CONF-920262 - -

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

CONF-920262--
DE93 007491

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

Dr. F. A. Nichols
Project Manager

U. S. Department of Energy

Dr. J. M. Perez
Program Manager

Edited by:

F. A. Nichols and D. K. Moores

Issued: January 1993

## 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.

9. Improvements in wear life of ferrous and non-ferrous die materials for medium-volume applications in engine manufacture.

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.

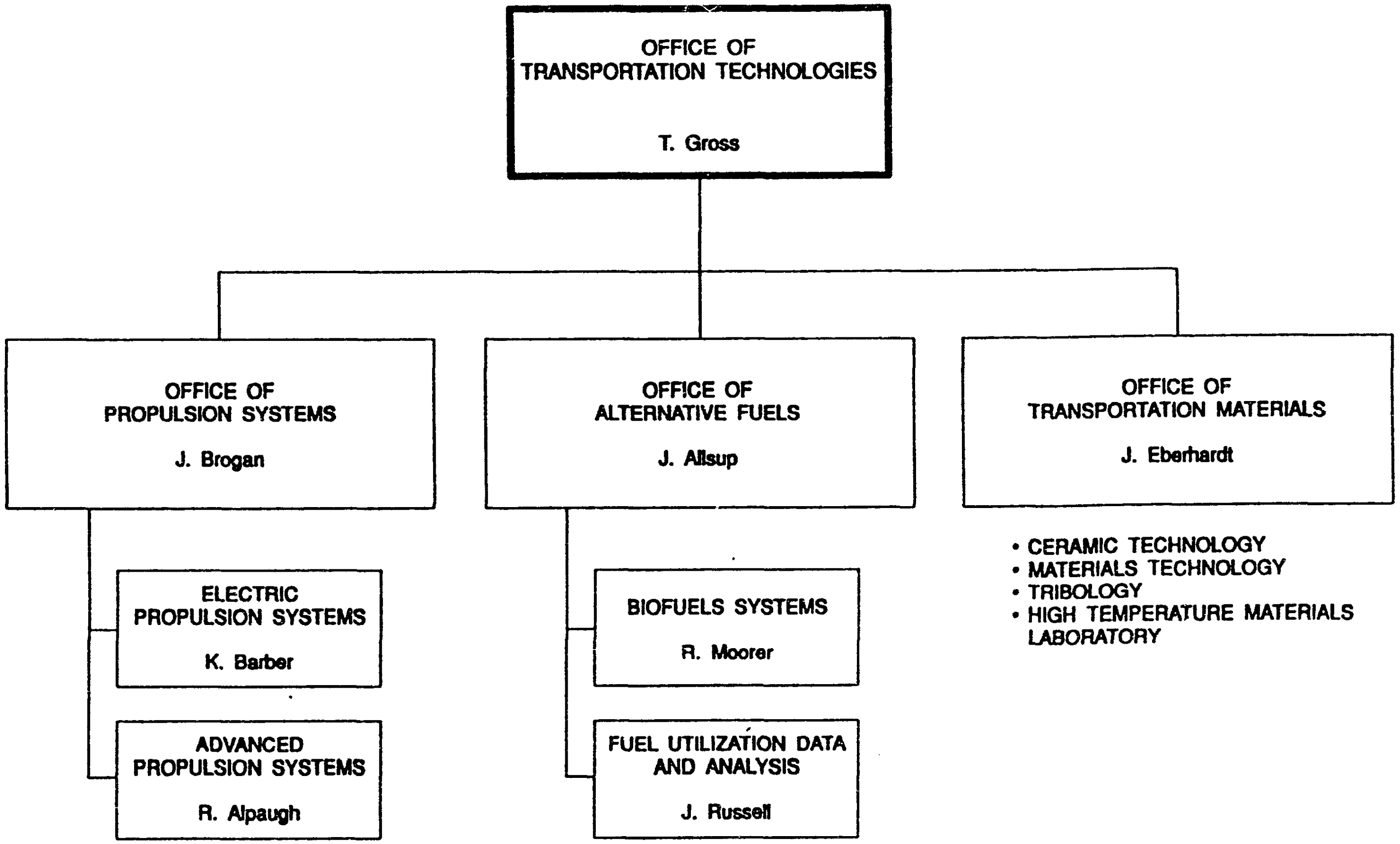
### 2.2 OFFICE OF TRANSPORTATION TECHNOLOGY (OTT).

**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.

# Office of Transportation Materials

## Organization of the Office of Transportation Technologies



OFFICE OF TRANSPORTATION TECHNOLOGIES
T. Gross

OFFICE OF PROPULSION SYSTEMS
J. Brogan

ELECTRIC PROPULSION SYSTEMS
K. Barber

ADVANCED PROPULSION SYSTEMS
R. Alpaugh

OFFICE OF ALTERNATIVE FUELS
J. Allsup

BIOFUELS SYSTEMS
R. Moorer

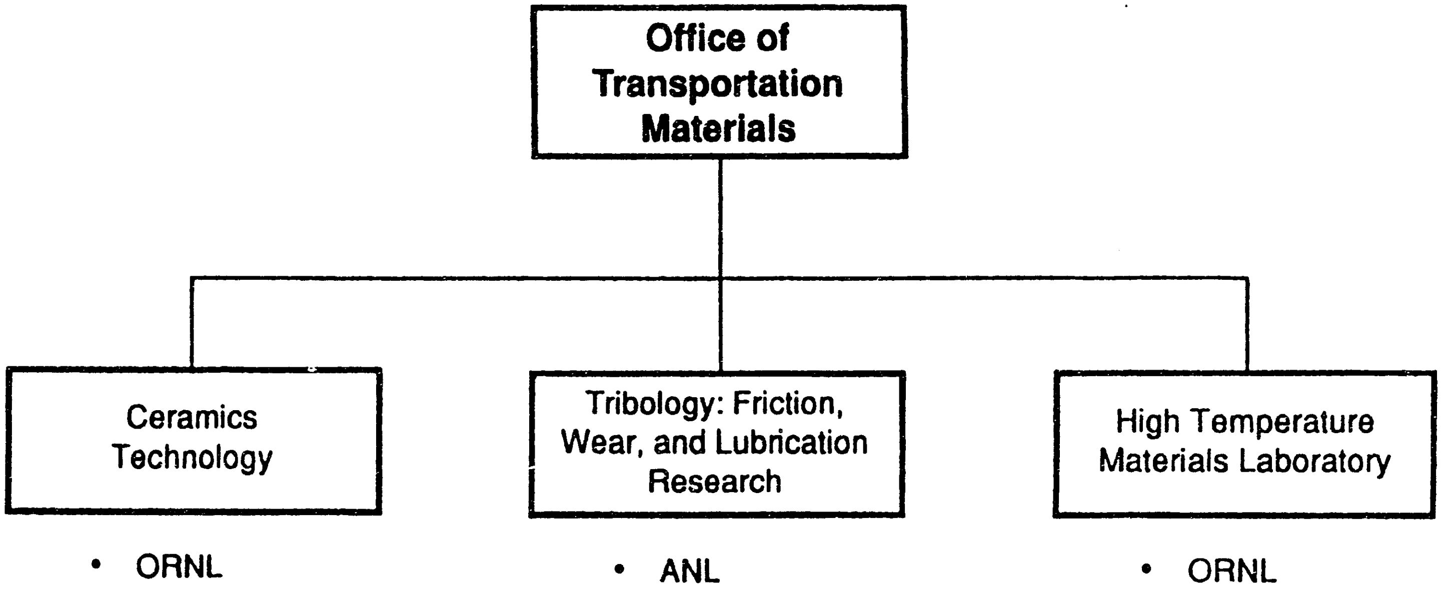
FUEL UTILIZATION DATA AND ANALYSIS
J. Russell

OFFICE OF TRANSPORTATION MATERIALS
J. Eberhardt

- CERAMIC TECHNOLOGY
- MATERIALS TECHNOLOGY
- TRIBOLOGY
- HIGH TEMPERATURE MATERIALS LABORATORY

# Office of Transportation Materials

## Current Program Structure of OTM



**Office of Transportation Materials**

Ceramics Technology
- ORNL

Tribology: Friction, Wear, and Lubrication Research
- ANL

High Temperature Materials Laboratory
- 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

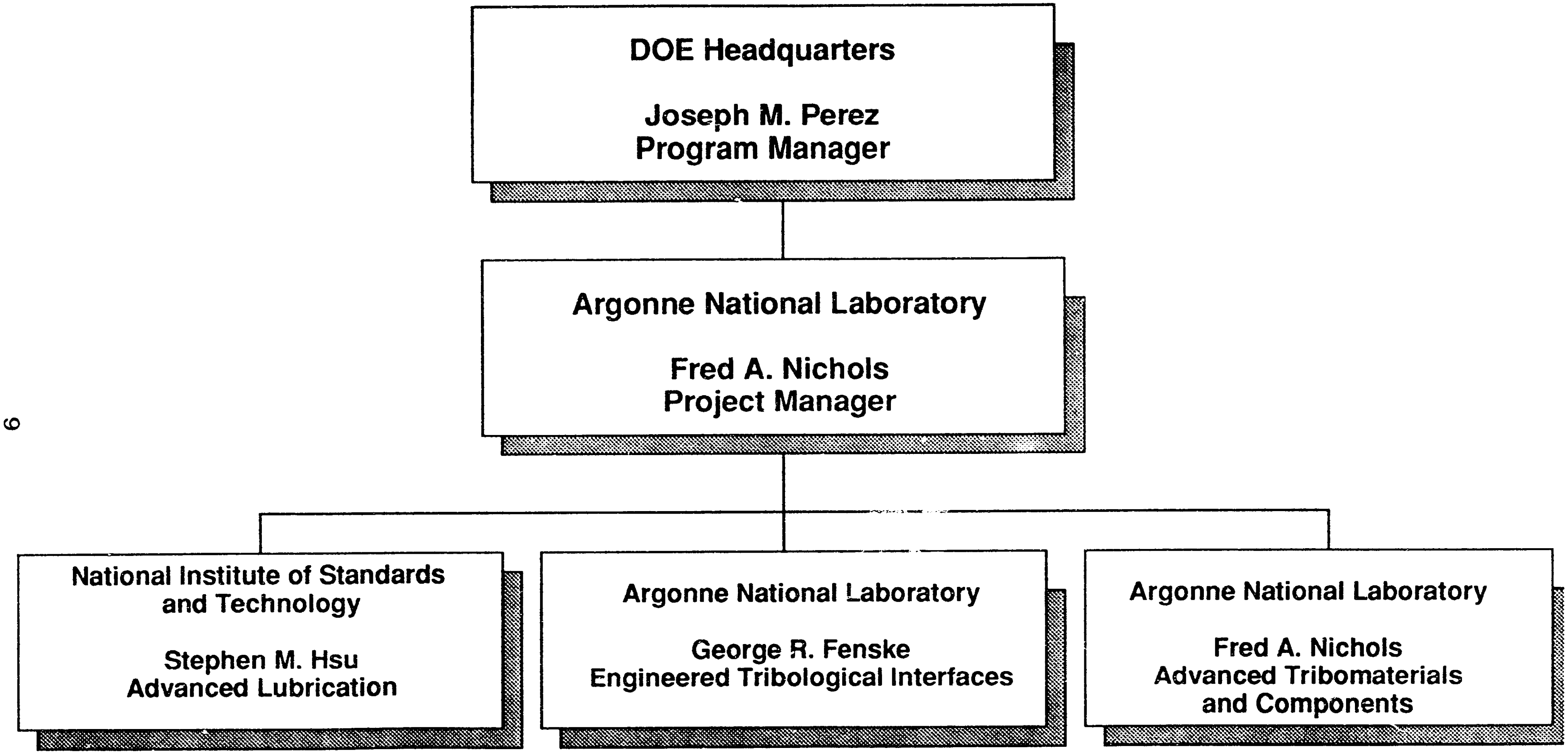

DOE Headquarters
Joseph M. Perez
Program Manager
Argonne National Laboratory
Fred A. Nichols
Project Manager
National Institute of Standards and Technology
Stephen M. Hsu
Advanced Lubrication
Argonne National Laboratory
George R. Fenske
Engineered Tribological Interfaces
Argonne National Laboratory
Fred 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

# Office of Transportation Materials

## Tribology Program

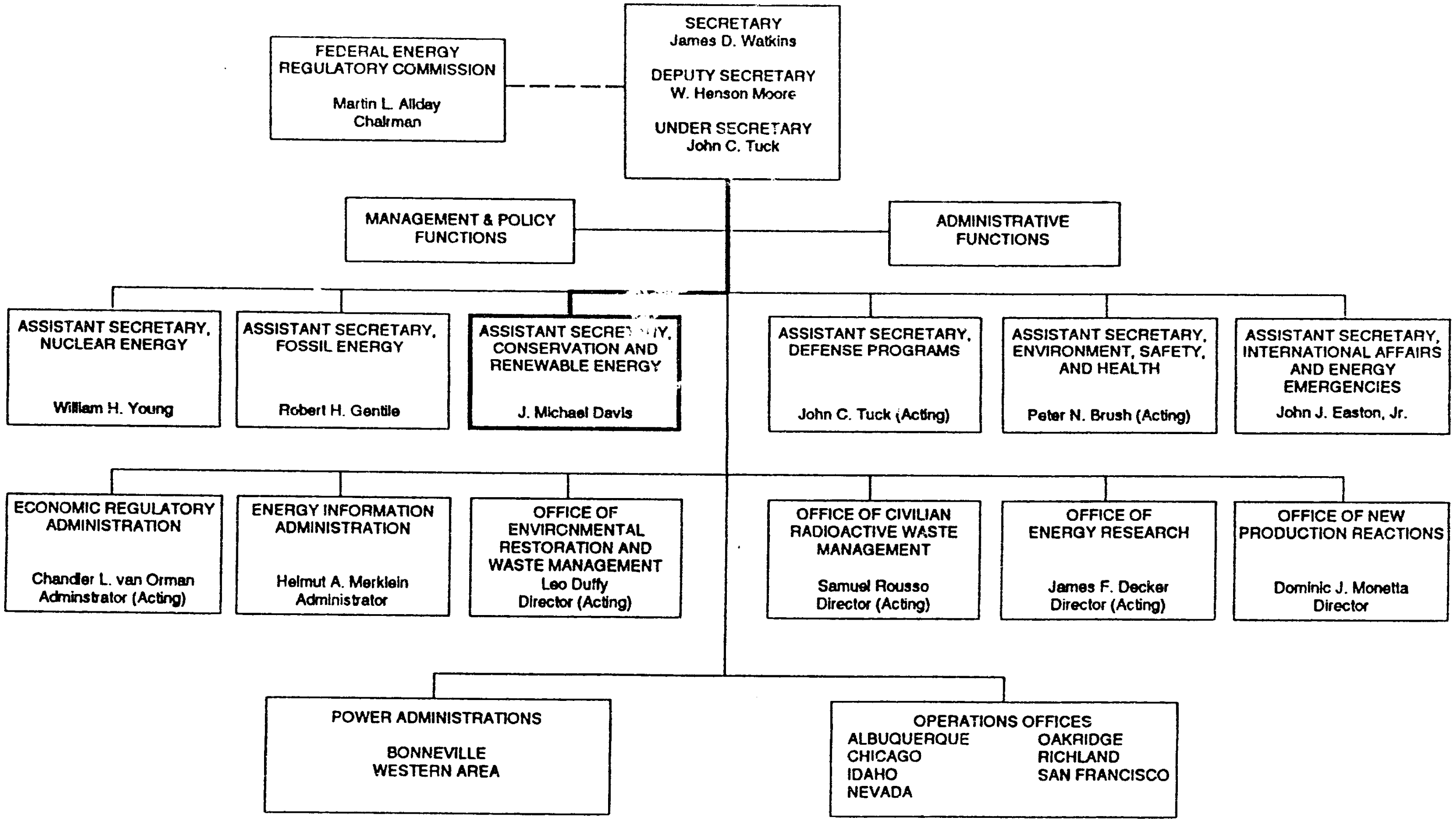
**Joe Perez** **CE-34**
Tribology Program Manager

