1.4 - 2.0 g cm⁻³
    - Hardness 8 to more than 9 on the Mohs Scale

- Non-hydrogenated (a-C) - <1 Atom % H
  - Density up to 3.1 g cm⁻³
    (Diamond = 3.51 g cm⁻³, Graphite = 2.26 g cm⁻³)
  - Hardness reported to equal or exceed diamond

245
Why Use DLC Films?

- Hardness
- Abrasion Resistance
- Friction and Wear
- Corrosion Resistance (Inertness)
- Low Permeability
- Optical Properties
- Electronic Properties
- Large Area Films
- Very Smooth
- Cost
- Excellent Adhesion to Glass, Metals, Plastics etc.
- Adaptable to Manufacturing and Applications
- Combinations of the Above
Structure and Properties of Diamond and Diamond-Like Films

- Introduction
- Natural Ila Diamond (The Standard)
- Importance of Structure and Composition
- Control of Structure and Properties
Diamond Properties Depend On Structure

- Mechanical
- Thermal
- Corrosion
- Optical
- Electronic
EFFECT OF NITROGEN ON MECHANICAL PROPERTIES

Strength, hardness, abrasion resistance of laboratory grade diamond
(after Chrenko and Strong\textsuperscript{20})

<table>
<thead>
<tr>
<th>Diamond</th>
<th>Colour</th>
<th>Nitrogen/ppm atomic</th>
<th>Cleavage/pressure\textsuperscript{a}/GPa</th>
<th>Hardness\textsuperscript{b}/GPa</th>
<th>Abrasion resistance\textsuperscript{c}</th>
</tr>
</thead>
<tbody>
<tr>
<td>70</td>
<td>Yellow</td>
<td>70</td>
<td>20.3</td>
<td>95</td>
<td>0.84</td>
</tr>
<tr>
<td>12</td>
<td>Yellow</td>
<td>20</td>
<td>---</td>
<td>106</td>
<td>1.31</td>
</tr>
<tr>
<td>82</td>
<td>Pale green</td>
<td>~2</td>
<td>24.5</td>
<td>---</td>
<td>1.72</td>
</tr>
<tr>
<td>15</td>
<td>Colourless</td>
<td>~0.3</td>
<td>---</td>
<td>110</td>
<td>3.05</td>
</tr>
<tr>
<td>87</td>
<td>Pale green</td>
<td>~0.1</td>
<td>~30.0</td>
<td>131</td>
<td>3.11</td>
</tr>
</tbody>
</table>

(a) Indentation on a (001) face with a spherical indenter
(b) Vickers indenter on a (001) face, with the diagonals of the indenter parallel to <100> direction.
(c) Grinding wheel test with 70 A\textsubscript{1203} grit and with grinding ratio expressed as volume of wheel wear in m\textsuperscript{3} divided by weight of diamond lost in gm.
HARDNESS AS A FUNCTION OF CRYSTAL FACE AND INDENTER ORIENTATION

Knoop hardness ($H_K$) of diamond - GPa (after Brookes$^{48}$)

<table>
<thead>
<tr>
<th>Plane</th>
<th>Direction</th>
<th>Type I</th>
<th>Type II</th>
</tr>
</thead>
<tbody>
<tr>
<td>(001)</td>
<td>[110]</td>
<td>81.0</td>
<td>89.0</td>
</tr>
<tr>
<td>(001)</td>
<td>[100]</td>
<td>96.0</td>
<td>101.0</td>
</tr>
<tr>
<td>(110)</td>
<td>[110]</td>
<td>86.0</td>
<td>92.0</td>
</tr>
<tr>
<td>(110)</td>
<td>[001]</td>
<td>106.0</td>
<td>113.0</td>
</tr>
<tr>
<td>(111)</td>
<td>[110]</td>
<td>55.0</td>
<td>75.0</td>
</tr>
<tr>
<td>(111)</td>
<td>[112]</td>
<td>62.0</td>
<td>108.0</td>
</tr>
</tbody>
</table>
ABRASION RESISTANCE IS A STRONG FUNCTION OF CRYSTAL PLANE AND DIRECTION OF CUTTING

 Depths of cuts made by bonded wheels, normalised to a depth of 10 \( (\lambda/2) \) in the softest direction (Wilks and Wilks\textsuperscript{54})

<table>
<thead>
<tr>
<th>Plane and Direction</th>
<th>Plane</th>
<th>Dodecahedron (011)</th>
<th>Cube (001)</th>
<th>Octahedron (111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direction</td>
<td>[100] [011]</td>
<td>[100] [110]</td>
<td>[112] [112]</td>
<td></td>
</tr>
<tr>
<td>Depth of cut ( (\lambda/2) )</td>
<td>10.0  1.8</td>
<td>8.5  1.1</td>
<td>3.9  2.1</td>
<td></td>
</tr>
</tbody>
</table>
ABRASION RESISTANCE IS A FUNCTION OF CRYSTAL PLANE AND DIRECTION

Fig. 11.1. The relative depths of cuts when abrading diamond facets near (111). The symbols $^0$ and $x$ correspond to the directions shown in the inset.
CLEAVAGE ON \{111\} DOMINATES FRACTURE

Theoretical cleavage energy for diamond

<table>
<thead>
<tr>
<th>Plane</th>
<th>Angle between plane and (111) plane</th>
<th>Cleavage energy/ J m(^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>0° and 70° 32'</td>
<td>10.6</td>
</tr>
<tr>
<td>332</td>
<td>10° 0'</td>
<td>11.7</td>
</tr>
<tr>
<td>221</td>
<td>15° 48'</td>
<td>12.2</td>
</tr>
<tr>
<td>331</td>
<td>22° 0'</td>
<td>12.6</td>
</tr>
<tr>
<td>110</td>
<td>35°16' and 90'</td>
<td>13.0</td>
</tr>
<tr>
<td>322</td>
<td>11° 24'</td>
<td>13.4</td>
</tr>
<tr>
<td>321</td>
<td>22° 12'</td>
<td>14.3</td>
</tr>
<tr>
<td>211</td>
<td>19° 28'</td>
<td>15.0</td>
</tr>
<tr>
<td>320</td>
<td>36° 48'</td>
<td>15.3</td>
</tr>
<tr>
<td>210</td>
<td>39° 14'</td>
<td>16.4</td>
</tr>
<tr>
<td>311</td>
<td>29° 30'</td>
<td>16.6</td>
</tr>
<tr>
<td>100</td>
<td>54° 44'</td>
<td>18.4</td>
</tr>
</tbody>
</table>

Note: to obtain a fracture surface energy, \(\gamma\), divide by 2.
Structure and Properties of Diamond and Diamond-Like Films

- Introduction
- Natural Ila Diamond (The Standard)
- Importance of Structure and Composition
- Control of Structure and Properties
PROPERTIES OF DIAMOND ARE SENSITIVE TO FILM STRUCTURE AND DEFECTS

• Structure Depends Strongly on Growth Conditions
• Mechanical and Physical Properties Correlate with Structure and Growth Conditions
• Films can be Designed and Grown for Specific Applications
DIAMOND FILM MORPHOLOGIES

PYRAMIDS (a)  MICRO-CRYSTALS (b)  PLATE-LIKE (c)

30µm  6µm  30µm
DATA FOR SAPPHIRE SLIDERS ON DIAMOND FILMS

![Graph showing data for sapphire sliders on diamond films. The graph plots nominal (T/N) against pass number. Three types of structures are compared: pyramids, micro-crystals, and plates.](image-url)
Figure 7. Scanning electron micrograph of a steel cutting chip removed as a steel ball slid against a diamond film with sharp facets.
FRICITION COEFFICIENTS OF DIAMOND AND DLC FILMS

Single Crystal Ila
- Typically 0.5 to 0.15, Except in Vacuum or at High Temperature

CVD Diamond Films
- After some Wear (Wong et al)
  Blocky, <100>  0.3>0.16  0.2
  Pyramidal, <110>  0.04> 0.11  0.035
  Microcrystalline  0.04  0.035

DLC Films - Both a-C:H and a-C
- Reported Values Range From 0.01 to 0.3, (Typically 0.1 to 0.2)
- Friction Coefficients Increase with High Humidity to 0.3 or 0.4
- Films Alloyed with Si Gave Values Near 0.05

- One Report W/O Data Said That Coating "Moving Parts Inside Automotive Engines" With DLC "Successfully Reduced Wear Rates"

Note: All above results depend on details of the test and materials
SOME OBSERVATIONS ON FRACTURE OF DIAMOND FILMS

- CVD Films Usually Fail Transgranularly Implying Strong Grain Boundaries

- Torch Grown Films Usually Fail Intergranularly Implying Weaker Grain Boundaries

- Cracks in Polycrystalline CVD Films Branch Suggesting That They May Be Tougher Than Single Crystals

- Microcrystalline CVD Films Are Slightly Softer and Deform Slightly in Indentation Tests Suggesting That They May Be Tougher Than Coarser Grained Polycrystalline CVD Films
"MICROCRYSTALLINE"

- Mixture of diamond and other bonding types

(-75% sp$^3$)

\[
\begin{array}{cc}
\text{Displacement (nm)} & \text{Displacement (nm)} \\
210 & 210 \\
220 & 220 \\
230 & 230 \\
240 & 240 \\
250 & 250
\end{array}
\]

Hardness = 37 GPa

Elastic Modulus = 370 GPa

(Collins et al)
THIN FILMS: DEPTH OF INDENT RELATIVE TO FILM THICKNESS

- Softer substrate - HCC on glass

![Graph of hardness versus indenter displacement](image_url)
Adherent films
- DLC 10 (sapphire)
- DLC 11 (ALON)

Non-Adherent films
- DLC 2 (sapphire)
- DLC 4 (sapphire)
- DLC 5 (sapphire)
RESULTS FOR DLC FILMS

"HCC" FILMS

<table>
<thead>
<tr>
<th>HARDNESS (GPA)</th>
<th>ELASTIC MODULUS (GPA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>40 - 60</td>
</tr>
<tr>
<td>10</td>
<td>100 - 120</td>
</tr>
<tr>
<td>15</td>
<td>130 - 170</td>
</tr>
</tbody>
</table>

MICROCRYSTALLINE MIXTURE

| 37 | 370 |
SUMMARY

• DLC FILMS

  Substrate properties affect measurements
  Film adherence affects measurements
  Hardness = 5 - 15 GPa
  Elastic modulus = 40 - 170 GPa

• DIAMOND FILMS

  "Hardness" is same as Type IIa (100)
  Elastic Modulus = 1280 GPA = Type IIa
GROWTH CONDITIONS CHANGE STRUCTURE AND THERMAL CONDUCTIVITY

Fig. 3. Thermal conductivity of diamond films for different methane concentrations.