1000 Independance Ave., SW
Washington, D.C. 20585

**Ph. (202) 586-2325**
**FTS (202) 896-2325**
**FAX (202) 586-7114**

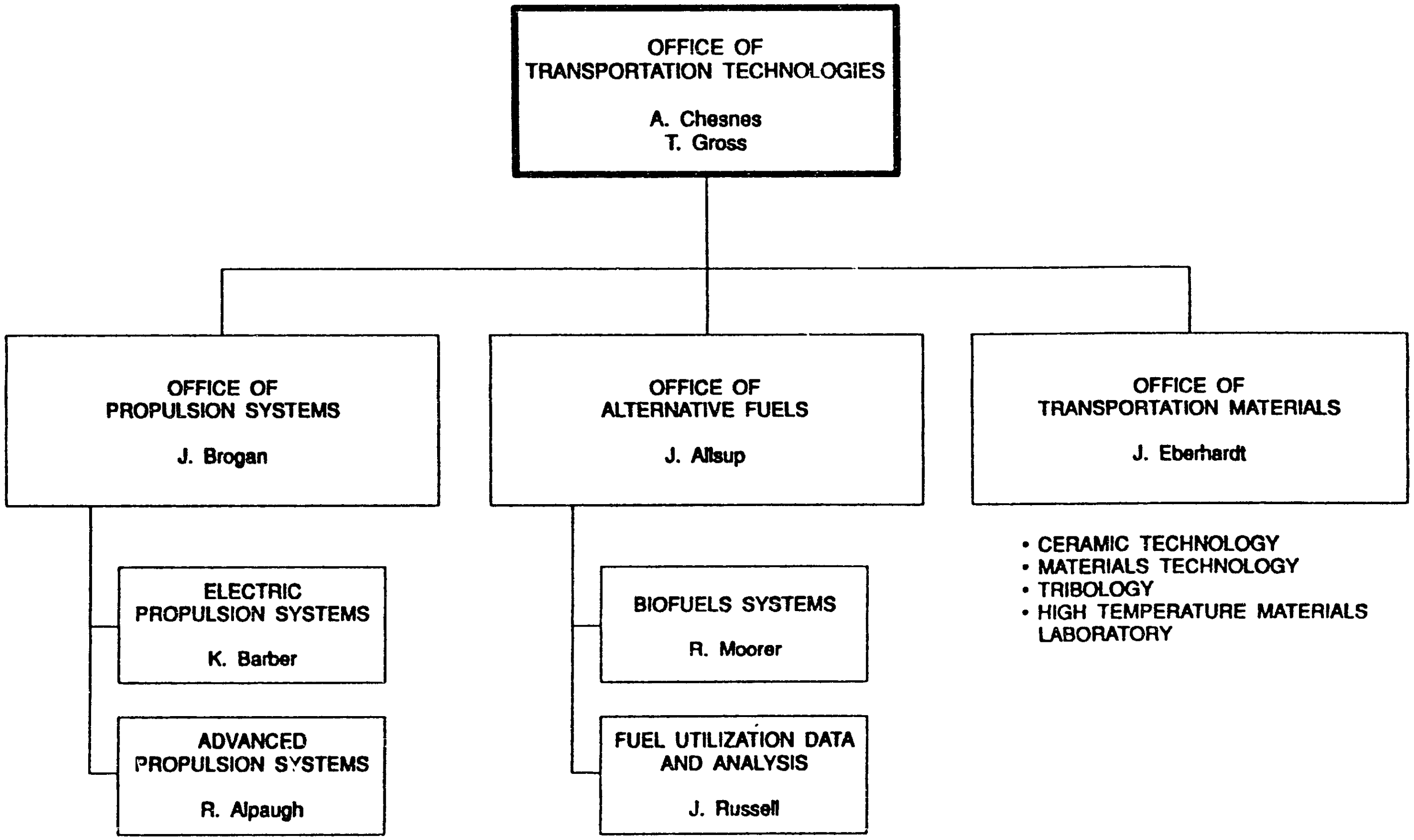
# Office of Transportation Materials

## THE DEPARTMENT OF ENERGY



# Office of Transportation Materials

## Organization of the Office of Transportation Technologies



OFFICE OF TRANSPORTATION TECHNOLOGIES

A. Chesnes
T. Gross

OFFICE OF PROPULSION SYSTEMS

J. Brogan

ELECTRIC PROPULSION SYSTEMS

K. Barber

ADVANCED PROPULSION SYSTEMS

R. Alpaugh

OFFICE OF ALTERNATIVE FUELS

J. Allsup

BIOFUELS SYSTEMS

R. Moorer

FUEL UTILIZATION DATA AND ANALYSIS

J. Russell

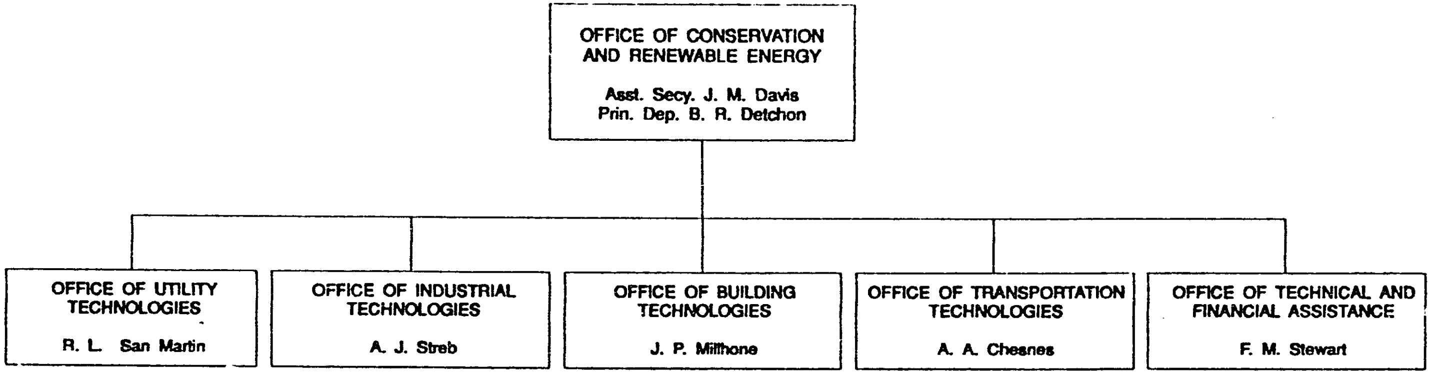
OFFICE OF TRANSPORTATION MATERIALS

J. Eberhardt

- CERAMIC TECHNOLOGY
- MATERIALS TECHNOLOGY
- TRIBOLOGY
- HIGH TEMPERATURE MATERIALS LABORATORY

# Office of Transportation Materials

## Organization of the Office of Conservation and Renewable Energy



OFFICE OF CONSERVATION AND RENEWABLE ENERGY

Asst. Secy. J. M. Davis
Prin. Dep. B. R. Detchon

OFFICE OF UTILITY TECHNOLOGIES

R. L. San Martin

OFFICE OF INDUSTRIAL TECHNOLOGIES

A. J. Streb

OFFICE OF BUILDING TECHNOLOGIES

J. P. Millhone

OFFICE OF TRANSPORTATION TECHNOLOGIES

A. A. Chesnes

OFFICE OF TECHNICAL AND FINANCIAL ASSISTANCE

F. M. Stewart

# Office of Transportation Materials

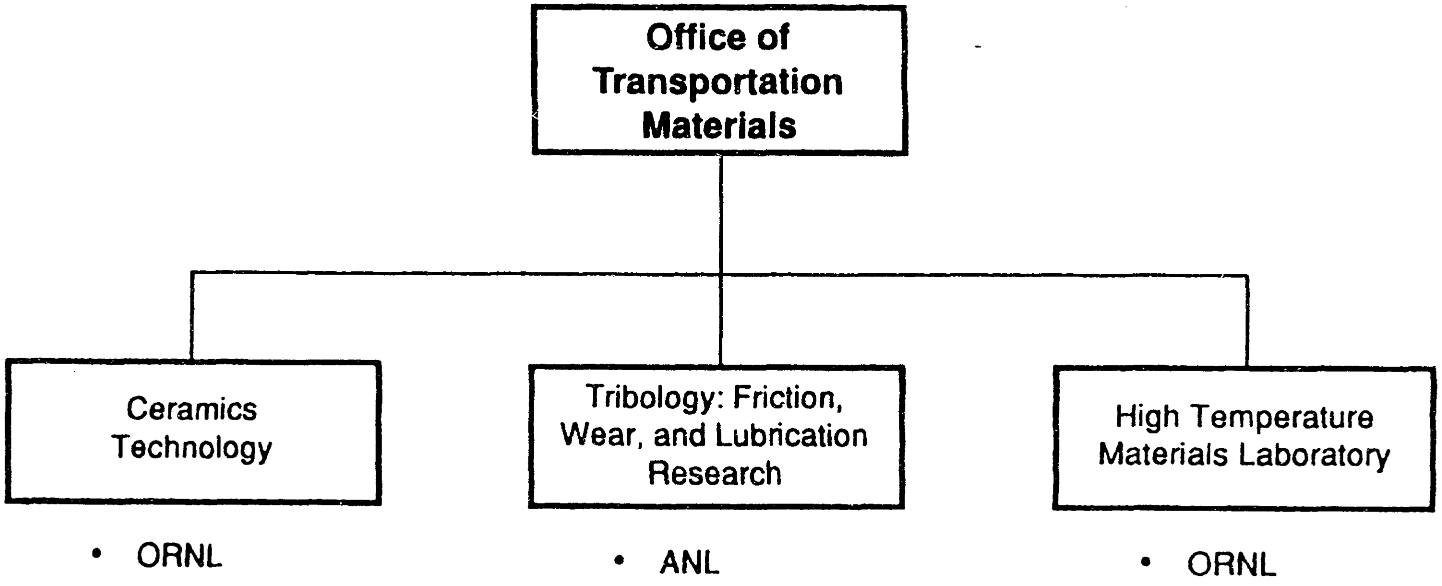
## Materials Development Program

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



**Office of Transportation Materials**

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

# Role and Mission

# 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

| | |
|---|---|
| **DOE-ECUT Tribology Program:** | **Long-range,**<br>**High risk,**<br>**Basic research** |
| **DOE-OTM Tribology Program:** | **Shorter-term,**<br>**Industry relevant** |

# Office of Transportation Materials

## Tribology Program

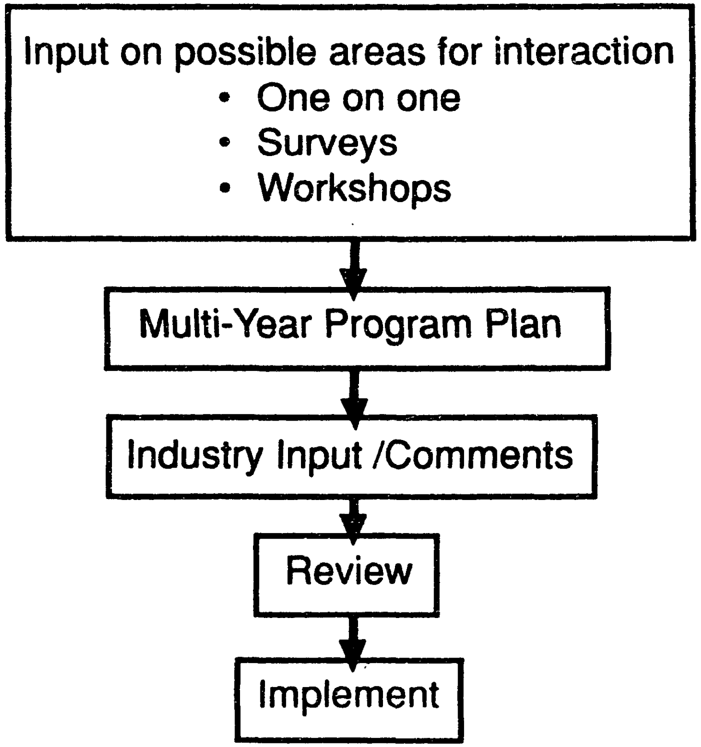
### Purpose

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)

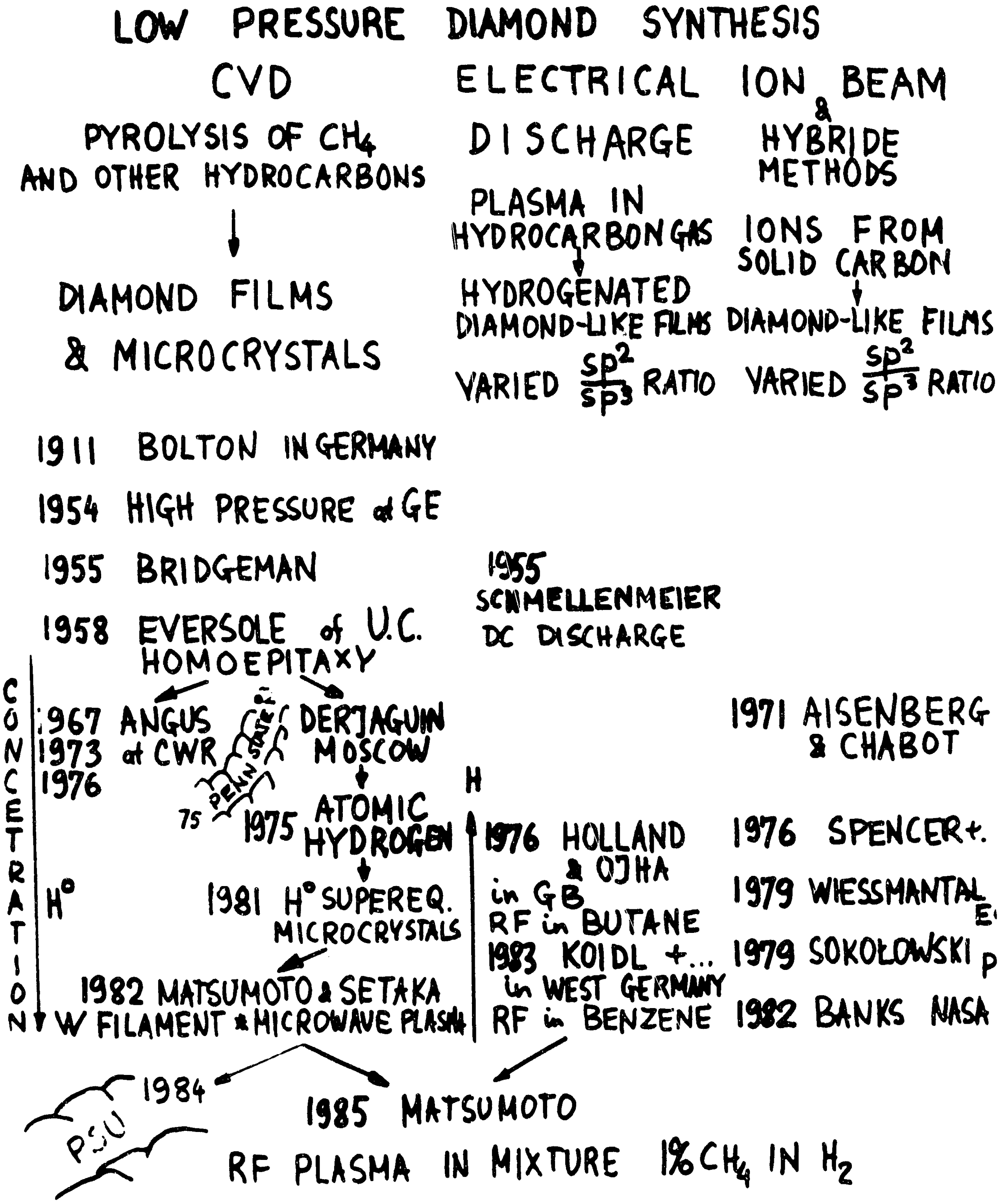
Denise Moores for outstanding arrangements

# DIAMOND FILMS: HISTORICAL PERSPECTIVE

**Russell Messier**
The Pennsylvania State University
Materials Research Laboratory
University Park, PA 16802

---

Presentation at: Diamond Films Workshop
Department of Energy
Argonne National Laboratory
February 4-5, 1992



# LOW PRESSURE DIAMOND SYNTHESIS

## CVD

PYROLYSIS OF $CH_4$
AND OTHER HYDROCARBONS

DIAMOND FILMS
& MICROCRYSTALS

## ELECTRICAL DISCHARGE

PLASMA IN
HYDROCARBON GAS

HYDROGENATED
DIAMOND-LIKE FILMS

VARIED $\frac{sp^2}{sp^3}$ RATIO

## ION BEAM & HYBRIDE METHODS

IONS FROM
SOLID CARBON

DIAMOND-LIKE FILMS

VARIED $\frac{sp^2}{sp^3}$ RATIO

1911 BOLTON IN GERMANY

1954 HIGH PRESSURE at GE

1955 BRIDGEMAN

1958 EVERSOLE of U.C.
HOMOEPITAXY

1967 ANGUS
1973 at CWR
1976

DERJAGUIN
MOSCOW

1975 ATOMIC
HYDROGEN

1981 H° SUPEREQ.
MICROCRYSTALS

1982 MATSUMOTO & SETAKA
W FILAMENT * MICROWAVE PLASMA

CONCENTRATION

H°

PENN STATE

75

1955
SCHMELLENMEIER
DC DISCHARGE

H

1976 HOLLAND
& OJHA
in GB
RF in BUTANE
1983 KOIDL +...
in WEST GERMANY
RF in BENZENE

1971 AISENBERG
& CHABOT

1976 SPENCER+.

1979 WIESSMANTAL

1979 SOKOŁOWSKI

1982 BANKS NASA

1984

PSU

1985 MATSUMOTO
RF PLASMA IN MIXTURE 1% $CH_4$ IN $H_2$

Sci. Am. 193 (1955)

# Synthetic Diamonds

1955

*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 1797 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 carb of course, is graphite. Diamond has density of 3.51 against 2.25 for graphite. Modern X-ray analysis has disclosed th structural differences between the Diamond crystallizes in a cubic syste with each atom symmetrically surround ed by four others, all at the same di tance and arranged at the corners of regular tetrahedron. Graphite cry lizes in the hexagonal system: the at are arranged in layers; within each lay the pattern is not greatly different fr the arrangement in diamond, but th layers are separated by comparativ large intervals. It is to this that graph owes its lubricating properties, for th layers can slip over one another und the action of weak mechanical forces.

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

Willard Gibbs's work in thermody namics at the turn of the 19th ce tury made it possible to say theoretic under what conditions carbon mi

DIAMONDS made in the General Electric Research Laboratory are enlarged about seven diameters. They were grown by H. P. Bovenkerk in the press depicted on the opposite page.

take the form of diamond in preference to graphite. Gibbs's studies made clear that graphite could not turn into diamond unless the "thermodynamic potential" of diamond was less than that of graphite. The thermodynamic potential plays for chemical reactions a role closely analogous to the ordinary potential of mechanics. Just as a weight falls from a higher to a lower position because its potential is less near the earth, so a chemical reaction tends to run in the direction in which its thermodynamic potential becomes less—or, expressing the rule more rigorously, a chemical reaction *can* run only in the direction in which its thermodynamic potential decreases.

Gibbs showed how to calculate the thermodynamic potential in terms of the specific heat, the thermal expansion and other measurable properties of materials. It appeared probable at the time, and later it became a certainty, that the thermodynamic potential of graphite is lower than that of diamond—which is another way of saying that under ordinary conditions graphite is thermodynamically the more stable form. It follows that if any transformation is to take place at all at ordinary temperatures and pressures, it is from diamond to graphite.

But there is a catch when it comes to using these considerations to predict what will happen. For although we can tell when a transformation may run, we cannot tell when it will run. Although diamond has thermodynamic permission to transform itself into graphite under ordinary conditions, it has no mandate to do so. (Thermodynamic stability is not the same as mechanical stability.) Everyone knows that diamonds do not spontaneously change to graphite, and my wife has worn her engagement ring these many years with no solicitude on that score.

The mathematical expression for the thermodynamic potential showed that if the pressure could be raised high enough, graphite would receive thermodynamic permission to transform, even at ordinary temperatures, to diamond. This pressure was calculated to be about 20,000 atmospheres. But here again permission does not mean that the reaction will inevitably run.

Just as we cannot say that graphite will change to diamond if only it has thermodynamic permission, so also we cannot say that when a carbon compound decomposes, or when carbon is precipitated from a solution, the form of carbon that separates will be the form thermodynamically preferred. We know from the thermodynamic potential that graphite is ordinarily the preferred form, but this does not enable us to say that the actual precipitate will be graphite and not diamond. As a matter of fact, there are many known instances in which an element's unstable form, corresponding to diamond, separates from a solidifying liquid or solution in preference to the more stable form.

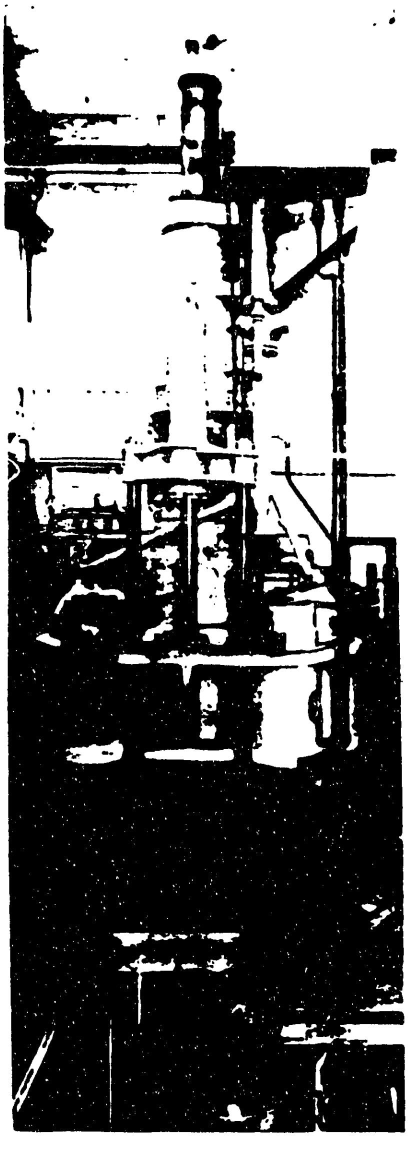
The possibility that diamond may be formed as an unstable phase under conditions where "nascent" (uncombined) carbon is liberated makes it impossible to rule out the chance of an accidental success. Thus I could never say to the hopeful amateur who walked into my office: "Your process *certainly* will not work." I could only say this when he proposed to transform graphite directly into diamond under thermodynamically impossible conditions. The aforementioned possibility has been one of the bogeys in the whole situation. Many geologists and mineralogists have been of the opinion that diamond is formed in nature under unstable conditions, which would mean that it might be a matter of anybody's lucky guess to find the proper conditions.

None of the sophistications we have considered entered into the early attempts to make diamonds. Many of those who made the attempt were guided simply by the fact that diamond is more dense than graphite, which naturally suggested the possibility that it might be formed by subjecting carbon to great pressure. There were then no means of producing anything like the 20,000 atmospheres later calculated to be necessary, but claims of success were numerous nonetheless.

One of the earliest and still most discussed attempts was by a Scotsman, J. B. Hannay, in 1880. He mixed hydrocarbons, "bone oil" and lithium, sealed the mixture in a wrought-iron tube and heated it to redness in a forge. All but three of 80 tubes exploded. (The pressure in the tubes could not have been more than one or two thousand atmospheres.) In the residue of the unexploded tubes it was said that diamonds of density 3.5 were found. The claim was accepted at its face value and reported in the London *Times* by N. Story-Maskelyne. Subsequent attempts by a number of experimenters failed, however, to reproduce Hannay's results.

The matter was reopened in 1943 by the discovery in a forgotten corner of the British Museum of a small exhibit labeled "Hannay's Diamonds." These were analyzed with X-rays by F. A. Bannister and Kathleen Lonsdale, and found to be certainly diamonds, and of a somewhat rare type at that. On the theory that it was unlikely that diamonds fraudulently inserted would be of this rare type, Bannister and Mrs. Lonsdale argued that Hannay's claim was probably genuine. But there was also contrary evidence, in particular, as pointed out by Lord Rayleigh, some known instances of bad faith on Hannay's part. It seems to be the present consensus that Hannay was a fraud. Mrs. Lonsdale recently told me that she now also inclines to that view.

Perhaps the best known experiments of all are those of the Frenchman Henri Moissan, made in the 1890s when he was



**HYDRAULIC PRESS** in which the diamonds were grown is capable of exerting a force of 1,000 tons. The pressure chambers are located below the floor level (*bottom*).

metal halide melts, obtaining feltable titanium dioxide fibers, and isolating the feltable titanium dioxide fibers from the metal halide melt.

---

### 3,030,184
### METHOD FOR PRODUCTION OF MAGNESIUM HYDRIDE

John P. Faust, Kenmore, Charles E. Fogle, Niagara Falls, and Theodore L. Heying, Tonawanda, N.Y., assignors to Olin Mathieson Chemical Corporation
No Drawing. Filed Aug. 21, 1958, Ser. No. [illegible]
8 Claims. (Cl. 23—204)

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 compound of the class RXX' wherein R 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.

---

### 3,030,185
### PROCESS FOR PRODUCING BORON TRICHLORIDE

Sheldon L. Clark, Kenmore, and Theodore L. Heying, Tonawanda, N.Y., assignors to Olin Mathieson Chemical Corporation, a corporation of Virginia
No Drawing. Filed Feb. 14, 1958, Ser. No. 715,474
2 Claims. (Cl. 23—205)

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, separately reacting the mixture of boron hydrides higher than decaborane in a second reaction zone at a temperature within the range from about 50° to 550° C. with a gas stream consisting essentially of chlorine, and recovering boron trichloride from the reaction products.

---

### 3,030,186
### MANUFACTURE OF HYDROGEN PEROXIDE

Donald F. Kreuz, Buffalo, and Leonard R. Darbee, Grand Island, N.Y., assignors to FMC Corporation, a corporation of Delaware
No Drawing. Filed May 16, 1958, Ser. No. 735,675
2 Claims. (Cl. 23—207)

1. In the production of hydrogen peroxide by the alternate reduction and oxidation of an alkylated anthraquinone as the working material carried in solution and wherein the working material is hydrogenated by passage through a fixed particulate catalyst bed of a noble metal catalyst deposited as a surface coating upon an inert solid carrier, that 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. of less than 0 03 cc. per gram.

---

### 3,030,187
### SYNTHESIS OF DIAMOND

William G. Eversole, Kenmore, N.Y., assignor to Union Carbide Corporation, a corporation of New York
No Drawing. Filed July 23, [redacted] Ser. No. 750,309
8 Claims. (Cl. 23—209.4)

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 selected from the group consisting of carbon monoxide and mixtures of carbon dioxide and carbon monoxide at temperatures between about 600° C. and about 1600° C and pressures above about 20 atmospheres.

---

### 3,030,188
### SYNTHESIS OF DIAMOND

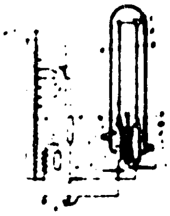
William G. Eversole, Kenmore, N.Y., assignor to Union Carbide Corporation, a corporation of New York
No Drawing. Original application July 23, [redacted] Ser. No. 750,309. Divided and this application Nov. 24, 1961, Ser. No. 154,836
9 Claims. (Cl. 23—209.4)

1. A process for growing diamond on diamond seed crystal which comprises providing diamond seed crystal; contacting said diamond seed crystal with a gas which is at least partially decomposable to a free methyl radical at temperatures between about 600° C. and about 1600° C. and pressures at which the partial pressure of the gas decomposable to a free methyl radical is less than about 75 millimeters of mercury.

---

### 3,030,189
### [illegible] OF [illegible] SUBSTANCES OF [illegible], PARTICULARLY ELECTRIC [illegible]

[illegible] and [illegible] Gutsche, Erlangen, and [illegible], Germany, assignors to [illegible]
[illegible]
8 Claims. [illegible]



5. A method of producing an electric semiconductor of high purity, comprising contacting the peripheral surface of an elongated carrier body of the same material as the semiconductor with a gas comprising a chemical compound of the material, the carrier body being heated by passing an electric current through the elongated body lengthwise thereof, the heating being to a temperature sufficiently high to cause chemical conversion of the chemical compound to said material and deposition of the latter on the lengthwise extending peripheral surface of the carrier body, stretching the enlarged body, in a crucible-free zone-pulling process, by pulling an end region thereof in a direction away from the opposite end region while melting a zone of limited longitudinal dimension by heating means having no contact with said zone, the molten zone being caused to be displaced longitudinally with respect to the body during the pulling, whereby an elongated section of reduced cross-section is produced in the body, contacting at least part of the reduced section, employed as heated elongated carrier body, with a gaseous chemical compound of the said material to enlarge said piece by deposition of the material thereon.

---

### 3,030,190
### METHOD OF CHEMICAL TESTING OF OILS

Walter P. [illegible], [illegible], and [illegible], Germany, assignors to Shell Oil Company, New York, N.Y., a corporation of Delaware
No Drawing. Filed Apr. [illegible], 1960, Ser. No. [illegible]
Claims priority, application Germany May 25, 1959
6 Claims. (Cl. 23—[illegible])

1. A method of determining the [illegible] number of mineral oils which are subject to contamination with

1968

JOURNAL OF APPLIED PHYSICS VOLUME 39, NUMBER 6 MAY 1968

# 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 cound 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,[3] Suits,[4] Lander and Morrison,[5] and Angus.[6] In addition, claims of successful low-pressure syntheses were made by Brinkman[7] and Eversole,[8] 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 the 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.[5]

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 supersaturated 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-

---

[*] Present address: NASA, Lewis Laboratories, Cleveland, Ohio.

[1] P. W. Bridgman, Sci. Am. 193, 42 (1955).

[2] F. P. Bundy, H. T. Hall, H. M. Strong, and R. H. Wentorf, Nature 176, 51 (1955).

[3] A. R. Ubbelohde and F. A. Lewis, *Graphite and Its Crystal Compounds* (Oxford University Press, London, 1960), p. 62.

[4] C. G. Suits, *The Synthesis of Diamond—A Case History in Modern Science*, A paper presented before the American Chemical Society, Rochester, New York, Nov. 3, 1960, Reference is made to an unpublished report by R. A. Oriani and W. A. Rocco.

[5] J. J. Lander and J. Morrison, Surface Sci. 4, 241 (1966).

[6] J. C. Angus, *Synthesis of Diamonds*, unpublished report, Nov., 1961.

[7] J. A. Brinkman, U.S. patent No. 3,142,539, July 28, 1964.

[8] W. G. Eversole, Canadian patent No. 628,567, October 3, 1961.

АКАДЕМИЯ НАУК СССР

Ордена Трудового Красного Знамени
Институт физической химии

DERYAGIN FEDOSEEV
Б. В. ДЕРЯГИН, Д. В. ФЕДОСЕЕВ

# GROWTH of DIAMOND
# РОСТ АЛМАЗА
# and И ГРАФИТА GRAPHITE
# ИЗ ГАЗОВОЙ ФАЗЫ
# from GAS PHASE

Издательство «Наука»
Москва [illegible]

## ОГЛАВЛЕНИЕ

Предисловие . . . . . . . . . . 3

PRINCIPLES OF NUCLEATION THEORY
1. ОСНОВНЫЕ ЗАКОНОМЕРНОСТИ НУКЛЕАЦИИ 5
- 1. Теория гомогенной нуклеации . . . . . . . . 5
- 2. Влияние поверхностных сил на образование и свойства новой фазы . . . . . . . . . 15
- 3. Теория гетерогенной нуклеации . . . . . . 22

GROWTH OF GRAPHITE FROM GAS PHASE
2. РОСТ ГРАФИТА ИЗ ГАЗОВОЙ ФАЗЫ . . . . . 34
- 1. Физико-химическая теория роста графита . . 34
- 2. Экспериментальная проверка предложенной теории роста графита . . . . . . . . . 36
- 3. Рост графита в неизотермических условиях . . . 42
- 4. Нитевидные кристаллы графита . . . . . . . 44

KINETICS OF PHYSICO-CHEMICAL SYNTHESIS OF DIAMOND
3. КИНЕТИКА ФИЗИКО-ХИМИЧЕСКОГО СИНТЕЗА АЛМАЗА 52
- 1. Из истории синтеза алмаза . . . . . . . . . 52
- 2. Кинетика роста алмаза на алмазных порошках 58
- 3. Циклический метод наращивания алмазных порошков . . . . . . . . . . . . 71
- 4. Механизм роста алмаза . . . . . . . . . 76
- 5. Синтез алмаза из смесей углеводородов (неаддитивность скоростей реакций) . . . . . . 83
- 6. Фракционирование стабильных изотопов углерода . . . . . . . . . . . . 88
- 7. Определение удельной поверхности порошков 90

EPITAXIAL FILMS OF DIAMOND AND WHISKERS
4. ЭПИТАКСИАЛЬНЫЕ АЛМАЗНЫЕ ПЛЕНКИ И НИТЕВИДНЫЕ КРИСТАЛЛЫ . . . . . . . 98
- 1. Синтез и свойства алмазных пленок . . . . . 98
- 2. Импульсный способ наращивания алмаза . . 103
- 3. Нитевидные и изометричные кристаллы алмаза 105

Литература . . . . . . . . . . . . 112

[illegible] FILMS & WHISKERS

## 4. ЭПИТАКСИАЛЬНЫЕ АЛМАЗНЫЕ ПЛЕНКИ И НИТЕВИДНЫЕ КРИСТАЛЛЫ

HYPOTHETICAL SOLVENT

### [illegible] и свойства [illegible] пленок

[illegible] эпитаксиальн[illegible] бы[illegible] получены [illegible] скорости роста алмаза [illegible] большие ско[illegible] [illegible] сравнительно [illegible] [illegible] растворитель, который не действовал бы на алмаз, [illegible] графита. Все усилия [illegible] были [illegible] направлены [illegible] на подавление [illegible] значительной скорости роста алмаза. [illegible] пленок [illegible] с на[illegible] алмаза [illegible] размером [illegible] алмазных [illegible]ков. Небольшие [illegible] алмазных [illegible] кристаллах получены [illegible] значительно превышающие линейные ско[illegible] [illegible] 8.