Fig. 4. Raman spectra of diamond films for different methane concentrations.
GROWTH CONDITIONS CHANGE STRUCTURE AND THERMAL CONDUCTIVITY

\[ \kappa \text{ (W/cm}^\circ\text{C)} \]

GROWTH RATE (\( \mu \text{m/h} \))

To be published in
Journal of Applied Physics
The Thermal Conductivity of CVD Diamond Films on Silicon

J. E. Graebner
J. A. Mucha
L. Seibles
G. W. Kammlott

AT&T Bell Laboratories
Murray Hill, NJ 07974
THERMAL CONDUCTIVITY IS BETTER FOR FILMS WITH A NARROW 1332 CM$^{-1}$ RAMAN LINE

![Graph showing thermal conductivity vs. Raman line width](Image)

Figure 4. Thermal conductivity $\kappa(T = 25^\circ C)$ vs. linewidth $\Delta\nu$ of the diamond-like Raman line at 1332 cm$^{-1}$ for the CVD films listed in Table 1. The dashed line is to be published in the Journal of Applied Physics: The Thermal Conductivity of CVD Diamond Films on Silicon.

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THERMAL CONDUCTIVITY OF DIAMOND FILMS CAN BE DIRECTIONAL BECAUSE OF STRUCTURE

Fig. 5 Thermal conductivity vs. temperature for sample A (squares) and B (circles). The thermal conductivity for heat flowing parallel to the plane of the film is given by open symbols, perpendicular by closed symbols. $k_{||}$ for single-crystal Type IIa diamond (Ref. 15) is shown by the dot-dashed line. The intrinsic conductivity of sample B is given by a dashed line, based on a model described in the text.

Anisotropic Thermal Conductivity in CVD Diamond

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B. Bacon*
L. Seibles

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W. Banholzer
General Electric Research Center
Schenectady, N.Y.
THERMAL CONDUCTIVITY OF DIAMOND FILMS CAN BE A FUNCTION OF THICKNESS WHEN THE STRUCTURE CHANGES WITH THICKNESS.

Fig. 4 Measured thermal conductivity, $\kappa_{\text{obs}}$, at 25°C for five samples (squares). The line through the $\kappa_{\text{obs}}$ data is a 3-term polynomial (Eq. 2) least-squares fitted to the data. The dashed curve is the derived local conductivity $\kappa_{\text{local}}$ as a function of position in the sample (Eq. 3). The horizontal dashed line indicates the typical conductivity reported for single-crystal high-quality (Type Ib)
EFFECT OF GRAIN SIZE ON THERMAL CONDUCTIVITY

Unusually High Thermal Conductivity in Diamond Films

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AT&T Bell Laboratories
Murray Hill, New Jersey 07974

J. A. Herb and C. F. Gardinier
Crystallume, Inc.
Menlo Park, CA 94025

Local conductivity at 25°C vs. grain size in CVD diamond films, obtained from Figs. 3 and 4. The solid circles and the dashed curve have the same meaning as in Fig. 4. The horizontal dashed line indicates the typical conductivity reported for single-crystal high-quality (Type IIa) diamond.

Fig. 5
SOME OBSERVATIONS ON OXIDATION OF DIAMOND FILMS

Single Crystal IIa
- Begins to be Significant at 700 C in air or Oxygen
  (100) 0.15 x10^-4 mm min^-1
  (110) 0.8 x10^-4 mm min^-1
  (111) 01.5 x10^-4 mm min^-1

CVD Diamond Films
- Depends on Structure -- Consistent With Single Crystal Data for Good Quality Films
- Microcrystalline Films Oxidize Much More Rapidly (Usually Contain sp^2 material)

DLC Films - Both a-C:H and a-C
- a-C:H Loses Hydrogen and Decomposes Above 400 C
- Estimated to be 10 Times Faster Than CVD Films

Oxygen Plasma Etching seems to follow qualitatively in the same order
Structure and Properties of Diamond and Diamond-Like Films

- Introduction
- Natural Ila Diamond (The Standard)
- Importance of Structure and Composition
- Control of Structure and Properties
TRANSMISSION SPECTRA OF BROAD BAND INFRARED OPTICAL MATERIALS

- CsI (3mm)
- Zinc Selenide (7mm)
- Zinc Sulfide (5mm)
- Gallium Phosphide (5mm)
- Diamond IIA (1mm)

EXTERNAL TRANSMITTANCE vs. WAVELENGTH (micrometers)
Control of Structure and Properties

- Evolution of Microstructures
  - Amorphous
  - Microcrystalline
  - Torched Growth - Porous Material
  - Uniform Non-textured Fine Grained Material??
  - Mixed Size Equiaxed Grains
  - Columnar Textured Structure

- Van der Drift
- Homoeopitaxial Crystals
- Heteroeopitaxial Crystals

- Adhesion/Interfacial Properties
- Planar

- Chemical Bonding
- Cobalt Problem
- Thermal Coefficient of Expansion

- Brazing
- Sintering??
- Mechanical
- Uniformity and Quality Control
DIAMOND FILM MORPHOLOGIES

PYRAMIDS

(b)

PLATE-LIKE

30μm

6μm

30μm
The growth of diamond materials must be controlled to optimize their structure for specific applications.

- Crystal perfection/defects are important to properties.
- Crystal orientation and morphology are also important to the properties.
- Crystal perfection and morphology are functions of growth conditions and can be controlled.

We have made good progress toward this goal.
Hypothesis #1

THE PERFECTION/DEFECTS INCORPORATED INTO THE CRYSTAL STRUCTURE DURING THE GROWTH PROCESS ARE RELATED TO THE STRUCTURE OF THE GROWING CRYSTAL SURFACE.
Hypothesis #2

THE DEVELOPMENT OF TEXTURES IN DIAMOND FILMS IS THE RESULT OF "THE SURVIVAL OF THE FASTEST GROWING CRYSTALLITES."

This is van der Drift's "Principle of Evolutionary Selection" and can explain the development of textured materials.

It serves as a guide for growing selected textures and the surfaces on which growth will occur.
van der Drift's
"Principle of Evolutionary Selection"

- Random nucleation
- Competitive growth
  Nuclei with the fastest growing crystallographic direction direction perpendicular to the substrate envelop and over-grow the less favorably oriented ones.

THIS LEADS TO A TEXTURE (CRYSTALLITE ORIENTATION)
WITH THE FASTEST GROWING DIRECTION PERPENDICULAR TO THE SUBSTRATE.
Fig. 4a. Starting from random-orientated equidistant (10)-bounded “cubic” crystals in a two-dimensional space and assuming infinite surface diffusion even along the substrate, the intercrystal boundaries (dashed lines) as well as the crystal front at different times (at $t = 0$, $t = 5 \Delta t$, and $t = 25 \Delta t$ in which $\Delta t$ is the shortest time required for two neighbouring nuclei to meet one another) are constructed. It is shown how the evolutionary selection leaves the crystals with their ⟨11⟩-direction (arrows) nearly perpendicular to the substrate.
FILMS EXHIBIT TYPICAL PYRAMIDAL "(111)" MORPHOLOGIES

- Cubo-octahedral Crystallites
- Twinned Microstructure

1% methane
1050°C
Cubo-octahedral shapes reveal the ratio of growth rates in the \langle100\rangle and \langle111\rangle directions. The \langle100\rangle/\langle111\rangle value is given.
[111] faces have rough micro-faceted surfaces
[100] faces are smooth
The fractured edge of a free standing film shows the rough faceted surface and the columnar grain structure.
TEM shows ubiquitous twinned structures
At 920°C and below films are microcrystalline.
Microcrystalline material is full of micro-twins and defects.
In a narrow range near 950C square [100] Facets develop
The grains contain no twins or stacking faults
Grainboundary regions included very defective material.
The initial nuclei are randomly oriented cubo-octahedra.
Cub-octahedral shapes reveal the ratio of growth rates in the $<100>$ and $<111>$ directions. The $<100>/<111>$ value is given.
After 20 hours the $<100>$ texture is clearly developed.
X-RAY TEXTURE DIAGRAM FOR DIAMOND FILM GROWN AT 930–950°C USING 1% CH₄ IN HYDROGEN