[illegible] вопрос [illegible] пара[illegible] [illegible] высокими линейными скоро[illegible] [illegible] быть разъяснена [illegible]. Для [illegible] каждого нового [illegible] необходимо, чтобы спа[illegible] [illegible] критически[illegible]. Вероятность [illegible] площади, [illegible] между [illegible] двух за[illegible] площади [illegible] этот промежу[illegible] вместится [illegible] атомов, то ли[illegible] скорость [illegible] равной частному от деления рас[illegible] соседних атомных слоев на интервал времени между образо[illegible] критических зародышей. Если бы эта закономерность [illegible], то линейная скорость роста, прямо [illegible] площади грани, была бы пропорциональна [illegible] размеров кристалла. Однако этот закон справед[illegible] [illegible] оговоркой.

К[illegible] площадь кристаллической грани [illegible] известные гра[illegible] либо за время появления на ней второго критического за[illegible] [illegible] достичься, либо это не сможет произойти [illegible] грань кристалла не является идеально гладко выло[illegible] [illegible] и состоит из террас, разделенных ступеньками. [illegible] каждой террасы [illegible] на ней [illegible] образоваться [illegible] зародыш

ATOMIC HYDROGEN:
1. CATALYTIC e.g. Pt

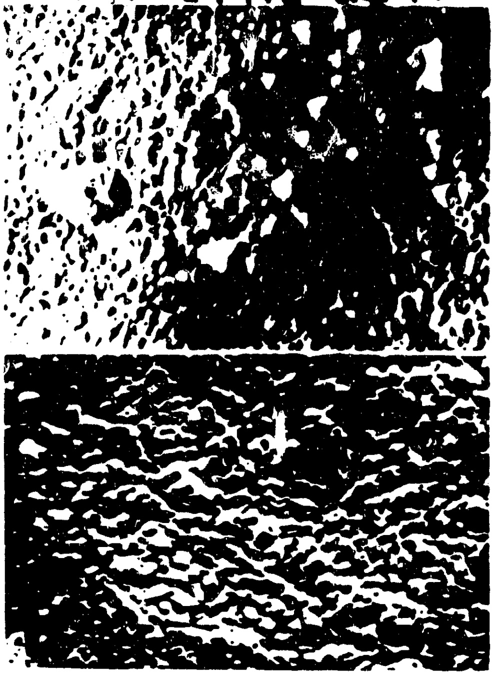


Рис. [illegible]

Таким образом, [illegible] максимальная линейная скорость роста граней равна расстоянию между соседними слоями, деленному на среднее время между появлением двух [illegible] критических зародышей на одной и той же террасе. Размеры террас не [illegible] различны у разных кристаллов и на разных гранях [illegible] ся, например уменьшаться по мере роста кристалла. В [illegible] нем случае рост кристалла замедляется.

Иначе обстоит дело с блокированием [illegible] щимся графитом, образующимся на [illegible] новь растущие как эпитаксиальные [illegible] щиеся трехмерные зародыши графита [illegible] родышей алмаза, не способны заместить [illegible] графита, поэтому блокирование каждой [illegible] купным действием кристаллических зародышей графита [illegible] вательно образующихся и растущих на ней [illegible] того время, по истечении которого процесс блокирования [illegible] ски прекращает или в определенной степени замедляет [illegible] ший рост алмаза, не зависит от размера кристалла и не [illegible] его увеличением. Отсюда понятно, почему [illegible] большими кристаллами (3—4 [illegible]) можно было получ[illegible] линейную скорость роста, чем для порошков.

На ранних стадиях кристаллизации из газа заметно проявляется эффект декорирования, т. е. фиксации деталей строения поверхности реального кристалла. На рис. 54 показано автодекорирование вы[illegible] алмазом поверхности затравочного кристалла алмаза на начальной стадии кристаллизации. При дальнейшем росте появляются отдельные островки новой фазы (рис. 55 а), которые затем, сливаясь, образуют сплошной фронт кристаллизации (рис. [illegible]).

Чтобы увеличить скорость роста алмаза, необходимо удалять графит. Травителем для селективной газификации графита может

SELECTIVE GASIFICATION OF GRAPHITE

Рис. 54. Автодекорирование поверхности [illegible] кристаллизации [illegible]

2. ELECTRICAL DISCHARGE,
3. W FILAMENT

служить водород. Как было показано в предыдущей главе, разбавление углеродсодержащего газа водородом сильно уменьшает скорость роста графита, но почти не отражается на скорости роста алмаза. Также известно, что водород хорошо травит графит при давлениях до [illegible] атм и температуре 1000° С [45]. Однако можно предположить, что на графит действует именно атомарный водород. При понижении давления молекулярного водорода концентрация атомарного водорода увеличивается пропорционально корню квадратному из общего давления. Поэтому для газификации используют высокие давления.

1. Однако можно каталитически [88] или с помощью электрического
2. разряда [89] создать сверхравновесную концентрацию атомарного водорода. Так, в работе [48] для удаления графита с алмазных по-
3. рошков использовался атомарный водород, генерируемый нагретой вольфрамовой нитью.

Соединение в одном реакторе двух процессов — роста алмаза (и графита) из углеродсодержащего газа и каталитического получения атомарного водорода в непосредственной близости от затравочного монокристалла алмаза — позволило авторам совместно с Н. Д. Поляковой получить и исследовать структуру достаточно толстых эпитаксиальных алмазных пленок.

Структурные исследования, проведенные [illegible] дифракции медленных электронов под малыми углами, [illegible] создать следующую картину роста. Первоначально растет [illegible] совершенного монокристалла (рис. 56, а), затем его структура ухудшается и наряду с монокристаллическими участками растет поликристаллический алмаз (см. рис. 56, б). На следующей стадии растет как алмаз, так и графит, причем алмаз сохраняет монокристальную структуру, что видно по линиям Кикучи, которые часто бывают двойными вследствие наследования двойниковой структуры кристалла-затравки. Далее растет поликристаллический алмаз совместно с графитом и наконец один графит (см. рис. 56, в). Ниже приведены результаты расчета и табличные значения межплоскостных расстояний на стадии, соответствующей рис. 56, [illegible]

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $d_{изм}$, Å | 2,06 | 1,27 | 1,073 | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| $d_{табл}$, Å | 2,[illegible] | 1,26 | 1,[illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |

Некоторые свойства алмазных эпитаксиальных пленок изучены в работах [90]. Микротвердость алмазных пленок измерялась методом вдавливания трехгранной алмазной пирамиды на приборе ПМТ-3. Глубина вдавливания составляла [illegible] мкм. Измеренная величина микротвердости равнялась 9600 ± 400 кГ/мм², что соответствует данным для природного алмаза.

Элементный состав пленок по данным микрорентгеноспектрального анализа, проведенного на приборе MS-46 («Камека»), отвечает содержанию углерода 99,5 ± [illegible] %. Плотность пленок синтетического алмаза, определенная по скорости флотации для трех образцов, оказалась равной [illegible] ± [illegible] г/см³. Показатель преломления

1981

Journal of Crystal Growth 52 ([illegible]) 219–226
© North-Holland Publishing Company

# VAPOR 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 reached 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 0.0009 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 crystalline 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 ~$1 \times 10^{-13}$ Torr. An acceptable growth rate (about 1 μm/h) requires that the carbon vapor pressure over diamond phase exceed $10^{-6}$ 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 $C_3$-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 determines 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.

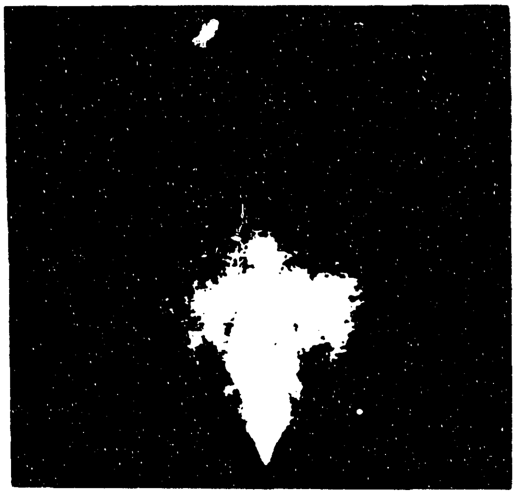


Fig. 1 Electron diffraction pattern ($E = 65$ keV) of a diamond film 0.8 μm thick, grown on {110} face of a natural diamond crystal at a growth rate ~0.4 μm/hour.

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 microtwin 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

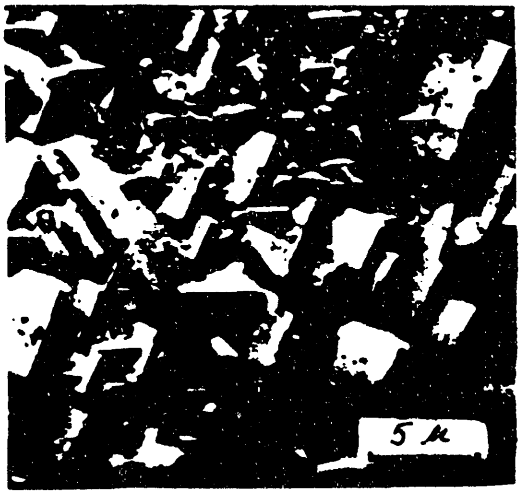


Fig. 2. Diamond layer ~4 μm thick, grown at a rate of ~2 μm/hour on {111} face of a natural crystal.

hydr
pitax
diam
CTR
of at
expe
thetic
table

4. Se

Int
the p
sible
line
dopir
~10
condu
Meas
demo
layers
X-ray
centr.
paran
[16].
tivity
levels
sites.
(up tc
is pra
appea
to bo
pensa
boron

DIAMOND ON DIAMOND

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

of a 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

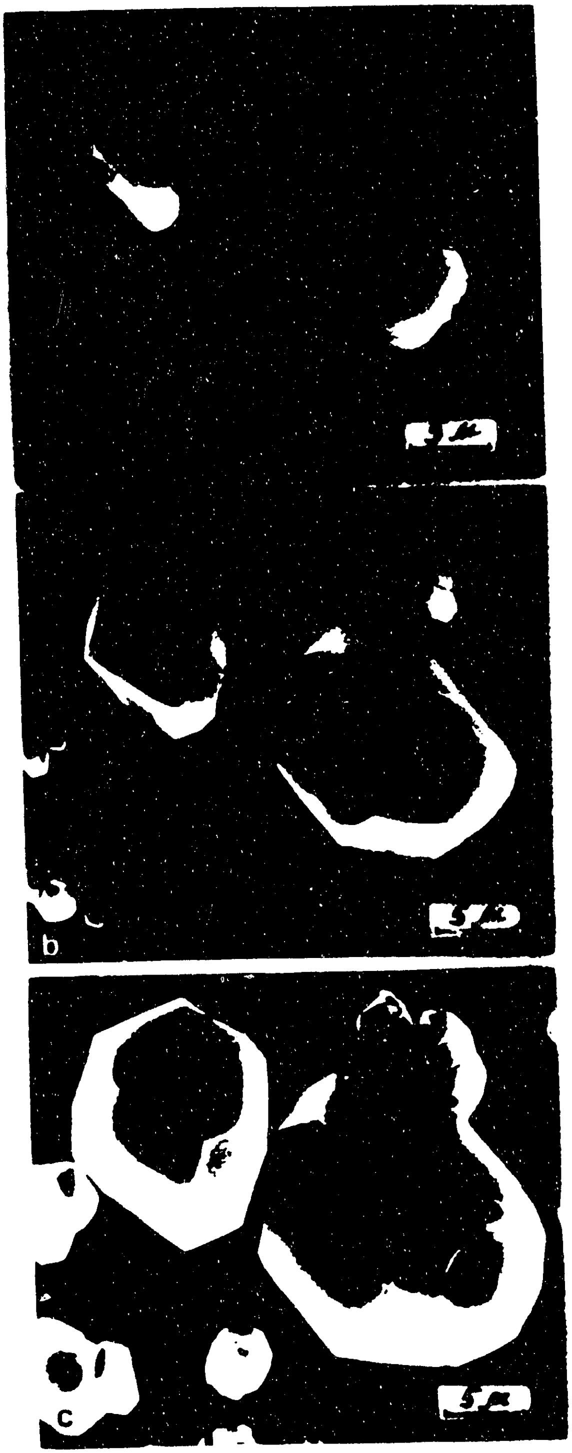


Fig. 5. Growth of diamond crystals on copper substrate: (a) area of substrate with two rounded-shape diamond seed crystals, (b) and (c) same area after 15 and 30 min of crystallization, respectively.

Japanese Journal of Applied Physics
Vol. 21, No. 4, April, [illegible] pp. L183–L185

1982

# Vapor Deposition of Diamond Particles from Methane

Seiichiro MATSUMOTO, Yoichiro SATO, Mutsukazu KAMO
and Nobuo SETAKA

*National Institute for Research in Inorganic Materials,*
*1-1 Namiki, Sakura-mura, Niihari-gun, Ibaraki 305*

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

Microcrystalline diamond has been formed on silicon or molybdenum substrates by vapor 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 scattering.

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),[1-3] ion-beam techniques,[4-6] and plasma-induced vapor deposition.[7-10] The carbon films obtained by these techniques are often termed diamondlike, 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.[3,6,8,9]

On the other hand, Deryagin *et al.*[11] 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 mechanism has been given by Spitsyn *et al.*[12] Diamond crystals were grown on diamond, 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 deposition chamber, in which a tungsten filament was mounted near the substrate, 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; flowrate, ca. 10 ml/min, temperature of deposition chamber, 800–1000°C; filament temperature, ca. 2000°C. The temperature of the deposition chamber was measured by a thermocouple in contact with the silica substrate holder, as shown in

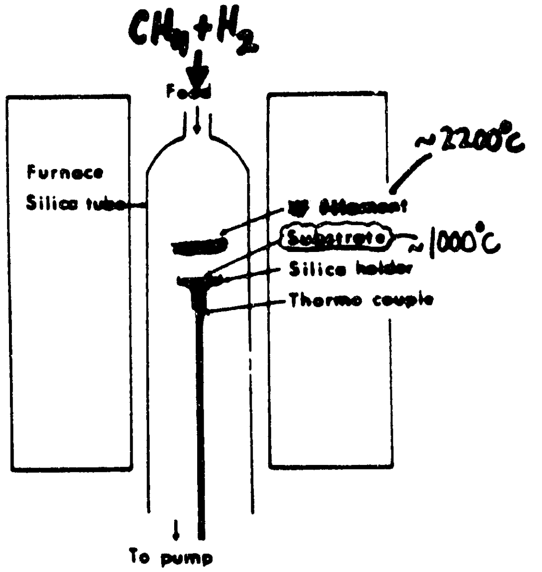


Fig. 1. Schematic diagram of deposition chamber.

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 morphologies resemble that observed with crystals deposited by chemical transport in a closed system.[11,12] Film-like regions are also formed by the contact of crystals, as Fig. 2(b) shows. 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

Jpn. JAP 21, L183 (1982)

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 800°C.

SEM MORPHOLOGY

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

| Observed | | Reported (ASTM 6–675, Diamond) | | |
|---|---|---|---|---|
| *d* (Å) | *I* | *d* (Å) | $I/I_1$ | *hkl* |
| 2.06 | s | 2.06 | 100 | 111 |
| 1.26 | r | 1.261 | 25 | 220 |
| 1.08 | s | 1.0754 | 16 | 311 |
| 1.03 | w | — | — | 222 |
| $0.89_3$ | w | 0.8916 | 8 | 400 |
| $0.81_8$ | m | 0.8182 | 16 | 331 |
| 0.727 | m | 0.7280ᵃ | | 422 |
| 0.685 | m | 0.6864ᵃ | | 511, 333 |
| 0.633 | w | 0.6305ᵃ | | 440 |
| 0.603 | m | 0.6029ᵃ | | 531 |

ᵃ Calculated from the reported values of $a_0 = 3.5667$ Å.

TED CRYSTAL STRUCTURE

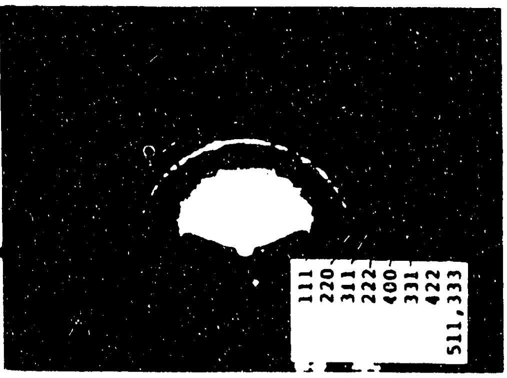
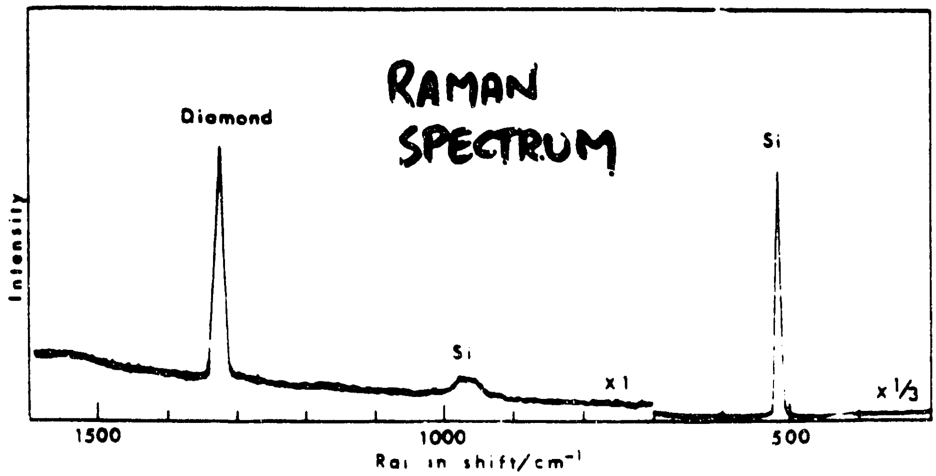


Fig. 3. Reflection electron diffraction of diamond particles deposited on silicon.