Si (1,0,0) PARALLEL TO C (1,0.2,0)
Growth Conditions Determine the Internal and External Morphology of Diamond Films

**SEM**

**Microcrystalline**
- smooth surface
- very fine grain size (<0.2 μm)
- poor crystal perfection

900°C

**TEM**

(100) & (111) Facets
- sharp angular faceted surfaces
- grain size of 2-30 μm
- good crystal perfection but twins and stacking faults

1050°C

(100) Facets
- flat, square facets
- grain size of 2-30 μm
- very good crystal perfection, no twins or stacking faults
- grain boundaries contain some less perfect material
- tends to be highly textured

930°C
TEXTURED MATERIAL GROWN WITH BOTH (001) AND 
{111} FACES HAS A CENTRAL VOLUME GROWN FROM A 
(001) FACE SURROUNDED BY MATERIAL GROWN FROM {111} 
FACES.
<100> textured films with (100) facets have smooth surfaces and columnar grains.
It is possible to change the growth conditions to produce a $<100>$ texture with (111) facets.
CVD DIAMOND GROWTH CONDITIONS CAN BE CONTROLLED TO PRODUCE THE FULL RANGE OF CRYSTAL HABITS

\[ R = 0.6 \]

\[ R = 1.7 \]
FILMS CAN BE GROWN WITH A <111> TEXTURE AND LARGE {111} FACETS PARALLEL TO THE SUBSTRATE.
FILMS GROWN WITH THE RATIO OF GROWTH RATES OF THE \(<100>/\langle111\rangle\) NEAR 0.6 PRODUCE \(<111\rangle\) TEXTURED MATERIAL WITH \(\{100\}\) FACETS.
SUMMARY

- Crystal perfection and morphology are functions of growth conditions and can be controlled.

  Crystallite shape indicates the relative rates of growth in the <100> and <111> crystallographic directions

  The van der Drift model predicts texture development

  The growth face is very important to control twinning

- The manipulation of texture and thereby surface morphology and internal crystal perfection is an important step in optimizing CVD diamond films for applications.
SUMMARY

- Unique new Dimond-Like Carbon (DLC) products are possible.
- Some properties of DLC films may approach those of natural diamond.
- Properties are a strong function of structure and hydrogen content and can be controlled over a wide range by the growth processes.
- Hard DLC films are generally limited to a few microns in thickness but are relatively easy to make and can be applied at room temperature to a wide variety of substrates.
SUMMARY

- Unique new CVD diamond products are possible.

- Properties of CVD diamond films can compare favorably with natural diamond.

- Properties are anisotropic, a strong function of structure and crystal perfection (including composition).

- Crystal perfection and morphology are functions of growth conditions and can be controlled.

- The manipulation of texture and thereby surface morphology and internal crystal perfection is an important step in optimizing CVD diamond films for applications.
Control of Structure and Properties

- Evolution of Microstructures
  - Amorphous
  - Microcrystalline
  - Torch Grown - Porous Material
  - Uniform Non-textured Fine Grained Material
  - Mixed Size Equiaxed Grains
  - Columnar Textured Structure
    - Van der Drift
  - Homoepitaxial Crystals
  - Heteroepitaxial Crystals

- Adhesion/Interfacial Properties
  - Planar
    - Chemical Bonding
      - Cobalt Problem
    - Thermal Coefficient of Expansion
  - Brazing
  - Sintering

- Mechanical

- Uniformity and Quality Control
SUMMARY

- Unique new Dimond-Like Carbon (DLC) products are possible.

- Some properties of DLC films may approach those of natural diamond

- Properties are a strong function of structure and hydrogen content and can be controlled over a wide range by the growth processes

- Hard DLC films are generally limited to a few microns in thickness but are relatively easy to make and can be applied at room temperature to a wide variety of substrates.
SUMMARY

- Unique new CVD diamond products are possible.
- Properties of CVD diamond films can compare favorably with natural diamond.
- Properties are anisotropic, a strong function of structure and crystal perfection (including composition).
- Crystal perfection and morphology are functions of growth conditions and can be controlled.
- The manipulation of texture and thereby surface morphology and internal crystal perfection is an important step in optimizing CVD diamond films for applications.
Potential Transportation Applications for Diamond Films

Robert A. Hay and Patrick M. Stephan
Norton Diamond Film
Northborough, MA
Overview of Diamond Films and Diamond-Like Coatings

Freestanding or Thick Film Diamond
Size
Properties
Overview of Diamond Films and Diamond-Like Coatings

Geometric Capability
Size Capability
Substrate Selection
Overview of Diamond Films and Diamond-Like Coatings
<table>
<thead>
<tr>
<th>Substrate</th>
<th>CVD Diamond</th>
<th>DLC</th>
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</thead>
<tbody>
<tr>
<td>Silicon Nitride</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Silicon Carbide</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Aluminum Oxide</td>
<td>No</td>
<td>Maybe</td>
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<tr>
<td>Steels</td>
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<td>Yes</td>
</tr>
<tr>
<td>Tungsten Carbides</td>
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<td>Yes</td>
</tr>
<tr>
<td>Other Carbide Formers</td>
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<td>Yes</td>
</tr>
<tr>
<td>Glass</td>
<td>Maybe</td>
<td>Yes</td>
</tr>
</tbody>
</table>
Characteristics of Diamond Films

- High Hardness (Wear Resistance)
- High Stiffness
- High Corrosion Resistance
- Low Mass
- High Thermal Conductivity
- Low Friction Coefficient
- Thermal Stability
- Thermal Shock Resistance
- Low Thermal Expansion
# Properties

<table>
<thead>
<tr>
<th>Properties</th>
<th>Natural Diamond</th>
<th>CVD Diamond</th>
<th>PCD</th>
<th>DLC</th>
<th>Tungsten Carbide (ISO K10)</th>
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<td>Hardness GPa</td>
<td>56-102</td>
<td>70-100</td>
<td>50-80</td>
<td>25-50</td>
<td>18</td>
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<tr>
<td>Young's Modulus GPa</td>
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<td>630</td>
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<td>Thermal Conductivity W/m K</td>
<td>600-2000</td>
<td>600-1400</td>
<td>560</td>
<td>-</td>
<td>110</td>
</tr>
<tr>
<td>Temperature Limit Deg. C</td>
<td>600-650</td>
<td>700</td>
<td>600</td>
<td>200-400</td>
<td>600</td>
</tr>
</tbody>
</table>
Potential Benefits

- Longer Component Life
- Fuel Savings
- Noise Reduction
- Better Thermal Management
- Higher Package-Specific Output
Potential Component Applications for Diamond Films

- Valve Train Components
- Piston Rings
- Piston Pins
- Cylinder Liners
- Gears
- Window Coatings
- Fuel Nozzles

- Brakes
- Bearing Surfaces
- Low Friction Pads
- Heat Sinks
How Do We Get There From Here?

Diamond Thin Film, Nozzles, Valve Train
Diamond-Like Coating, Gears, Valve Train
Freestanding Diamond, Nozzles, Heat Sinks
How Do We Get There From Here?

- Surface Characteristics
- Adhesion Strength
- Wear Resistance
- Temperature Capability
- Thickness and Coverage
How Do We Get There From Here?

Benefits Analysis
Cost/Price Relationships
Barriers Analysis
Technical Feasibility
Technical Issues
- Nucleation on different substrates
- Adherence
- Film growth mechanisms
- Film structure and quality

Scale-up
- Large sizes
- Complex shapes

Other
- System capacity
- Growth rates
- Handling systems
Conclusions

Three Viable Technologies
Need considerable amount of development
Near-term commercial applications
Panel 1 - Comparative Evaluation of Deposition Technologies

Panel Members:

Chairman: George R. Fenske, Argonne National Laboratory

David K. Benson  National Renewable Energy Laboratory
Deepak Govind Bhat  GTE Valenite Corporation
Yu-Lin Chen  Allison Gas Turbine Division, GM
Roy Gat  Case Western Reserve University
Mike Kelly  Stanford University
James E. Lawler  University of Wisconsin
Dennis C. Nagle  Martin Marietta Labs.
Duane Outka  Sandia National Laboratories
Roland J. Pitts  Natl. Renewable Energy Laboratory
Gopal Subray Revankar  Deere & Co.
Frank Stodolsky  Argonne National Laboratory
Vish V. Subramaniam  Ohio State University
Mahendra Kumar Sunkara  Case Western Reserve University
Paul J. Wilbur  Colorado State University
Ming-Show Wong  Northwestern University
William E. Woolam  Southwest Research Institute

This working group attempted to evaluate/compare the different types of deposition techniques currently under investigation for depositing diamond and diamond-like carbon films. Table I lists the broad types of techniques that were considered for depositing diamond and diamond-like carbon films. After some discussion, it was agreed that any evaluation of the various techniques would be dependent on the end application. Thus the next action was to list the different areas where diamond and DLC films could find applications in transportation. These application areas are listed in Table II. Table II intentionally does not go into great detail on applications because that subject is dealt with specifically by Panel #4 - APPLICATIONS TO TRANSPORTATION. The next action concentrated on identifying critical issues or limitations (see Table III) that need to be considered in evaluating the different processes. An attempt was then made to rank different broad categories of deposition techniques currently available or under development based on the four application areas (Table II) and the limitations (Table III). These rankings/evaluations are given in Tables IV and V for diamond and DLC techniques, respectively. Finally, the working group tried to identify critical development and research issues that need to be incorporated into developing a long-term program that focuses on diamond/DLC coatings for transportation needs.
Deposition Technologies

Techniques for depositing diamond and diamond-like-carbon films are listed in Table I. For diamond films, CVD processes that were considered include: laser-assisted, hot-filament, plasma-assisted (microwave), and halogen-based CVD. Two other techniques considered were combustion-flame processes and plasma (arc)-jet processes. While this is not a complete list of all of the techniques/processes (and variants thereof) known to be under investigation for depositing diamond films, the working group felt that these were the more prominent ones and that techniques/processes not listed (e.g. biased hot-filament, low- or high-pressure rf-discharge, etc.) would be similar to those listed. For example, the LANL process, currently under development to combine hydrogen and carbon at elevated temperatures in a fluidized-bed reactor to deposit diamond coatings would come under the combustion-flame process in Table I.

Techniques for producing DLCs are also listed in Table II. Again, not all processes are listed. The DLC processes are primarily based on PVD and energetic-beam technology (or combinations of both).

Application Areas

The first action was to list the different areas where diamond and DLC films could find applications in transportation. These application areas are listed in Table II. Table II intentionally does not go into great detail on applications because that subject is dealt with specifically by Panel #4 - APPLICATIONS TO TRANSPORTATION. The first application area on thermal management takes advantage of the high thermal conductivity of diamond films to help dissipate heat generated either by mechanical means (e.g. brakes or cutting operations), or ohmic heating (high-power-density electronic components). It was also noted that diamond/DLC films could be used to control the thermal loading of the interior compartment by controlling the amount of light transmitted.

The second application area identified, Optics, is concerned with the use of diamond (and perhaps DLC) films as optical coatings for windows.

The third area deals not only with the use of diamond/DLC films in end-use tribological applications (e.g. cylinder liners, fuel injectors, etc.), but also with manufacturing practices (e.g. machining, etc. of components)

The fourth application area deals with using diamond/DLC coatings in fabricating sensors used in transportation, e.g., pressure, temperature, and emission sensors.
Comparative Limitations

The discussion in this section focused on determining the critical factors that need consideration in ranking/evaluating the different processes listed in Table I for the application areas listed in Table II. Substrate preparation refers to special pre-deposition treatments (such as scratching the surface with diamond or some other abrasive material) to enhance the nucleation of diamond crystals during the initial stages of film growth. While these steps may be required for diamond films, they are not required for DLCs. Growth rates may also be a limiting factor for some of the processes (e.g. PA-CVD) but not for others (Arc-Jet). The size of the component for currently available diamond techniques may be an issue depending on the application, but not necessarily for many of the DLC processes which are more mature.

Substrate deposition temperature is currently a major limiting factor for most diamond deposition processes (depending on what one would consider as being an acceptable growth rate). Deposition temperatures below the annealing temperature of steel components are highly desirable. Cost is always a critical factor particularly if these techniques will be used in treating components produced in large quantities. Surface finish is another critical factor particularly for tribological applications that demand smooth surfaces to prevent severe wear of the mating surface. In some instances (e.g. material cutting, grinding, etc.), however, a smooth surface may not be as critical.

The maximum thickness that can be deposited may be critical depending on the process and type of film (diamond or DLC). Thick diamond coatings (in excess of 3-4 mm thickness) are commercially available today. For DLCs, the thickness is usually less than several micrometers.

Adhesion is another critical factor that limits applications. If the coating does not adhere to the surface under typical operating conditions, the coating is useless. Adhesion appears to be more of an issue for diamond coatings than for DLCs. Diamond films are often difficult to nucleate and grow on all but a few materials (typically strong carbide formers), while DLCs can be applied on a wider range of materials particularly if an intermediate bond-coat is employed.

Thermal conductivity is not a limiting factor for diamond films; in fact the thermal conductivity of diamond films is one of its outstanding properties. DLCs on the other hand, because of their amorphous nature, have very poor thermal conductivities, and thus are inappropriate for thermal-management applications.

The geometry limitation in Table III refers to the capability of the different techniques to coat components with complicated shapes. Line-of-sight processes such as the ion-beam techniques would have difficulty coating interior surfaces. CVD processes on the other hand may be more appropriate for interior surfaces provided activated species can be transported to the interiors.

Finally, thermal oxidation of the coatings needs to be considered. Diamond films are stable up to temperatures of approximately 800°C (depending on the environment) while DLCs start to crystallize (to graphite) at temperatures above 300-400°C.
Ranking/Evaluations

Tables IV and V summarize the ranking of the different techniques identified in Table I for the 4 application areas listed in Table II. The critical limiting factors that the working group members felt were crucial in evaluating the different techniques are listed for each application area. For thermal-management applications, the limiting factors include: growth rates, substrate temperatures, cost, thermal conductivity, and thermal oxidation. Based on these factors, the group felt that the Arc-Jet technology is most promising as a proven technology for thermal-management applications. Plasma-assisted CVD (microwave) and hot-filament CVD processes were rated as the next two most promising proven technologies. The columns denoted by "Pot" denote technologies (PA-CVD, halide-assisted CVD, and Arc-Jet) that the group felt had significant potential for thermal-management applications.

For optics applications, the more promising, proven technologies include PA-CVD, Arc-Jet, and HF-CVD, while halide-CVD and combustion-flame processes offer potential.

Under tribological applications, PA-CVD, Arc-Jet, and HF-CVD were noted as most promising techniques (these three techniques are the most mature of the different techniques listed, and thus it is not surprising to see them listed in the top of the "Proven" processes). PA-CVD was listed as having potential because it may be possible to form cubic BN films. Halide-based CVD techniques were also listed as having potential because of their potential ability to deposit films at low substrate temperatures.

For sensor applications, the PA-CVD and HF-CVD were noted as being the most promising proven technologies. Arc-Jet technologies were not considered because of high deposition temperatures. Laser-assisted CVD techniques have potential because of their ability to develop complex diamond patterns that may be incorporated into the sensors.

The results of the ranking exercise for DLC processes are given in Table V. Because of the poor thermal conductivity and thermal oxidation properties of DLCs, it was felt that these types of films (and hence their deposition processes) should not be considered at all for thermal management and sensor applications. Consequently, all of the processes listed in Table V received a "0", signifying that they should not be considered. For optical coatings, sputter-deposition techniques were considered to be very mature, and thus were rated as most promising of the proven technologies. Ion-assisted techniques and PA-CVD were also noted as being promising "proven" processes.

For tribological applications, all of the processes, with the exception of laser-ablation-PVD appeared to be equally promising as proven technologies.

Recommendations:

After evaluating the different processes for depositing diamond and DLC coatings, the working group attempted to identify key issues that need to be addressed in furthering the utilization of diamond and DLC films in transportation applications. These issues fell into one of two categories: one dealing with research issues and the other dealing with technology-development issues.
The research issues that need to be addressed in bringing diamond and DLC coating technologies to the point where they can solve the thermal-management, optic, tribological, and sensor needs of advanced transportation systems are as follows:

1) Growth Rates: The growth rates of the current processes used to produce diamond and DLC films are not sufficiently high to make them economically attractive for transportation applications. Growth rates are typically on the order of several micrometers per hour (with the exception of plasma arc-jet processes). Increases in the range of two to three orders of magnitude are needed.

In order to increase the overall growth rates of the deposition processes, research is needed to understand the nucleation and growth of diamond and DLC films and how the multitude of process parameters influence these processes.

2) Substrate Temperature: The substrate temperatures required for diamond-film growth are too high for many materials. Typical deposition temperatures for diamond films are in the 800 to 1000°C range. Deposition temperatures (without reduced growth rates) below 400 to 500°C are desirable for use on heat-treated steel components (assuming adherent diamond coatings can be deposited on steels).

Research on nucleation and growth at low substrate temperatures is needed to address this issue.

3) Adhesion: Adhesion is a critical factor that limits the application of diamond films. A general (but not necessarily sufficient) criterion for good adhesion is to use a material that is a strong carbide former (iron and steels are an exception).

Research is needed to identify the properties that determine the adhesion of diamond films and how the different deposition processes can be modified to improve the adhesion of diamond and DLC films.

4) Surface Finish: Polycrystalline films deposited by many of the techniques listed in Table I are comprised of faceted crystals. The resulting surfaces can be rough and thus unacceptable for some applications. Research on the nucleation and growth mechanisms of diamond films would provide information on controlling the surface roughness. Post-deposition surface-finishing procedures may offer an alternative approach to obtain the desired surface morphology.

Once the technological barriers have been overcome, a number of process-development issues need to be addressed. These issues include:
1) Scalability: Can the desired process be scaled up in size to coat not only prototypic components, but also eventually be adapted for long-term and potentially high-volume manufacturing runs?

2) Controllability: Is the desired process controllable, and if so what are the critical process parameters that need to be monitored and controlled?

3) Cost/Marketability: Can the cost be brought down to reasonable levels acceptable to industry? Precisely what are the markets for these diamond/DLC film processes?

Summary:

Within the time allotted, a number of practical deposition processes that currently exist for forming diamond and DLC coatings were evaluated with respect to 4 application areas (thermal management, optics, tribology, and sensors). The group identified a number of promising technologies that currently exist for diamond-film deposition. These include processes based on hot-filament and microwave-plasma CVD and arc-discharge. For DLC coatings, it was noted that this is a relatively more mature field in terms of processes than the deposition of diamond films. There are a number of applications where DLCs are routinely used, particularly in the magnetic recording field. It was also noted that although the group considered 4 application categories in assessing the different processes, a more thorough assessment needs to be performed for each specific application once it has been identified.