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 to the substrate, and background due to weak luminescence, as Fig. 4 shows. Raman scattering from to amorphous



RAMAN SPECTRUM

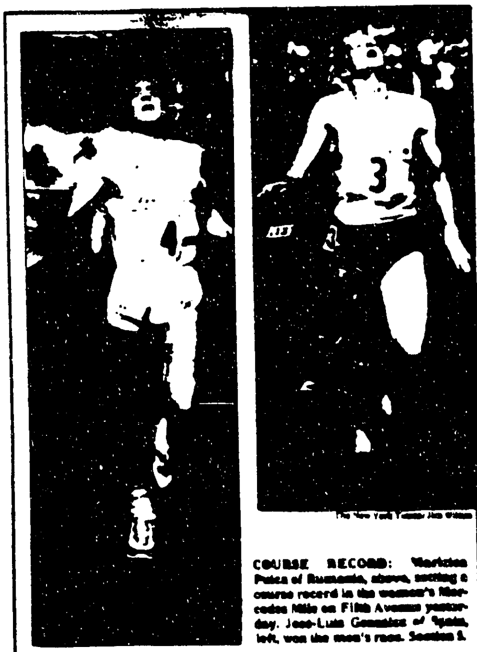
Fig. 4. Raman spectrum of as-grown specimen silicon substrate. 441.6 nm line of He–Cd laser was used for excitation.

: PERSONAL FINANCE, A PLANNING GUIDE, SECTION

"All the News That's Fit to Print"

The New York Times

VOL.CXXXV .... No. 46,897 — NEW YORK, SUNDAY, SEPTEMBER 14, 1986



The New York Times/Jim Wilson

**COURSE RECORD:** Maricica Puica of Rumania, above, setting a course record in the women's Mercedes Mile on Fifth Avenue yesterday. José-Luis Gonzalez of Spain, left, won the men's race. Section 5.

# 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. DIONNE Jr.

Special to The New York Times

WASHINGTON, Sept. 13 — While national attention has focused on the elections that will determine which party controls the Senate, political leaders say the Republican Party, remarkably, is likely to avoid any serious losses in the House of Representatives this year.

Experts from both parties agree that the Democrats will maintain control of the House but that their chances for dramatic gains are minimal.

The analysts are speaking instead of the Democrats' picking up 10 to 15 seats, much less than has often been the case when one party has controlled the White House for six years. The average shift has been 40 seats in the last three elections held at such a time: 1974, 1966 and 1958.

### Estimate Is Subject to Change

Both sides caution that dramatically bad economic news, such as a continuation of this week's slide in the stock market, could alter the picture substantially.

"I thought we were in pretty good shape in October of 1982," said Joseph Gaylord, executive director of the National Republican Congressional Committee. But when the national unemployment rate rose to over 10 percent in mid-October of that year, Republicans all over the country dropped sharply in the polls.

Both parties agree that the estimates of a Democratic gain of 10 to 15 seats, while realistic, are as much a guess as they are the result of careful analysis. The figure has been popular with each side partly because it would allow each to claim victory.

The Republicans could cite it as a minimal loss, while the Democrats could say they had restored themselves to within about 10 seats of where they were when President Reagan was first elected in 1980.

"We've been in the ring six years with the heavyweight champ and we only lose 10 seats?" said Martin D. Franks, executive director of the Democratic Congressional Campaign Committee. "That's not much of a loss."

As for the Republicans, Mr. Gaylord

Continued on Page 38, Column 4

Associated Press

Nicholas S. Daniloff and his wife, Ruth, in Moscow yesterday.

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

By PHILIP TAUBMAN

Special to The New York Times

MOSCOW, Sept. 13 — The Soviet Union presented new espionage charges against an American correspondent today and said the United States was holding East-West relations hostage to the case.

The charges were presented by Gennadi F. Gerasimov, Foreign Ministry spokesman, at a news briefing. He said the Soviet Government had "irrefutable" evidence that the correspondent, Nicholas S. Daniloff of the magazine U.S. News & World Report, had "acted on instructions" of an American diplomat, Murat Natirboff, who ended an assignment here this summer.

The Soviet Government press agency, Tass, in reporting Mr. Gerasimov's briefing, identified Mr. Natirboff as Moscow station chief of the Central Intelligence Agency.

Jaroslav Verner, a spokesman for the United States Embassy, said Mr. Natirboff's title at the embassy was counselor for regional affairs.

[In Washington, a White House spokesman repeated the Government's assertion that Mr. Daniloff was not a spy and had never worked for an American intelligence organization. At the State Department, a spokesman declined to provide information about Mr. Natirboff.]

Mr. Natirboff is the second embassy official to have been linked by the Soviet authorities to Mr. Daniloff. Last Monday the Government newspaper Izvestia said Mr. Daniloff had been alluded to in a letter from Paul M. Stombaugh, an embassy staff member who was expelled in June 1985 for what Moscow said was espionage.

### Daniloff Again Denies U.S. Link

Mr. Daniloff, who was released from prison Friday into embassy custody pending trial, told The Associated Press that he "would not dignify the charges by commenting on them."

Earlier, in a written statement read by his wife, Ruth, he said, "I have no official or secret relationship with any intelligence agency."

The custody arrangement under which Mr. Daniloff was released from jail also involved the release in New York of Gennadi F. Zakharov, a Soviet employee of the United Nations, who faces espionage charges in the United States.

Mr. Daniloff, who is free to move about Moscow but must check in with

Continued on Page 14, Column 1

# New Era of Technology Seen In Diamond-Coating Process

By MALCOLM W. BROWNE

Scientists have discovered a way of coating objects with thin films of synthetic diamond, an achievement that they believe has opened a new era for electronics, optics, machine tools, chemical processing and military technology.

Experts said that diamond-coating processes would be cheap enough, moreover, to make diamond film a common manufacturing material. Although many diamond films will be no more visible to the unaided eye than coatings of transparent lacquer, they will radically improve the quality of the objects they coat.

Long-wearing tools and bearings coated with diamond film and powerful new optical systems for scientific instruments, communications and weapon systems are just some of the many intended applications. Others are scratch-proof lenses and windows, ultra-high-fidelity diamond loudspeakers and a new generation of high-speed solid-state devices impervious to the radiation of nuclear blasts. Diamond coatings could improve a range of devices extending from the most advanced rocket engines to humble razor blades, experts say.

### Impact on Society

Some scientists suggest that diamond film could have an impact on society comparable to that of the advent of cheap aluminum after the invention of the electric extraction process 100 years ago.

Developments in recent months have been so rapid and dramatic that a wide cross section of American industry and the Pentagon's Strategic Defense Initiative Organization, which is developing a space-oriented defense against intercontinental missiles, have joined the drive to exploit diamond coatings.

Scientists at Pennsylvania State University are among the leaders in diamond-film research, and Penn State held a conference on Wednesday to inform American industry of the latest developments and possibilities.

### Soviet and Japanese Advances

Some of the biggest news came from abroad. The Soviet Union has succeeded in developing diamond films more than one millimeter thick, and next year, Sumitomo Electric Industries of Japan is expected to begin producing the world's first diamond computer chips.

Representatives of more than 40 companies, including many of the

Continued on Page 38, Column 1

**Today's Sections**

1 ——— News
2 ——— Arts and Le
3
4 ——— The Week in
5
6

# *Why Stocks F Anxiety, With*

By LEO

*The precipitous stock market d on the New York Stock Exchange*

1986

REDAKTÖR LARS RYDING, Tel. 08-13 51 56.

# Diamanter av sumpgas!

**Att tillverka diamanter av vanlig simpel sumpgas är nu fullt möjligt. Det kan bli en vardagsvara i förskärare, glasögon och kanske framför allt i datorernas chips. En av följderna av detta revolutionerande nya kan bli att diamanter blir betydligt mindre sällsynta och exklusiva.**

Harry Bökstedt

En sällsynt geologisk skapelse uppstigen ur jordens inre, eller en högteknologisk produkt tillverkad i laboratoriet under extremt höga tryck — det har hittills varit vår bild av diamanten. Som verktygsmaterial hårdare än något annat ämne, som adelsten den dyrbaraste och skönast gnistrande av alla. Men nu händer det saker som snart kan komma att göra diamanter betydligt mindre sällsynta och exklusiva. Man har upptäckt att det går att tillverka diamant av vanlig simpel sumpgas. Det kan bli en vardagsvara i förskärare, glasögon, och kanske framför allt i datorernas chips. Diamant har unika egenskaper som kan revolutionera halvledarindustrin, spår entusiasterna.

Bakom den nya tekniken för diamanttillverkning ligger en tio år gammal sovjetisk upptäckt. Just den härkomsten kan i och för sig vara värd ett utropstecken. Sovjetunionen har inte precis skämt bort oss med banbrytande tekniska framsteg.

## Sovjet först och sist

När tidskriften Fortune (13 oktober) publicerade en av experter utförd rangordning av de fyra teknikjättarna i världen hamnade Sovjetunionen på jumboplats inom samtliga de fyra "high tech" områden som betygsättningen gällde, men låg klart bäst till i fråga om utvecklandet av nya material — och detta inte minst tack vare upptäckten av den nya metoden att tillverka diamant.

(Övriga områden var elektronik, bioteknik och optoelektronik, och jämförelsen gjordes mellan USA, Japan, Västeuropa och Sovjet.)

Det mest förbluffande är kanske att de moderna diamantfabrikanterna har brutit med vad som kan kallas för naturprincipen, alltså de förhållanden under vilka diamanter har uppstått i jordens innandöme.

I geologiska handböcker brukar det kort och gott heta att diamanter endast kan bildas vid ett tryck som är lika stort som trycket på 125—150 km djup under jordytan. Därifrån har de dyrbara stenarna sedan transporterats högt upp i jordskorpan vid vulkanutbrott. Naturliga diamanter förekommer i sedimentära bergarter och framför allt i flodavlagringar, där de hamnat genom vittring och det rinnande vattnets spel.

## Endast kol

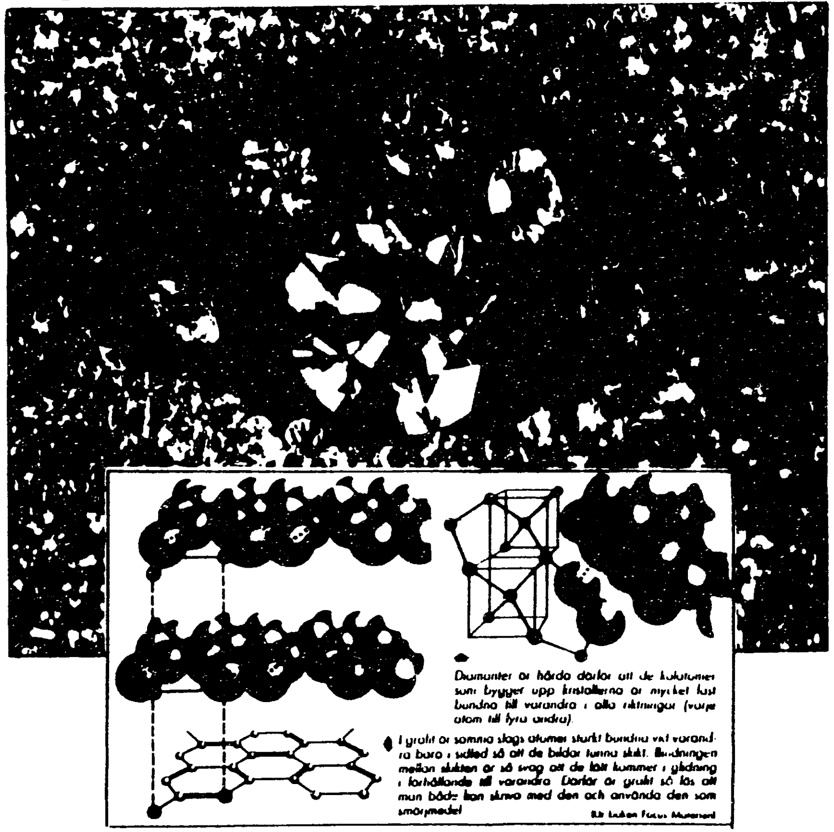
Kemiskt sett är ren diamant ingenting annat än kol. Det avslöjade den berömde franske kemisten Lavoisier år 1792, när han förbrände diamant tillsammans med syre och alltihop gick upp i rök, närmare bestämt gasen koldioxid.

Diamant är den ena av grundämnet kols kristallformer. Den andra är grafit, som ser ut att vara något helt annat, och är avgjort mera kolliknande. Det är svartgrått till färgen, och lämpar sig utmärkt att skriva med, i blyertspennor t ex — därav namnet efter det grekiska "grafein" = skriva.

Det som gör de båda kristallerna så kolossalt olika är att atomerna binds vid varandra på olika sätt. I diamant ingår alla atomer i ett hårt och oupplösligt tredimensionellt gitter. Grafit består av enkla sinsemellan löst sammanfogade atomskikt, som lätt halkar på varandra — så lätt att grafit också kan användas som ett utomordentligt smörjmedel.

## Asea först

När man började tillverka konstgjorda diamanter (för industribruk) gick man in för att kopiera den naturliga processen. Det var vid mycket högt tryck — c:a 70 tusen atmosfärer, och hög temperatur — c:a 2 000 grader, som Asea 1953 lyckades framställa de första syntetiska diamanterna av grafit. Det skedde i samarbete med Baltzar von Platen och med hjälp av en av denne och Hans Lårker konstruerad press. Ungefär i samma veva gjorde General Electric om samma bedrift.



Diamanter är hårda därför att de kolatomer som bygger upp kristallerna är mycket fast bundna till varandra i alla riktningar (varje atom till fyra andra).

I grafit är samma slags atomer starkt bundna vid varandra bara i sidled så att de bildar tunna skikt. Bindningen mellan skikten är så svag att de lätt kommer i glidning i förhållande till varandra. Därför är grafit så lös att man både kan skriva med den och använda den som smörjmedel.

[illegible]

Men långt innan dess hade kemister drömt om att åstadkomma en utfällning av diamantkristaller genom förångning av någon enkel kolförening. En sådan är kolvätet metan eller sumpgas, som inom parentes sagt inte luktar någonting alls.

Och som tidskriften Science berättar (28 november) kunde faktiskt en forskare vid amerikanska Union Carbide år 1958 ta patent på en metod att framställa tunna diamantfilmer genom stark upphettning (pyrolys) av metan.

Dessvärre gick det inte att utnyttja upptäckten. Samtidigt med diamantkristallerna bildades också grafit, som en "förorening", som det var svårt att bli av med.

Det är det problemet som sovjetiska forskare har löst. 1977 kunde Boris Derjaguin vid Institutet för fysikalisk Kemi i Moskva och hans kollega D V Fedosejev rapportera att de funnit ett sätt att förhindra att grafit fälls ut. Det består i att låta upphettningen av kolvätet ske i närvaro av atomärt väte (väte i form av enskilda atomer, och inte som vanliga 2-atomiga vätemolekyler).

Några år senare visade Derjaguins grupp att det med en sådan metod går att få ett sammanhängande diamantskikt att växa med 1 mikrometer per timme. Besökare i laboratoriet i Moskva fick där [illegible] tunna diamantfilmer som ersatts på underlag av plast. Även metaller kan tjäna som substrat för sådana filmer.

Nyheterna från Moskva gav eget genljud i USA, kanske därför att amerikanerna innerst inne tvivlade på att det verkligen kunde vara så pass tekniskt enkelt och billigt att göra diamanter. Därmed missade man uppföljningen av ett tekniskt genombrott.

Det gjorde däremot inte japanerna. Redan 1982 började forskare vid institutet för materialforskning i Ibaraki ta fram nya förbättrade versioner av den sovjetiska diamanttekniken och numera arbetas det med diamantfilmer i närmare tjugotalet laboratorier vid universitet och industrier i Japan.

Det har också den nya kunskapen raskt omsatts i praktiska tillämpningar. Några företag sägs redan vara färdiga att släppa ut sådana på marknaden. Från Sony väntas sålunda en ny högtalare för hypertrogen ljudåtergivning, där hemligheten sitter i att högtalarkonen är överdragen med en diamanthinna.