The group also noted that there are a number of significant differences between diamond and DLC coatings that place limitations on the end-use of these coatings. Notable are the low thermal-conductivity and thermal-oxidation properties of DLCs compared to diamond films that limits the applicability of DLCs for sensors and thermal management. The surface roughness of DLCs make them very attractive for tribological applications compared to diamond films.

It was further noted that new/novel processes and deposition chemistries (e.g. halogen-assisted CVD) need to be explored particularly for diamond-film deposition.

Specific development and research goals were identified. Research and development effort is strongly needed to obtain higher growth rates, to lower the deposition temperature, improve the surface roughness, and the adhesion of diamond and DLC films.
**TABLE I: Deposition Techniques**

**Diamond Films**

Chemical Vapor Deposition Processes

- laser assisted CVD (LA-CVD)
- hot filament CVD (HF-CVD)
- plasma-assisted (micro-wave) CVD (PA-CVD)
- halogen activated CVD (hal-CVD)

Combustion Flame (FLAME)

Plasma (Arc-Jet)

**Diamond-Like Carbon Films**

Physical Vapor Deposition

- electron-beam evaporation (EB-PVD)
- sputtering (SPT-PVD)
- CVD (CVD-PVD)
- laser ablation (LA-PVD)

Ion-Beam Deposition (IBD)

Ion-Assisted Deposition (IAD)

Plasma-Assisted CVD (PA-CVD)
### TABLE II: Transportation Application Areas

1) **Thermal Management**
   - heat dissipation (hot spots)
   - electronic components (high power density)
   - heat loading through windows
   - manufacturing (cutting tools)

2) **Optics**

3) **Tribology**

4) **Sensors** (e.g., mechanical devices to measure pressures and temperatures)
<table>
<thead>
<tr>
<th></th>
<th>PCDs</th>
<th>DLCs</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>substrate preparation (nucleation)</td>
<td>x</td>
</tr>
<tr>
<td>B</td>
<td>growth rates</td>
<td>x</td>
</tr>
<tr>
<td>C</td>
<td>component size</td>
<td>x</td>
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<td>D</td>
<td>substrate temperature</td>
<td>x</td>
</tr>
<tr>
<td>E</td>
<td>cost</td>
<td>x</td>
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<tr>
<td>F</td>
<td>surface finish</td>
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<tr>
<td>G</td>
<td>maximum coating thickness</td>
<td>x</td>
</tr>
<tr>
<td>H</td>
<td>adhesion</td>
<td>x</td>
</tr>
<tr>
<td>I</td>
<td>grain-size, crystallites, heteroepit.</td>
<td>x</td>
</tr>
<tr>
<td>J</td>
<td>thermal conductivity</td>
<td>x</td>
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<tr>
<td>K</td>
<td>geometry</td>
<td>x</td>
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<tr>
<td>L</td>
<td>thermal oxidation</td>
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**TABLE III: Comparative Limitations**
**TABLE IV: Ranking of Diamond-Deposition Processes**

<table>
<thead>
<tr>
<th>Thermal-Magmmt</th>
<th>Optics</th>
<th>Tribology*</th>
<th>Sensors</th>
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</thead>
<tbody>
<tr>
<td>(B, D, E, J, L)</td>
<td>(F, G, H, I)</td>
<td>(C, D, F, H, K, L)</td>
<td>(H, J, L)</td>
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<tr>
<td>Prvn**</td>
<td>Pot**</td>
<td>Prvn</td>
<td>Pot</td>
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<tr>
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<td>-----</td>
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</tr>
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<td>PA-CVD</td>
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<td>*</td>
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<td>hal-CVD</td>
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<td>FLAME</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Arc-Jet</td>
<td>1</td>
<td>*</td>
<td>1.2</td>
</tr>
</tbody>
</table>

*Also includes wear-resistant coatings for optics.

**“Prvn” – refers to proven technologies for specified field.
“Pot” – refers to technologies that have significant potential in specified field.

*Denotes technologies that have potential.
### TABLE V: Ranking of DLC-Deposition Processes

<table>
<thead>
<tr>
<th>Thrml-Mngmnt</th>
<th>Optics</th>
<th>Tribology</th>
<th>Sensors</th>
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<tbody>
<tr>
<td>[B. D. E. J. L]</td>
<td>[F. G. H. I.]</td>
<td>[C. D. F. H. K. L]</td>
<td>[H. J. L]</td>
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<tr>
<td>Prvn</td>
<td>Pot</td>
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<td>CVD</td>
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<td>0</td>
<td>-</td>
</tr>
<tr>
<td>LA-PVD</td>
<td>0</td>
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<tr>
<td>IBD</td>
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<td>D</td>
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</tr>
<tr>
<td>PA-PVD</td>
<td>0</td>
<td>0</td>
<td>2,</td>
</tr>
</tbody>
</table>

*A '0' denotes these techniques should **not** be considered.
**Refers to technologies that have potential.
aProtective coatings for low-heat-load windows.
bIR windows.
Panel 2 – Properties of Diamond and Diamond-like-Carbon Films

Panel Members:

Chairman: P. J. Blau, Oak Ridge National Laboratory

- O. O. Ajayi, Argonne National Laboratory
- P. F. Bartelt, Deere & Co.
- R. H. Baughman, Allied Signal
- B. Bhushan, Ohio State University
- R. E. Clausing, Oak Ridge National Laboratory
- C. V. Cooper, United Technologies Research Center
- M. T. Dugger, Sandia National Laboratories
- A. Freedman, Aerodyne Research, Inc.
- J. Larsen-Basse, National Science Foundation
- Y. Y. Liu, Argonne National Laboratory
- N. R. McGuire, Caterpillar
- R. F. Messier, Penn State University
- G. L. Noble, John Crane, Inc.
- M. H. Ostrowski, John Crane, Inc.
- A. Purohit, Argonne National Laboratory
- B. D. Sartwell, Naval Research Laboratory
- R. Wei, Colorado State University

Goals of this Panel

This panel attempted to identify and prioritize research and development needs in determining the physical, mechanical and chemical properties of diamond and diamond-like-carbon films (D/DLCF). Three specific goals were established. They were:

1. To identify problem areas which produce concern and require a better knowledge of D/DLCF properties.
2. To identify and prioritize key properties of D/DLCF to promote transportation applications.
3. To identify needs for improvement in properties-measurement methods.

Each of these goals is addressed subsequently.

Problem Areas

Problem areas delineated by the panel were identified as being either short-term (ST) issues (urgent needs), long-term (LT) issues (requiring significant times for effective solution), or as having elements of both (S/LT). These problem areas are summarized as follows:
There was general agreement that there is a need for specific guidance from the transportation industry (i.e., engine manufacturers, parts manufacturers, materials suppliers) as to which specific properties need to be improved. This guidance is critical for those developing new methods to produce D/DLCF. [ST]

A need was expressed for a comprehensive data base for the properties of D/DLCF. This activity should begin at once and be continued as the technology matures. [S/LT]

There is a lack of standard tests (e.g., ASTM test methods) for use to determine the properties of D/DLCF. [S/LT]

Standard reference materials on which to validate D/DLCF property-measurement methods are not available but should be developed. [ST]

There is a need for better quality-control (QC) methods which can use one or two key properties to qualify products for use. Often it is not possible, economically and/or technically, to perform a large number of tests on each lot of material. Key QC tests, which are well-correlated to performance, should be developed. [S/LT]

Considerations Bearing on Problem Areas

There was a sense that certain factors affect the degree to which government laboratories should be involved with industrial efforts to promote and develop D/DLCF technology. There considerations included the following:

1. There is no question that property requirements will be driven by end use. Applications information arising from the other panels should be considered in setting priorities.

2. Pending the identification of specific target applications, R&D should be directed at generic technical issues.

3. Research is needed to link D/DLCF properties with their microstructures and the underlying mechanisms of material behavior.

4. Combinations of key properties may be more important than individual properties alone.

5. The properties of D/DLCF must be taken in the context of a total materials system which contains the substrate-material properties as well.

Prioritization of Needs for D/DLCF Properties

A poll of the panel members indicated the following order (1=highest) of importance in properties determination for D/DLCF used in transportation applications:
1. tribological properties
2. mechanical properties
3. thermal properties
4. chemical properties
5. electro/optical properties.

It is recognized that the above priorities may be different for specific applications (for example, thermal management for circuit chips may rank much higher in regard to automotive microcomputer-system needs). Therefore, the list resulted from a consensus on applicability to the general area of transportation technology.

There was an attempt to further break down the top two properties needs on the above list into more specific areas. Those tribology areas receiving at least three votes from panel members were the following:

<table>
<thead>
<tr>
<th>Subject</th>
<th>No. of Votes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. friction</td>
<td>13</td>
</tr>
<tr>
<td>2. wear</td>
<td>13</td>
</tr>
<tr>
<td>3. better surface-morphology...</td>
<td>10</td>
</tr>
<tr>
<td>4. rolling-contact-fatigue...</td>
<td>5</td>
</tr>
<tr>
<td>5. lubrication of D/DLCF</td>
<td>4</td>
</tr>
<tr>
<td>6. scuffing-reduction properties</td>
<td>3</td>
</tr>
</tbody>
</table>

Similarly, mechanical-properties areas receiving the most votes were as follows:

<table>
<thead>
<tr>
<th>Subject</th>
<th>No. of Votes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. adhesion</td>
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<tr>
<td>2. hardness</td>
<td>8</td>
</tr>
<tr>
<td>3. residual stress</td>
<td>4</td>
</tr>
<tr>
<td>4. fracture toughness</td>
<td>3</td>
</tr>
<tr>
<td>5. elastic properties</td>
<td>2</td>
</tr>
</tbody>
</table>

Prioritization in Needs for Better Properties-Measurement Methods

There were five areas in which better D/DLCF properties-measurement methods were felt to be needed. These are:
1) Better methods for reporting (i.e., improved completeness of methodology) are needed for friction and wear data, including the more consistent use of units.