Diamantklädda och därmed garanterat repfria glasögonlinser och flygplansfönster är andra aviserade produkter. Verktyg av olika material kan få en oanad hållbarhet och hårdhet om de överdras med ett tunt diamantskikt. Kökskniver som är vassa som rakknivar och aldrig blir slöa, är kanske något att se fram emot.

## Diamantfeber i USA

Sent omsider har också amerikanerna gripits av diamantfeber. I år har forskare vid [illegible] framgångsrikt tunnfilmer av diamant på kiselsubstrat genom att hetta upp en blandning av väte och metan med mikrovågor, omtalar Science. Ett företag i Palo Alto i Kalifornien, Crystallume, har i ett par år arbetat på att utveckla egna diamantprodukter.

Det som för närvarande framför allt stimulerar forskningen kring denna nya materialteknik i USA är planerna på det strategiska rymdförsvaret. Projektet "Stjärnornas krig" kommer att kräva fabulösa nya material, som i många avseenden överträffar allt som står att få i dag. Exempelvis för sådana skyddsfönster för optiska linser, som ångdeponerade diamantfilmer kan bilda. För att inte tala om de möjligheter som de nya diamanterna öppnar för datorer och annan elektronisk utrustning.

Och då gäller det inte bara materialets hårdhet och hållbarhet, även om det kan komma väl till pass bl a för att klara av skivminnen som lätt kan skadas av läs- och skrivhuvudet.

## Bättre värmeledare

Nej det är andra egenskaper som gör diamantfilmerna speciellt intressanta i sammanhanget. Bl a att diamant är en bättre värmeledare än något annat ämne.

Störande värmeutveckling är ett stort bekymmer när man vill packa in så många transistorer som möjligt i en integrerad krets och fylla sin utrustning med så många kretskort som möjligt. Med kretskort av diamant skulle värme ledas bort utan att man behövde ordna med extra kylning av komponenterna.

Det skulle också vara möjligt att tillverka själva transistorerna av diamant. Japanska forskare har gjort tunnfilmer av diamant till fungerande halvledare genom att dopa dem med bor och fosfor. De elektriska egenskaperna hos diamant anses göra ämnet till ett många gånger bättre halvledarmaterial än kisel.

Det skulle också finnas andra goda sidor hos diamantchips. De skulle utan särskilda skydd kunna placeras i en bilmotor eftersom de tål både hög temperatur och smuts. De är relativt okänsliga för strålning och skulle därför vara mycket tjänliga i kommunikationssystem i rymden.

## Något extra

Som halvledarmaterial har diamant ytterligare en egenskap som gör det till något extra. Elektronhastigheten är så hög i ämnet att det skulle kunna arbeta snabbare än galliumarsenid som f n innehar hastighetsrekordet bland halvledarna.

Diamant kan tydligen bli ett mirakelmaterial, men än är man långtifrån där. Hur användbara de förångade tunnfilmerna är återstår att prova i praktiken. Kommer de att kunna tillverkas i stora kvantiteter? Det är också en förutsättning för ett eventuellt genombrott.

En annan fråga är hur det skulle gå med diamanternas [illegible] om de skulle börja [illegible] och det [illegible] till råga på allt.

# U.S. HISTORY
# DIAMOND VAPOR GROWTH

[at practical rates]

| | |
|---|---|
| pre-1985 | Results. Little Belief! |
| 1985 | Cautious Belief. |
| 1986 | Belief! Cautious Acceptance. |
| 1987 | We're Behind! ⇒ START! |
| 1988<br>↓ | We're all in for the long-haul. |

THE
TOLEDO
BLADE

# Soviets On Cutting Edge Of Earth's Diamond Age

By MICHAEL WOODS
Blade Science Editor

MOSCOW — Historians who chronicle human progress in terms of new materials that change society will never know 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 huge 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 Deryaguin mused. His thumb and forefinger lazily caressed a small wafer of material coated with diamond in the process that he and Dimitri Fedoseyev invented a decade ago.

"Yes, maybe so."

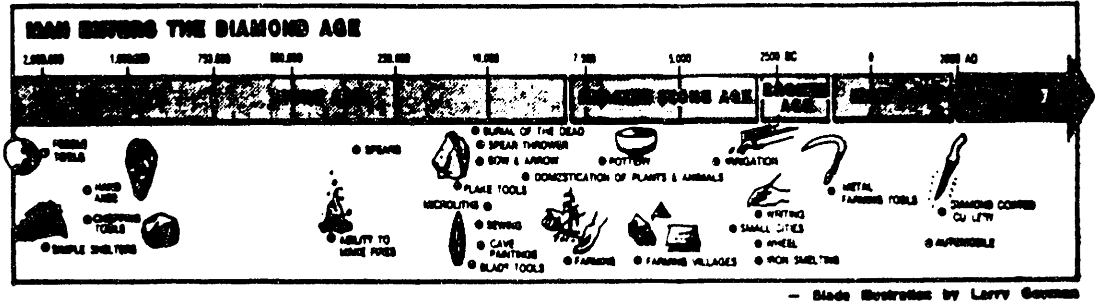
Although they published a detailed report on the process in 1977, scientists around the world ignored it — for reasons that are unclear.

### Shrug Of Bewilderment

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

During the last year, Drs. Spitsen, Deryaguin, 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 1886 — the year of the invention of the process that made aluminum widely available.



— Blade Illustration by Larry Gousman

That process, developed by Charles Hall and Paul Heroult, 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. Deryaguin 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. Deryaguin 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.

### Films 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. Deryaguin 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 stereo speakers, scratch-proof airplane windows and camera lenses, and diamond-coated computer chips that dissipate heat very rapidly.

Dr. Spitsen 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

THE BLADE: TOLEDO, OHIO,

# 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. Spitzen 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.

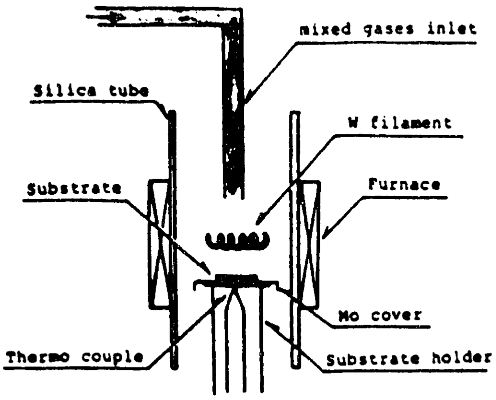
When the plasma comes into contact with an object, carbon atoms accumulate on its surface in the specific crystalline form of diamond.

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 Sovietsare 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 cited many pleasant encounters with American scientists. Dr. Spitzen expressed the hope that political differences would not hinder scientific cooperation between the United States and the USSR.

ALL
HYDROCARBON GASES
MAKE DIAMOND $\approx$ SAME



Heated Filament
CVD

Fig. 1. Schematic diagram of thermal CVD apparatus.

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

| | | |
|---|---|---|
| methyl alcohol | $CH_3OH$ | |
| ethyl alcohol | $C_2H_5OH$ | ← Vodka, Sake |
| isopropyl alcohol | $(CH_3)_2CHOH$ | |
| 2-methyl-2-propanol | $(CH_3)_3COH$ | |
| acetone | $CH_3COCH_3$ | ← Nail Polish Remover |
| isopropyl ether | $[(CH_3)_2CH]_2O$ | |
| diethyl ether | $C_2H_5OC_2H_5$ | |
| methyl acetate | $CH_3COOCH_3$ | |
| acetaldehyde | $CH_3CHO$ | |
| trimethylamine | $(CH_3)_3N$ | |

From Y. Hirose and Y. Terasawa
Jpn. JAP 25, L519 (1986)

March 29 '88
The Yomiuri Shimbun

# 2回以上売買16%

## 都区部の土地取引　民間企業同士が67%

61年、都白書

東京都区部の土地取引の六件に一件は、一年間に二回以上売買され、その転売の七割が民間企業間の取引で占められていることが、二十八日東京都がまとめた「土地白書」で明らかになった。地価狂乱を演出したといわれる企業の〝土地転がし〟の実態が具体的データで裏付けられたのは初めて。この白書、昨年一年[illegible]一年間に二回[illegible]千四百十八件で全体の一三・九%を占めた。このうち、年間三回以上転売されたケースは二百九十九件にものぼった。

これら転売取引のうち、民間企業同士の取引が最も多く六七%。特に売り主が法人だったのは八八%で、千代田区では九三%、港区、新宿区は九〇%と、都心三区の土地が企業によって転がされた実態を示している。

この結果、企業所有の宅地も増え、特に区部では昨年に比べて百三十五㌶も増加しているのに対し、個人所有の土[illegible]

[illegible]これら〝土地転がし〟による地価高騰で〝マイホームの夢〟を奪われたのが一般の都民。都が昨年の公示地価を参考に試算したところでは、三千万円で購入できる区部の土地はわずか二十八平方㍍、大阪の百七十平方㍍、横浜の百二十九平方㍍に比べて最も狭い。さらに、六十一年までは、三千万円の資金で何とか手が届いた西多摩地区の土地（百五十平方㍍）も、昨年は約四千九百万円と遠く及ばず、わずかに西多摩地区の土地だけとなった。百五十平方㍍の土地を区部で手に入れようとすると、中心区は七億四千万円、外周区一億二千万円と、夢物語となってしまったことも白書は示している。

---

# 職住近接を促進へ

## 建築規制の見直し諮問

越智伊平建設相は二十八日、都心での職住近接化を目[illegible]に、現行の建築基準法に基づく建築規制を見直す方針を[illegible]審議会（丹下健三会長）に諮問した。

現行法では、「商業地域」など八種類の用途地域ごとに、容積率、建ぺい率、日影規制、用途制限などの規制が細かく定められているが、例えば、商業地域にオフィス併設の住宅建設を誘導するような規制の仕組みはない。また、研究所的な性格が強い工場でも、一律に商業地域への建設が禁じられているなど社会的需要に合わない規制も多い。

このため、審議会では、二年後の六十五年春ないしは六十六年春の答申を目標に、これらの建築規制を抜本的に見直すことになったもの。

都心の商業地域で、オフィス併設の住宅建設を誘導するための建築規制緩和など、住宅関係の規制見直しは六十五年をメドに、工業地域関係の規制の見直しは、六十六年を目標に答申を受ける。

---

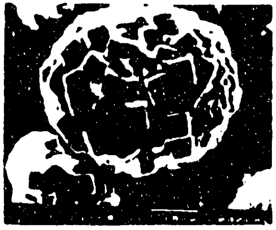
# ダイヤ簡単に作れます

DIAMONDS

## ガスバーナーとシリコン基材で

ただ今最大0.2ミリ　切削工具に応用

日本工業大・広瀬助教授開発



炎で作ったダイヤモンドの電子顕微鏡写真（下の白い線の長さが10ミクロン＝0・01ミリ）

プロパンでも都市ガスでも、とにかく燃やせばダイヤモンドができる、というダイヤ合成法としてはこれまでになく簡単な方法を、日本工業大学（埼玉県南埼玉郡宮代町）の広瀬洋一・助教授が見つけた。法政大学で開かれている第三十五回応用物理学関係連合講演会できょう発表する。

地下百数十キロの超高圧高温下。そこで炭素原子が立体的に規則正しく手をつなぎ合って生まれたのがダイヤモンドだ。人工ダイヤの合成法も、五―六万気圧、摂氏千四百―千八百度という地下深部並みの条件下で炭素を原料に作る高圧法がある。また、メタンガスなどを原料に、〇・一―〇・〇一気圧という低圧に保ち、シリコンなどの基材を八百度前後に熱して、基[illegible]「気相法」という方法もある。広瀬助教授の方法は、気相法の一種だが、常圧でしかも普通の空気中でできるため、真空ポンプや丈夫な容器などの装置を必要としないのが特徴。

作り方は本当に簡単だ。まずプロパンガスなりアセチレンガスなどの炭素を含むガスをバーナーで、シリコン基材に吹き付ける。ガスの中の炭素原子が基材上にたたきつけられて次第に成長しダイヤになる、という仕組みだ。

ただし、ただ炎を吹きつければいいわけではない。炎には明るく燃えている外炎と、白っぽい内炎とがあるが、外炎は酸化作用があるため、炭素原子が一酸化炭素か二酸[illegible]て、ダイヤを析出させるには、不完全燃焼で酸素が不足している内炎を基材に吹きつけなければならず、その位置の調節が極めて難しい。また、基材温度は八百度から九百度までに調節する。炎の温度も一おそらく千五百度[illegible]の条件さえ整えれば、学校の理科室でも簡単にできるという。エックス線回折及びラマン分光分析という、物質特有の性質を調べる検査の結果、ダイヤであることも確認した。

現在、最大の粒は一時間か[illegible]（〇・二ミリ）のダイヤ。今注目を浴びている半導体の材料としては、従来の気相法によるダイヤの方が適しているようだが、切削工具とか曲面へのコーティングには、この方法が威力を発揮するものと見られる。

---

新幹線公害

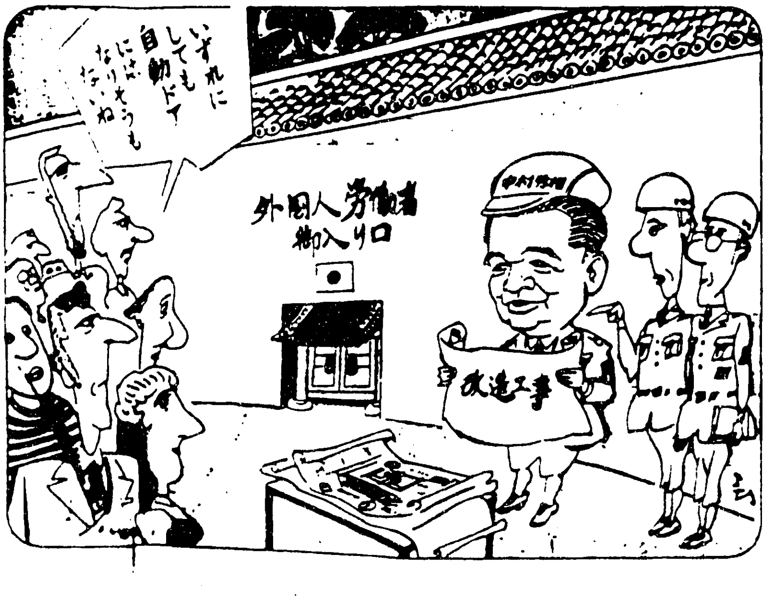
# 調整委が初の調停へ

## 大阪市民の申請を受理

一昨年十一月からのスピードアップ実施により激化している新幹線の騒音、振動問題で、国の公害紛争処理機関である「公害等調整委員会」（委員長　新見嘉実・前名古屋高裁長官）は二十八日、大阪市内の沿線住民七人による調停申請を受理、調停に乗り出した。申請はJR東海に対し、「環境基準より厳しい自主基準を設け、それを超えた場合にしか対策を講じていないのは違法」として、防音・防振工事費用の支払いをもとめたもの。新幹線公害については、また[illegible]な、[illegible]になった[illegible]初めてで、注目される。

申請を行ったのは、大阪市東淀川区瑞光二の九の三、不動産業西原昭久雄さん（四三）ら同区瑞光二丁目と大隅一丁目に住む七人。いずれもJR大阪駅から約五キロ離れ、新幹線のレールからの距離は数―四十メートルと近い。

申請書によると、西原さんらがJR東海に対して求めているのは住宅の防音・防振工事費用約五千六百万円の支払い、もしくは工事の実施。またそれが不可能な場合は午後九時以降の運転中止を求め、住民が設置したテレビ受信用共同アンテナの設置費用約二百[illegible]



いよいよ「ナンモン」に取り組む　牧野　圭一

translated by M. Suzuki
April 3,'88

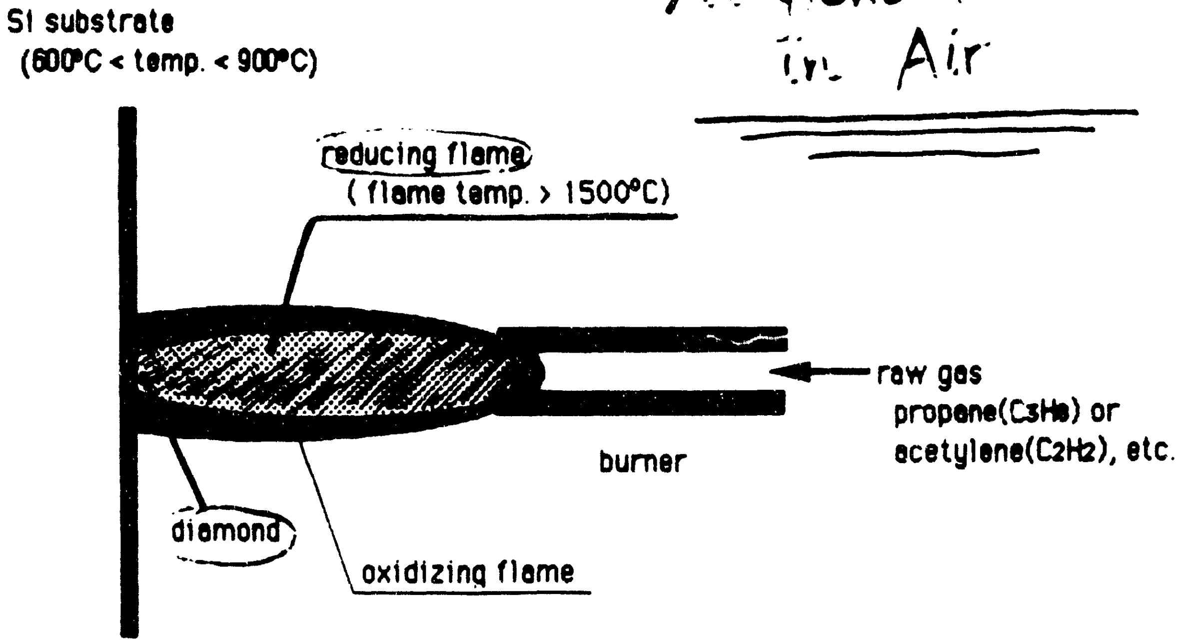
# You can make diamond easily!