2) Several areas of adhesion testing were identified as being significant. These included development of standard reference materials for adhesion testing, better means to develop quantitative rankings, more repeatable and reproducible methods for adhesion testing, better methods to discriminate between shear and tensile properties of D/DLCF, and better tests for scratch, pull, bend, bulge and indentation.

3) Thermal-conductivity test methods should be developed aimed at specific applications (as ASTM test methods). Special test methods are needed for films under 0.1 micrometer in thickness.

4) The hardness of thin films is very difficult to measure. New methods to prepare surface for hardness tests without altering properties should be developed.

5) Indentation fracture-toughness testing methods have serious drawbacks. Improved methods for D/DLCF are needed.

**Recommendations**

In summary, Panel #2 on Properties had the following recommendations:

1. Properties data for D/DLCF cannot stand alone. Data must be accompanied by an understanding of materials fundamentals.

2. Special techniques, tailored for measuring the properties of D/DLCF, are urgently needed. Some of these techniques should be standardized, for example, as ASTM test methods, and reference materials to validate new standard test methods are needed as well.

3. The panel recommended establishing an initial round-robin program to develop a D/DLCF properties database.

4. Tribological behavior, mechanical properties, and thermal properties have high priority for D/DLCF in transportation applications. A series of specific property rankings were developed.
Panel 3 - Characterization

Panel Members:

**Chairperson**: Robert A. Erck, Argonne National Laboratory

- Ali Erdemir, Argonne National Laboratory
- Albert Feldman, Natl. Inst. of Standards and Technology
- Jeffrey T. Glass, North Carolina State University
- Jang-Hsing Hsieh, Argonne National Laboratory
- Rick Kleimer, Coors Ceramics
- Emil A. Lawton, JPL/Caltech
- Richard H. Lee, Argonne National Laboratory
- Carl J. McHargue, Univ. of Tennessee-Knoxville
- Xian Zheng Pan, Argonne National Laboratory
- Diane E. Peebles, Sandia National Laboratory
- Deming Shu, Argonne National Laboratory

This task of this panel was to identify and prioritize needs in the area of characterization of diamond and diamond-like-carbon (DLC) films for use in the transportation industry. Diamond has been extensively studied for many years, and DLC has been known and studied for two decades. Until recent advances in producing diamond and DLC films that were both inexpensive and suitable for covering large areas, it was not considered feasible that these materials could be mass-produced.

The physical properties of diamond have been well characterized. However, because diamond and DLCs have been extremely expensive and difficult to produce, especially in large quantities or over large areas, little work has been done to apply these materials to non-traditional applications. Thus, little work was done (aside from diamonds for abrasive applications) on investigating and determining how best to apply diamond and DLCs to solving problems in transportation technology. The deposition technologies (e.g., CVD diamond) are themselves very new, and much more work needs to be done on understanding how the processes operate on the molecular scale.

After some discussion, it was agreed that the Characterization panel should restrict itself to identifying needs in areas that would be of most use to manufacturers and users in producing and utilizing diamond and DLC coatings in industry. These characterization needs include:

1) in-situ monitoring during growth

2) relation of structure to performance

3) standards and definitions

The performance of any diamond or DLC surface depends critically on the properties of the surface of the film, the film itself (bulk), any interfaces that are contained in the film or between film and substrate, and the substrate. The Panel addressed three questions.
were some of these general systems that needed to be characterized, why is the information needed, and how will this information be obtained? Table I is a summary list of items identified by the Panel.

The Panel intentionally avoided discussing specific properties of diamond and DLC films; that topic is dealt with by Panel #2, Properties of Diamond and Diamond-Like Carbon. Nor did the Panel enumerate the various techniques for deposition; these are addressed by Panel #1, Comparative Evaluation of Deposition Technologies.

For any successful commercial utilization of diamond and DLC films, it was thought vital to be able to know which parameters are critical for the maintenance of quality and reproducibility during deposition. In addition, any practical production process will require in-situ monitoring of the deposition process. Without real-time “feedback,” quality during manufacturing is put in jeopardy. Thus, the Panel placed emphasis on process control, and on determining the relation between measured parameters, structure and performance. The following section lists some of the concerns expressed by panel members.

- It was felt that the characterization question should span the range from fundamental to applied. Fundamental research was needed to determine which parameters (and thus which techniques) would give the most useful (significant) information about the control of a particular technique. Applied research was needed to relate properties to performance during use.

- Characterization methods should be developed which allow monitoring the growing film during deposition. Because practical CVD methods of growing diamond and DLC films have only recently been discovered, the kinetics of these interactions, especially gas-gas and gas-solid interactions, is just beginning to be understood. It became clear that any practical deposition technology involves understanding and controlling reactions between molecular and atomic species existing in the gas phase and between the gas phase and the surface. Thus, the characterization task requires a means of measuring properties of molecular, atomic or excited species, and characterizing the interactions between these species and the growing surface.

- Any practical use of diamond and DLC coatings under mechanically loaded conditions will require good adhesion of the film to the substrate. A film that detaches will be worthless. Diamond’s thermal-expansion coefficient is a poor match to many common engineering materials, and good adhesion is necessary for film integrity under thermal cycling. At present, good bonding of diamond can be obtained to only a few classes of materials. Thus a means of assuring film/substrate bonding is needed, as well as a way of controlling film stresses during growth.

- It was emphasized that characterization techniques can be classified as destructive or non-destructive. For process monitoring, suitable non-destructive tests need to be developed.
A suitable characterization technique must be sensitive to the parameter or parameters that critically affect the performance of the product. Much work is still needed to clearly understand which characterization techniques would be most appropriate to study the particular film property to be measured. For example, Raman spectroscopy is highly sensitive to graphite impurities that are sometimes found in diamond films grown by CVD techniques. Thus, Raman spectroscopy would be extremely useful as a characterization tool if knowledge or control of the presence or absence of graphite were critical. However, if film properties were found to be critically related to grain size, for example, and the presence of graphite was immaterial, then Raman would be unsuitable. A characterization technique sensitive to grain size would need to be found.

A clear need was felt for the development of basic and applied understandings of the chemistry and structure of diamond and DLC films in order to engineer specific (desirable) properties. Many of the basic physical properties of these materials are well-measured and understood. However, because diamond and DLCs have been very expensive and difficult to produce, especially in large quantities or over large areas, it was never thought practical to apply these materials on a large scale to manufactured parts. Thus, little work has been done on understanding diamond and DLC films in terms of those specific properties useful for application to transportation. Thus, a gap in knowledge was seen in the relation of chemistry and structure to properties such as wear resistance, friction or compatibility with other materials.

For any production of diamond and DLC films on a commercial scale, some reliable and robust means of monitoring and feedback will need to be developed for use during production. At the present time, we lack knowledge and tools to monitor and characterize the production of films of diamond and DLC in-situ. This includes both monitoring of film nucleation and monitoring of growth. The initial nucleation of the film will be a critical step, so that characterization and feedback may be necessary to attain acceptable yields. It was thought that deposition rates would probably be slow and that some means of assuring film quality in-situ would be necessary to avoid lengthy deposition of a fatally flawed film.

Much additional work and understanding are needed to relate structure to performance. The term structure was not restricted to physical structure, but also includes chemical composition and impurities. The panel included in the "performance" category not only tribological aspects such as wear, environmental and high-temperature properties, but also radiation resistance and electrical properties. Information is needed about not only the film itself, but also about the surface, interfaces and substrate, as shown in Table I.

An experimental means of adhesion testing that is reproducible is needed for diamond and DLC films. However, no widely accepted direct means of testing thin films in general exists, making this challenge more difficult. A non-destructive means of ascertaining film adhesion would be ideal. An indirect test, in which a particular property that is related to adhesion is measured may be one way of approaching the problem, but much work needs to be done in this area.
• The extent of the information database for diamond, and especially DLC, is still very limited. It was speculated that some of the data published to date may have been obtained under poorly controlled conditions as researchers initially strove to understand the new deposition processes. A strong desire was expressed by panel members representing industry for a study and compilation of a database concerning critical process parameters and performance. It was felt that a published database, perhaps similar to the ACTIS tribology database, would be useful.

• A strong need for standards and standardized characterization procedures was felt. At present, no industry-wide specifications or procedures seem to have been developed for diamond or DLC that were designed for use by the transportation industry. A need exists for specifications that are practical and useful and that facilitate meaningful communication between all parties. Materials standards for microelectronic and thermal-management application were known to be available, but these were thought to be unsuitable as standards for tribological use. There was no consensus, though, as to which organization or organizations should be responsible for producing the standards.

• In addition to standards, it was felt that a round-robin testing program should be initiated, similar to the programs developed to characterize other materials. The results would be compared and potential problems identified. This would aid in assuring high standards and consistency.

• The topics of surface roughness, its effect on wear and friction, its means of measurement, and ways to polish diamond, were raised. It was felt that this topic was more properly addressed by Panel #2, Properties of Diamond and Diamond-Like Carbon.

• A film of high "quality" is always desirable. However, a good working definition of quality for various applications does not exist, although this term is often used in the area of diamond and DLC films. This lack of a good definition is particularly evident for DLCs, which, because very little is known about their atomic structure, poses greater challenges for understanding the relationship of structure to properties. It was felt that any definition of quality of a film must take into account not only bulk properties such as structure, composition, phase distribution, residual stresses, and so on, but also adhesion of the film to the substrate.

• Another parameter that affects film performance is the relative amount of $sp^2$ and $sp^3$ bonding and the hydrogen content of a DLC film. The performance of DLC films is poorly known in relation to these quantities, and means to measure these properties are not readily available.

• Because no transportation industry can afford to invest in all possible characterization tools, panel members felt a need for more information on the strengths and weaknesses of various characterization methods for different tasks. Because tight control on process parameters is difficult and expensive, it is necessary to know which parameters are most vital for growing reproducible
films. The desire was also expressed for information concerning which kinds of characterization techniques could be relied upon to maintain tight process control.

- Although there is much interest in diamond films for microelectronic applications, good mechanical or tribological properties may not require high-purity diamond. Indeed, DLC or hydrogenated DLC films can be grown which are very smooth and hard, and which can exhibit low friction. DLC films can be deposited at low temperatures. Thus, there is great need to find useful characterization techniques for these amorphous materials, of which very little is known at present of the structure. Progress is needed for defining nomenclature for evaluating and describing amorphous carbonaceous phases, whether they be DLC or hydrogenated DLC.

The Panel summarized and prioritized these concerns according to the following criteria:

1. Identify areas for characterization
2. Identify critical needs
3. Rank needs by priority
4. Recommendation

The following items are a prioritized summary listing of critical characterization needs:

1. Development of in-situ surface/near-surface characterization (and quality control) techniques.
2. Determine the relation of structure, impurities, etc. to performance, tribobehavior, environmental, high-temperature, etc. properties.
3. Understanding of nucleation/adhesion mechanisms.
4. Establish criteria for evaluating amorphous carbonaceous phases.
   - nomenclature for non-crystalline materials.
   - relationship between hydrogen content and sp²/sp³ bonding.
5. Determine the nature of diamond/DLC interaction with other surfaces (wear/polishing).
6. A working definition of "quality" for various uses.
7. A correlation of various characterization techniques.
A final recommendation was given by members of the Panel:

"Diamond and diamond-like materials have been identified as enabling technologies for increasing U.S. competitiveness in the transportation sector. Critical issues in characterization must be addressed to enable the transfer of these materials from research labs to end-users in manufacturing. The successful use of diamond and diamond-like materials in the transportation sector will require solutions of critical issues identified by this panel for characterizing the production of these materials, the materials themselves, the interactions of these materials with other materials and the development of suitable standards."
Table I

a) **What** properties/regions can be characterized?

- structure
  - bonding
    - SRO, LRO, IRO
  - orientation/texture defects
- composition
  - hydrogen content
  - impurities
  - phase distribution
- morphology

b) **Why** is characterization needed?

- need to develop basic and applied understanding of chemistry and structure to engineer specific properties
- need for specifications useful to manufacturers and users

c) **How** can properties be characterized?

- stylus
- interferometer
  - STM
  - SFM
  - light scattering
  - SEM
  - TEM
  - Raman
  - other existing techniques
  - other future techniques
Panel 4 – Applications to Transportation

Chairman: Fred Nichols, Argonne National Laboratory

Joseph Au
Rabi Bhattacharya
Bharat Bhushan
Dennis Blunier
Bruce Boardman
Larry Brombolich
Jim Davidson
Mike Graham
Nabil Hakim
Keith Harris
Rob Hay
Leonard Herk
Henry Hojnacki
Roy Kamo
Bill Nieman
Dave O'Neill
Marshall B. Peterson
Gene Pfaffenberger
Roger W. Pryor
Dave Rourk
Jim Russell
Walter Syntuta
Mike Tamor
Ted Vojnovich
Wally Yarbrough
Charles S. Yust

Sundstrand Aerospace
Universal Energy Systems, Inc.
Ohio State University
Caterpillar, Inc.
Deere & Co.
Compu-Tec Engineering
Vanderbilt University
Northwestern University
Detroit Diesel Corporation
Dubbeldee Harris Diamond Corp.
Norton Diamond Film
Southwest Research Institute
Intelligent Structures Incorporated
Adiabatics, Inc.
Allied-Signal Inc., R&T
3M
Wear Sciences
Allison Gas Turbine
Wayne State University
Intelligent Structures Incorporated
Superconductivity Publications, Inc.
Advanced Mechanical Technology, Inc.
Ford Motor Co.
USDOE
Penn State University
Oak Ridge National Laboratory

After considerable discussion, it was decided that the most effective manner in which this working group could serve the aims of the workshop was to compile a listing of current and anticipated future problem areas in the transportation industry where the properties of diamond and DLC films make them especially attractive and where the group as a whole could strongly endorse the establishment of DOE/Transportation Industry cooperative research efforts. It was further decided that it would not be fruitful at this time to attempt to create a prioritized ranking.

The problem areas identified for possible applications of diamond/DLC technology are compiled in the following pages, together with indications of current approaches. Also we have given brief indications of specific needs and the type of research program envisioned. We have attempted to give some idea of time scale required for the various efforts. Finally, we have indicated foreseeable payoffs if the technologies are successfully implemented.

They should demonstrate cost-effectiveness and transferability to production. Finally, successful processes should be sufficiently robust for day-to-day production-line variations.
Area #1

1. Problem
Valve guide/stem wear at high temperatures in advanced diesel and developmental low-heat-rejection engine.

2. Current Approach
4140 Steel valves/cast iron guides at 300–350°C

3. Needed
Diamond or DLC coating on either or both surfaces to extend operating temperature to 300–500°C and to reduce liquid lubricant requirement.

4. R&D Program Envisioned
Investigation of coating/material combinations with high-temperature, 20,000-hour capability; should provide lubricious interface.

5. Time – Scale
5–7 years.

6. Payoff
Maintain international competitive advantage, better fuel efficiency, reduced emissions.
Area #2

1. Problem
Piston ring/bore tribosystem needs improvement to decrease wear, oil consumption and emissions for gasoline, diesel and alternative fuels.

2. Current Approach
Coated piston skirts and rings/cast-iron or Al bores at ≈150°C for 500,000 miles (diesel), 100,000 miles (automobile).

3. Needed
Heavy-Duty Diesel: Serviceable ring/bore combination at ≈300°C for approximately 1,000,000 miles, 20% increase in cylinder pressure, reduced friction.

Automotive: Friction reduction at current temperatures for 200,000 miles.

4. R&D Program Envisioned
Identify/develop diamond/DLC materials (coatings)/processes for high-temperature (~300°C) tribological interfaces, e.g., plasma deposition, cvd/pvd. Develop improved piston ring/cylinder wall tribological computer models to guide research.

5. Time – Scale
5-7 years.

6. Payoff
Maintain international competitive advantage, better fuel efficiency, reduced emissions.
Area #3

1. Problem
Need increased load-carrying capacity for gears, power train and bearings in spark-ignited/diesel engines and vehicular drive trains, as well as in manufacturing.

2. Current Approach
Gears: Steel (various) with some type of wear-life-enhancement process.
Bearings: Typically lead-tin bronze bushings cast or sintered onto steel backs, with Pb-Sn overlay. Oil-lubricated.

3. Needed
Improvements in power-throughput capability to allow components with lower cost or smaller size to be used. Increase oil temperatures from ~120°C to ~150°C.

4. R&D Program Envisioned
Investigate diamond/DLC coatings or new surface treatments that offer reduced pitting/contact fatigue/abrasion, scoring or galling in comparison with conventional materials. Improved computer modeling of gears and bearings.

5. Time - Scale
8-10 years.

6. Payoff
Enhanced international competitiveness, improved reliability and design flexibility. Improved fuel economy/emissions due to higher cylinder pressure, injection pressure. Reduced friction from (possibly) higher sump temperatures. Decrease Pb in environment.
Area #4

1. Problem
Electric fuel pumps and fuel pump gears operate immersed in fuel. Potential wear areas include the commutator/brush interface. Concerns include potential abrasion and arcing. The effect of methanol fuel on these phenomena has not been established. Other rubbing contacts are potential concerns because of the poor lubricating ability of these (low-viscosity) fuels.

2. Current Approach
Issues are in the early stages of investigation.

3. Needed
Identification of materials/coatings (diamond/DLC) appropriate for commutator, brush and other applications with gasoline, methanol and admixtures.

4. Payoff
Improved reliability and design flexibility.
Area #5

1. Problem
Accelerated or bench tests used for selection of tribological materials do not always accurately model the effects of actual service. This deficiency may lead to unrealistic failure modes during testing, or conversely to unexpected failures during service. No widely accepted, quantitative adhesion evaluation method is presently available for bond strengths in excess of 69 MPa (10 ksi).

2. Current Approach
Test simulation: varies widely from case to case, ranging from well-defined and verified accelerated wear tests to arbitrary screening tests for wear and/or adhesion.

Modeling: Empirical experimental methods are used, unreliable for predicting wear under typical operating conditions.