(The Yomiuri Shimbun* March 29,'88, P2)

Dr. Hirose, an associate professor of Nippon INST. OF TECHNOLOGY ~~Kogyo 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 hold 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.

Acetylene Torch in Air



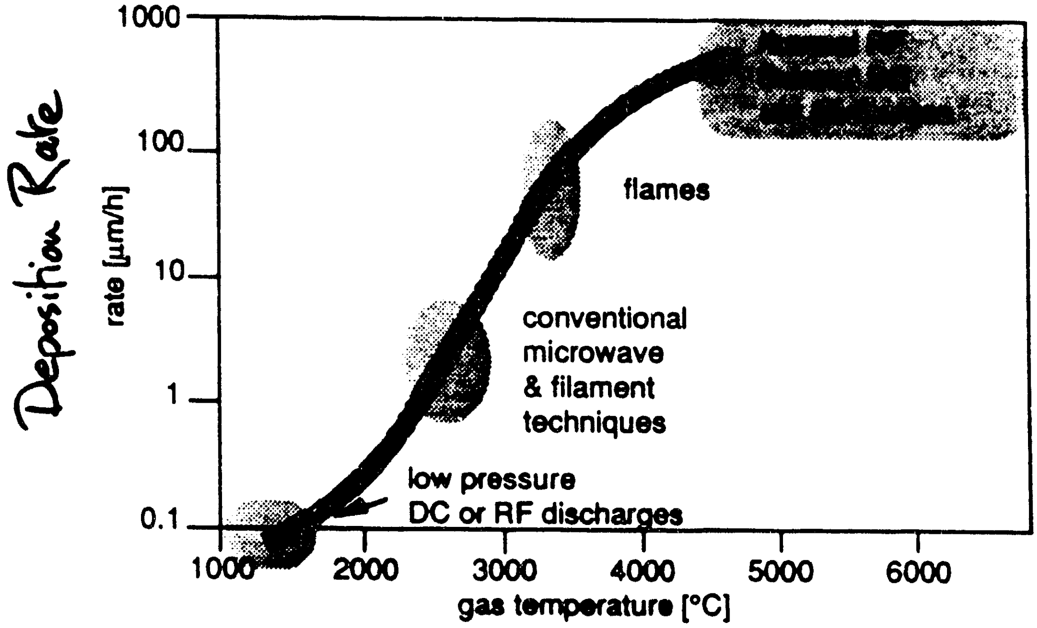
at an atmospheric pressure, in the air

A Schematic Image of the New Process

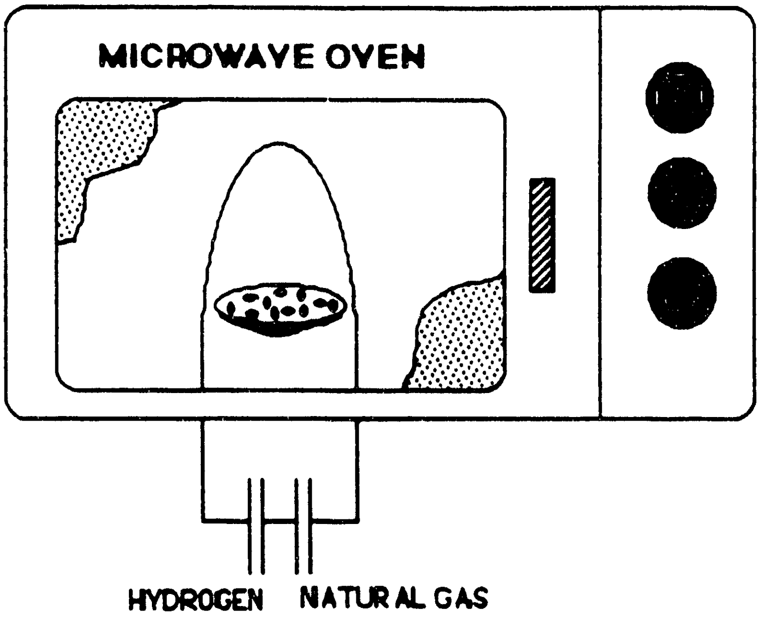
---

*The Yomiuri Shimbun is one of three big Japanese newspapers.

# Gas Temperature vs. Diamond Deposition Rate



from Bachmann and Lydtin
MRS Symp. Proc 165 (1989)



GE Process !
1986

# DIAMOND ⟷ DIAMOND-LIKE

**HOMOEPITAXY**

Acheived:

↓

**HETEROEPITAXY**

Indications: ß-SiC, c-BN

↓

**ORIENTED POLYCRYSTALLINE**

By controlling
deposition conditions and seeding

↓

**POLYCRYSTALLINE $\gtrsim 1\,\mu m$**

Typical: 800-1050°C
near-optimum 0.5%$CH_4$-$H_2$

*chemistry controlled*

↓

**POLYCRYSTALLINE $\lesssim$ ~~0.1~~ 0.5 µm**

Non-optimum conditions:
low Ts (< 500°C ↓ 300°C)
high %$CH_4$
oxygen additions
high nucleation density
bombardment (some)

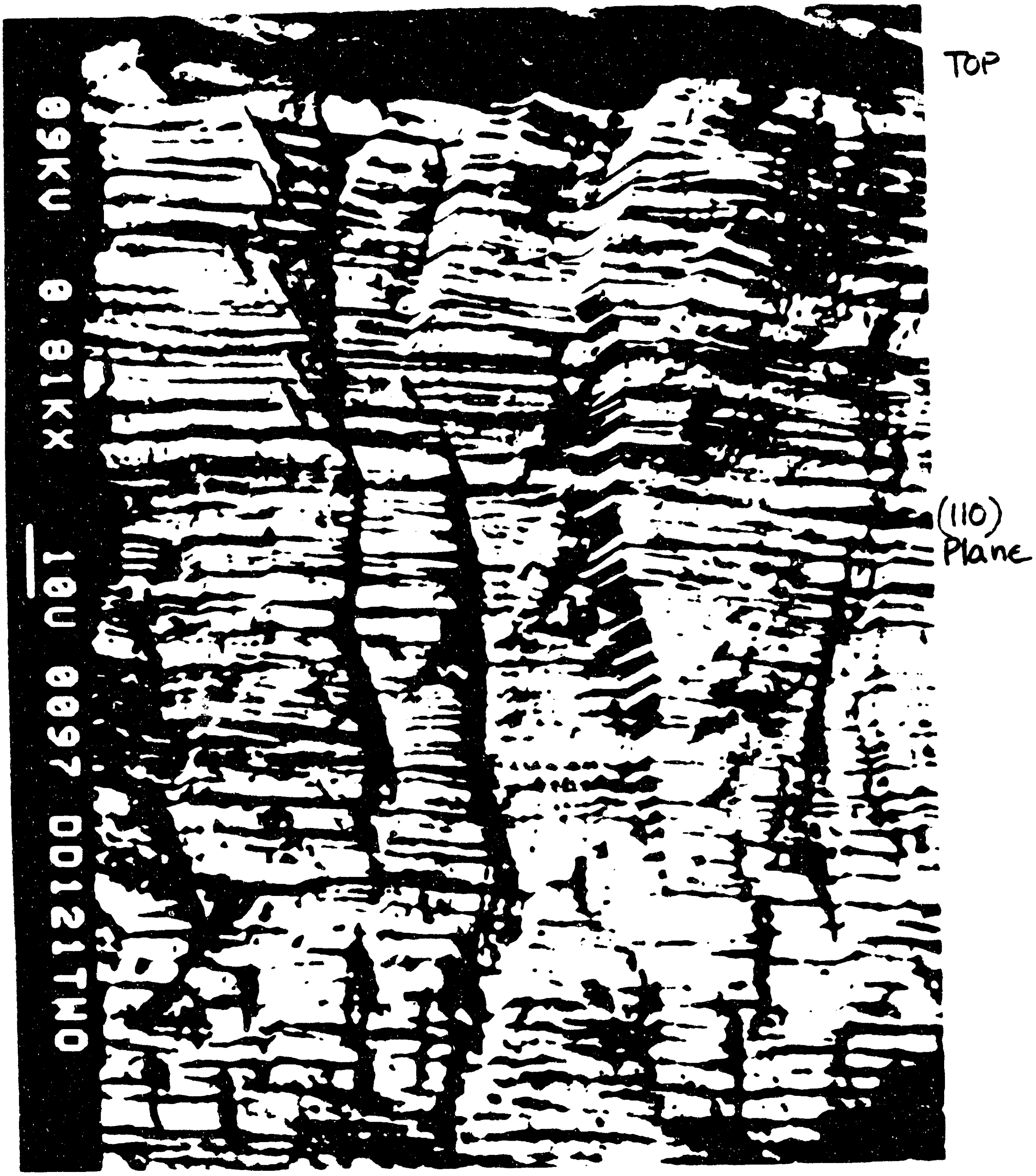
↓

**AMORPHOUS**

Low $T_s$
does a-C ($sp^3$) exist?
dense hydrocarbons

*bombardment controlled*

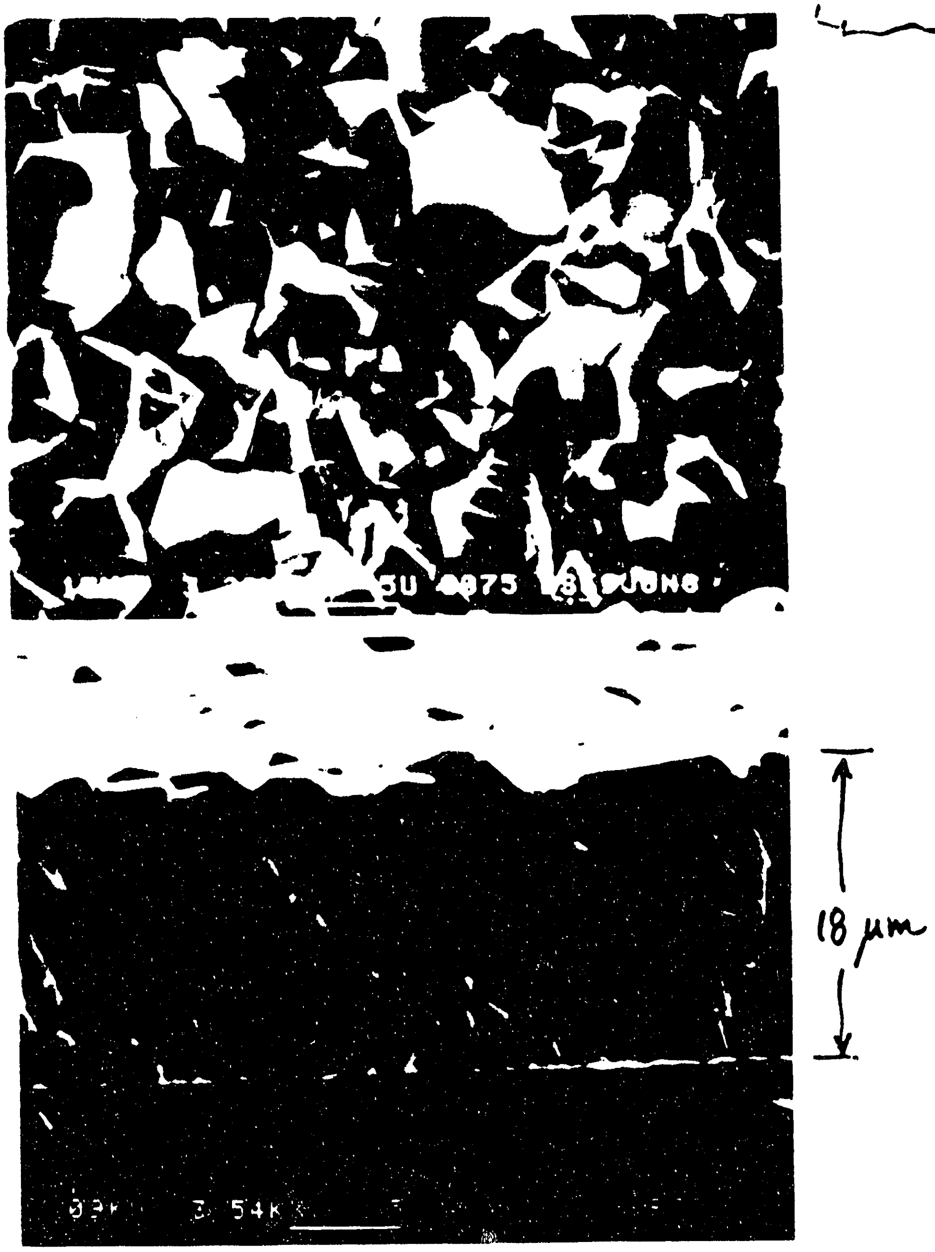
# HOMOEPITAXIAL DIAMOND



A. BADZIAN & T. BADZIAN

980°C
80 Torr
0.4% $CH_4$-$H_2$

## Diamond on Silicon

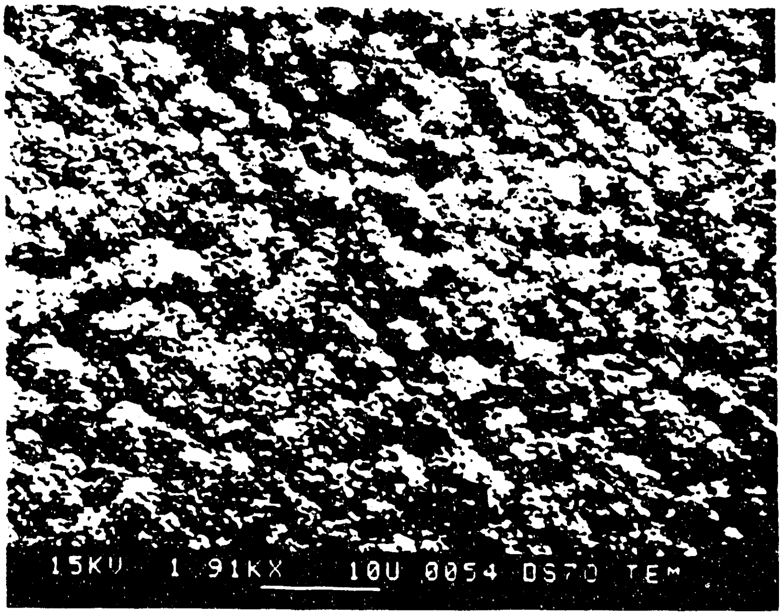


A.R. Badzian and T. Badzian
MCVD

# Diamond on Si

[illegible]
[illegible]
[illegible]