3. Needed
Systematic procedures for defining appropriate tests, especially for adhesion. Accurate modeling methods and properties of coatings, especially adhesion.

4. Payoff
Rapid material screening and validation, reduced costs and improved performance, shorter cycle time. Ability to predict component life and forestall premature failures.
Area #6

1. Problem
Injector plunger-barrel scuffing (adhesive wear) with diesel fuel, but especially with alternative (low-lubricity) fuels. Potentially also a problem with spark-ignition engines utilizing alternative fuels.

2. Current Approach
Typically, electroplated hard-chromium plunger with hardened steel bore, or nitrided plunger and bore. Very tight clearances required, e.g., 2.5 μm (100 μin) diametral. Fuel-lubricated, approximately 93°C (200°F). Axial load to 12 kN (2600 lbf), injection pressure = 172 MPa (25 ksi). Required life > 500,000 miles. Typically, tool-steel plunger, carburized steel injector cup with multiple holes formed by electro-discharge machining (EDM). Hole diameter approximately 200 μm (0.008 in). Diesel fuel contaminated with sulfuric acid/organic acids/combustion products, 150-315°C (300-600°F). Required life > 10,000 hrs or 700,000,000 cycles.

3. Needed
Injection pressure = 207 MPa (30 ksi), up to 1,000,000 miles for heavy-duty engines. Greater tolerance to low-lubricity fuels (e.g., low-S, low-aromatics fuel, arctic fuel, methanol, etc.). Reduce corrosion/erosion rates of spray holes by factor of 5.

4. Payoff
a) Develop scuffing- and wear-resistant coatings, as well as those for corrosion/erosion resistance.
b) Develop solid lubricating coatings.
c) Evaluate diamond-like-carbon coatings – need improved adhesion to steel.
d) Develop coating process for long, narrow bores (1/d > 3), e.g., conformal-plasma ion implantation.
e) Bench/screening tests and engine tests required.

5. Time – Scale
3-5 year R&D program to develop and evaluate processes.

6. Payoff
a) Improved emissions/fuel economy (higher injection pressure).
b) Improved durability & reliability with low-lubricity fuels.
c) Improved international competitiveness.
Area #7

1. Problem
Improved rolling-contact-fatigue (RCF) life of valve and injector cams and cam-roller followers is needed, for gasoline, diesel and gas-turbine engines.

2. Current Approach
Induction-hardened steel, powder-metallurgy and cast-iron cams, steel or ceramic rollers. Required life >500,000 miles (heavy duty) and 100,000 miles (automotive); oil-lubricated. Hertz stress approximately 1.4–2 GPa (200–300 ksi).

3. Needed
Increase injection pressure 20% without reducing RCF life. Improve lifetime for ceramic rollers.

4. R&D Program Envisioned
a) Evaluate thin-film ceramic PVD coatings on cam lobes.

b) Evaluate thin-film solid lubricating coatings on roller pin to reduce roller-pin friction, hence cam-roller traction.

5. Time – Scale
3 yr. R&D program.

6. Payoff
Increased fuel-injection pressure capability (improved emissions/fuel economy). Improved international competitiveness.
Area #8

1. Problem
Surfacing of light-weight materials for self-lubrication and resistance to scuffing.

Examples: Aluminum-block engine – cylinder–bore surface
Valvetrain components (valves, tappets, etc.)
Transmission case “hot spots”
Light–weight brake rotors
Air conditioning (A/C) compressor hardware

2. Current Approach
Use of inserts – e.g., bore liners (cast iron), valve seats, etc.
Use of heavier, wear-resistant (usually ferrous) alloys

3. Needed
Understanding of adhesion of surfacing layers, e.g., diamond/DLC to metals such as aluminum; modeling for mechanical surface behavior of bi-material couples; understanding of methodologies for selecting composite surfaces.

4. Time – Scale
3–5 years

5. Payoff
Reduced friction and energy consumption; manufacturing simplification (in some cases).
Area #9

1. Problem
The wear life of non-ferrous die materials is insufficient for medium-volume applications.

2. Current Approach
Hard-chromium plating is being evaluated for non-ferrous dies; for ferrous dies ion (plasma) nitriding mid-chrome coating and flame-hardening are used.

3. Needed
A wear-life-enhancement process that can be easily applied, give increased tool life, be repaired, stripped and retreated if needed.

4. R&D Program Envisioned
Hard-chromium plating and plasma-source ion implantation appear to be potential solutions. Could also employ diamond/DLC films.

5. Time – Scale
Process could be used immediately. R&D program could require 2-3 years.

6. Payoff
Benefits to U.S. auto-makers and other U.S. manufacturers.

Would obtain:

- cheaper tooling
- faster time to market; reduced lead time
- enhanced competition with foreign companies
Area #10

1. Problem
Develop diamond and/or DLC sensors and associated packaging systems, for harsh, transportation-related environments, for sensing temperature, force and various chemical conditions.

2. Current Approach
Usual approach has been simply to push silicon devices harder and harder; at present, we are up against the limits for Si sensors and further progress to more severe conditions requires a new material.

Needed
Operation at 500 to 800°C in exhaust environments. Many barriers to progress exist at ≈300°C, e.g., coolant, lubricant, air, fuel inlet.

4. R&D Program Envisioned
Integration of fragmented R&D in diamond electronics and sensors, as active and passive devices for on-board diagnostics.

5. Time - Scale
4-5 years

6. Payoff
Essential for selling automobiles in California with new emission/environmental requirements; enhance U.S. competitiveness in international markets.
Area #11

1. Problem
Abrasion/erosion of compressor blades, stator vanes in gas turbines, turbochargers, etc., where small amounts of wear can have drastic, deleterious effects. (Trouble in Saudi Arabia)

2. Current Approach
Replacement of components. This results in very costly loss in effective utilization.

3. Needed
Increase in abrasion resistance. Elimination of heavier materials which are now required for adequate abrasion resistance.

4. R&D Program Envisioned
Identify/develop diamond/DLC technology/processes for surfaces subject to highly abrasive conditions.

5. Time – Scale
4–5 years

6. Payoff
Reduced maintenance costs. Reduced down-time. Increased efficiency.
Area #12

1. Problem
Abrasion of windows on aircraft and automobiles.

2. Current Approach
Mostly uncoated windows are used.

3. Needed
Enhanced abrasion resistance, possibly combined with optical improvements, e.g., low heat transmission.

4. R&D Program Envisioned
Should include investigation of feasibility of float-line or post-line processes. Should also include possibility of non-glass windows.

5. Time – Scale
2–3 years

6. Payoff
Improvements in product, durability and safety.
**Area #13**

1. **Problem**

   Efficient utilization of electrical power/power transmission (power management) for electric vehicles and communications equipment.

2. **Current Approach**

   Si is used, with its low power capability.

3. **Needed**

   Higher-power switching and management.

4. **R&D Program Envisioned**

   Develop mosaic diamond, diamond-base sample and switch devices.

5. **Time – Scale**

   6–7 years

6. **Payoff**

   Extended vehicular range; improved safety, reliability and performance.
Area #14

1. Problem
Thermal fatigue from hot spots in combustion chamber, especially cylinder head.

2. Current Approach
Increase back-side (coolant side) flow rates and heat transfer. Increase material strength and thermal-fatigue resistance. Limit specific power.

3. Needed
Thin layer on top of firedeck surface to serve as heat distributor/spreader.

4. R&D Program Envisioned
Develop methodologies for practical applications of durable diamond coatings with very high thermal conductivity to eliminate “hot spots” within the combustion chamber. Validate same.

5. Time – Scale
2–4 years

6. Payoff
Enabling technology for increased specific power output for current and future-generation products. Improved emissions through elimination of radical sites.
Area #15

1. Problem
Machine/cutting tools for advanced materials, e.g., composites, ceramics.

2. Current Approach
Current programs on diamond-coated tools exist but are limited to non-ferrous substrates.

3. Needed
Diamond-coated tools for various substrates.

4. R&D Program Envisioned
Fill in gaps of current programs to cover all needs. Coordinate with National Center for Machining Sciences (NCMS).

5. Time - Scale
4–5 years

6. Payoff
Instantaneous productivity increase. Enabling technology for ceramics industry.
Area #16

1. Problem
Brake heating is a critical problem for heavy-duty trucks and aircraft.

2. Current Approach
Fins, radiators, water cooling, etc.

3. Needed
More efficient thermal management to eliminate overheating/failures.

4. R&D Program Envisioned
Diamond heat pipes and/or spreaders would be developed.

5. Time – Scale
4–5 years

6. Payoff
Improvement in safety and durability; weight reduction.
Area #17

1. Problem
Surfaces coated with diamond or DLC in the engine may not be compatible with the (conventionally) formulated engine oils. Also true for transmissions, gears, etc.

2. Current Approach
Diamond and DLC coatings are avoided in these systems.

3. Needed
Lubricants compatible with diamond and DLC that will not drastically alter other systems, materials, functions, etc.

4. R&D Program Envisioned
Develop practical lubricant (base-stock and additives) in the context of diamond/DLC coatings, applicable for tribological interfaces of real-life, near-term and advanced systems. Coordinate with current work on lubricants for ceramics.

5. Time – Scale
3-7 years

6. Payoff
Enabling technology for the utilization of diamond/DLC coatings in engine and power-transmission systems.
Area #18

1. Problem
Seals in many areas.

Note: Time did not permit elaboration on this area.
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