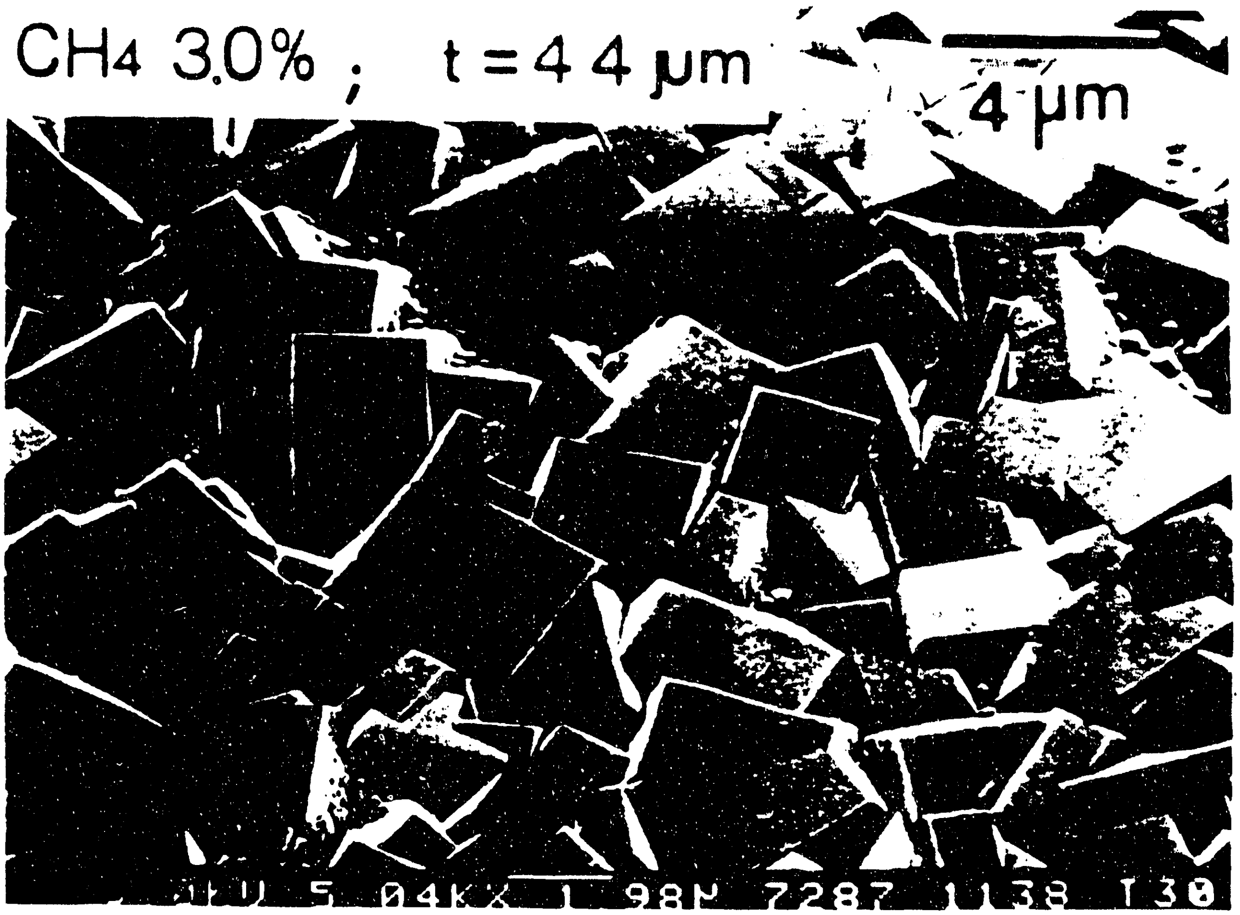
MPACVD



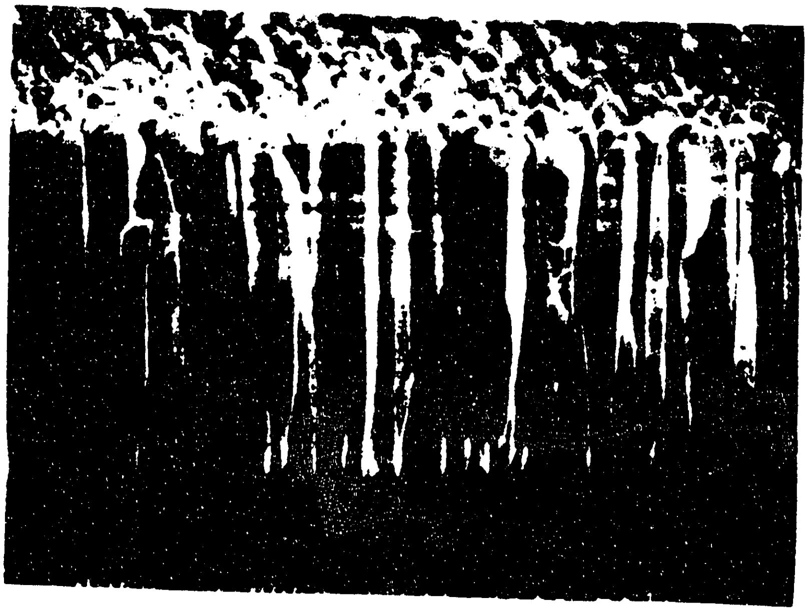
different substrate position

lower actual T

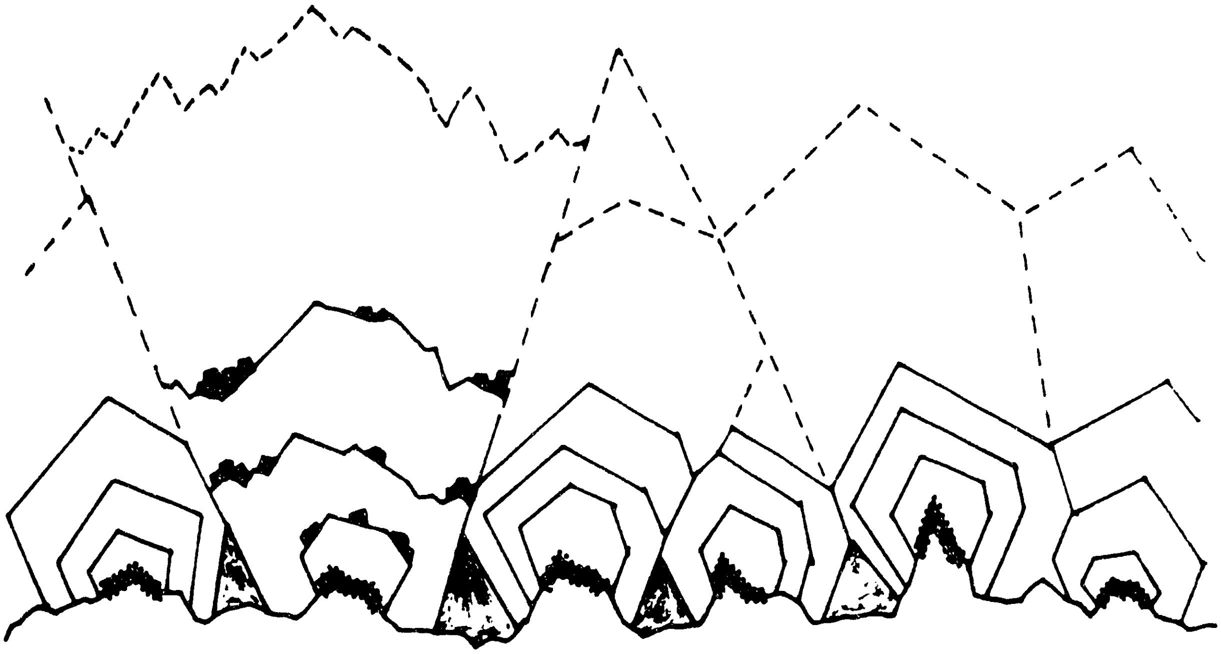
A. BADZIAN & T. BADZIAN



from Y. Sato (NIRIM)



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]

# PREFERENTIAL ORIENTATION

| | | | | |
|---|---|---|---|---|
| Windischmann<br>(MPACVD) | {111} | 800°C | ~1% $CH_4$ (low growth rate) | |
| | {110} | @ high T and % $CH_4$ | | |
| Parker<br>(MPACVD) | {110} | ~650°C | ~1 μm/hr) | |
| Wild<br>(HFCVD + MPACVD) | {110} | ~900°C | 1.5% $CH_4$ | twinning on {111} |
| Narayan<br>(dc plasma) | {110} | | | " |
| [illegible]<br>MPACVD) | {110} | | | |
| [illegible]<br>HFCVD) | {110} | at lower $T_s$ (~600°C) | | |
| Sato<br>(MPACVD) | {100} | 850°C | 3-4% $CH_4$ | low defects |
| Zeng<br>(MPACVD) | {100} | | | |
| Clausing<br>(HFCVD) | {100} | 950°C | | |
| | {110} | 900°C | | |
| Kaae<br>(HFCVD biased) | {100} | Similar Conditions | | SF and MT near Grain boundar |
| | {111} | | | SF and MT distributed throughout |

# DIAMOND
# PROBLEM AREAS

- High Quality
- Large Area Heteroepitaxy
- Adhesion
- Nucleation ⇒ Nucleation Density → Morphology
- Crystallite Size ⇒ Surface Roughness
  (Polishing required → 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

  ⇓

  Diamond has largest atom number density

  ⇓

  Large # of Unique Properties

- Diamond Technology ⟹ Metastable Material
  - can defects be reduced < during prep? / post-dep?
  - stable to high T's

- New Approach to Materials Synthesis
  - can it be generalized (eg. 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 純一

## 1. はじめに——ニューダイヤモンドとは

ダイヤモンドが，古く古代エジプトの時代からその高貴な輝き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維持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も古くから知られていたようで，聖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，加工工具材料としての利用につ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．

以来，ダイヤモンドそのものを始めとして各種の貴石，非常な難削材あるいは高精度を要する加工にダイヤモンドが工具材料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範囲は特殊な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者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上記の資源的束縛を離れるための努力が超高圧力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 年の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，ダイヤモンド砥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売上高で年間 700 億円以上，伸び率で年 15～20% になっている．

更に最近，大粒ダイヤモンドの静水圧法による製造，気相法による膜状ダイヤモンドの製造が可能になり，硬さを生かした切削・研削工具，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

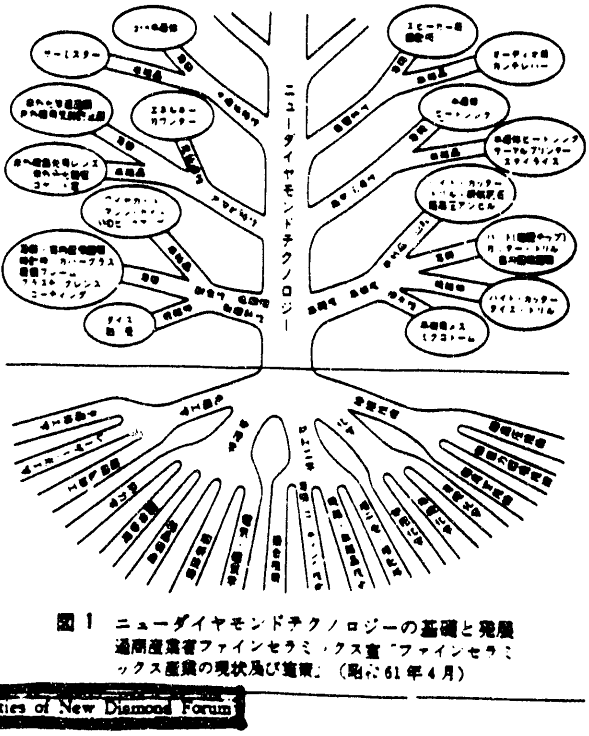


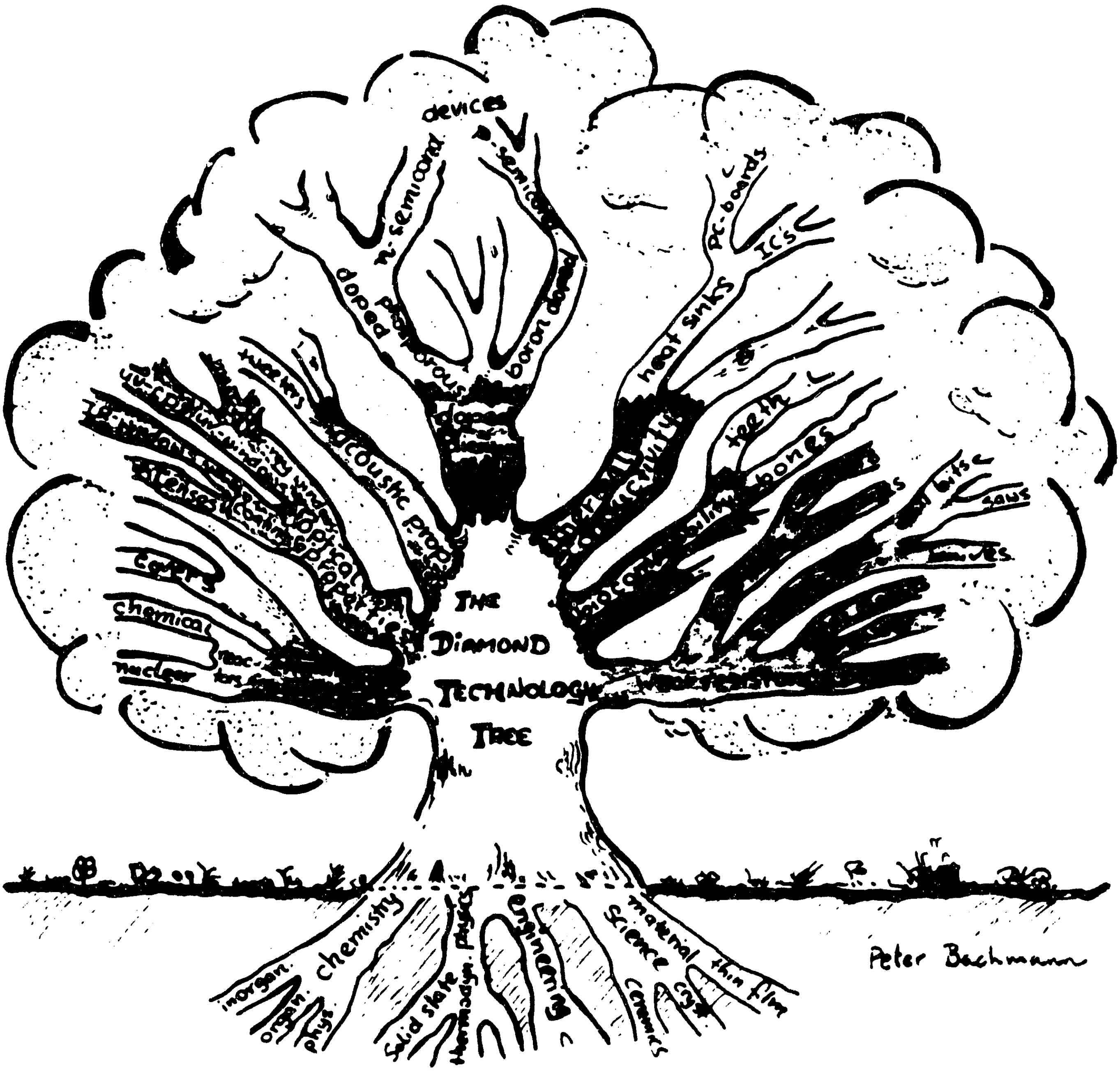
図 1 ニューダイヤモンドテクノロジーの基礎と発展
通商産業省ファインセラミックス室「ファインセラミックス産業の現状及び課題」（昭和61年4月）

---

Junichi SATO（Showa Denko K.K.）：Activities of New Diamond Forum

The basic development of new diamond tech. written by MITI, fine ceramic section, now and then.

1386



<u>the "diamond technology" tree</u>

# PROPERTIES

| Material<br>Property | Silicon | GaAs | Diamond |
|---|---|---|---|
| optical band gap [eV] | 1.1 | 1.4 | 5.5 |
| hole mobility [$cm^2$/V sec] | 600 | 400 | 1600 |
| electron mobility [$cm^2$/V sec] | 1500 | 8500 | 1900 |
| breakdown voltage [V/ cm] | $5 \times 10^6$ | $6 \times 10^6$ | $1 \times 10^7$ |
| electron velocity at high fields [V / sec] | $1 \times 10^7$ | $1 \times 10^7$ | $2.7 \times 10^7$ |
| dielectric constant | 11 | 12.5 | 5.5 |
| resistivity [Ω cm] | $10^3$ | $10^8$ | $>10^{12}$ |
| thermal conductivity [W / $cm^2$K] | 1.45 | 0.46 | 20 |
| thermal expansion coefficient [1/K] | $2.6 \times 10^{-6}$ | $5.9 \times 10^{-6}$ | $1.1 \times 10^{-6}$ |
| refractive index |  | 3.4 | 2.4 |
| Vickers hardness [kg / $mm^2$] | 1 000 | 600 | 10 000 |
| sound propagationvelocity [ m/ sec] |  |  | 18 500 |
| elasticity [N/ $m^2$] |  |  | $1.2 \times 10^{12}$ |
| density [g/ $cm^3$] |  |  | 3.5 |
| melting point [°C] | 1420 | 1238 | N/A |

# DIAMOND SCIENCE AND TECHNOLOGY

| | UNIQUE PROPERTIES | | APPLICATIONS |
|---|---|---|---|
| 1. | HARDEST MATERIAL KNOWN, 9000 KG/MM$^2$ | 1. | ABRASIVES, CUTTING TOOLS, SURGICAL KNIVES |
| 2. | HIGHEST VELOCITY (LONG 18000 M/SEC) | 2. | ACOUSTICS, SPEAKERS TO SAW DEVICES |
| 3. | HIGHEST THERMAL CONDUCTIVITY, 20 W/CM°C ++? | 3. | THERMAL MANAGEMENT, DENSE IC |
| 4. | MOST TRANSPARENT IN I-R, 225 NM-FAR IR | 4. | OPTICS (IR, VISIBLE) |
| 5. | HIGHEST HOLE MOBILITY 1600 CM$^2$/V-SEC, HIGHEST KEYES FIGURE OF MERIT | 5. | NEW ELECTRONICS |
| 6. | LOWEST FRICTION AMONG LOW-WEAR | 6. | TRIBOLOGY (BALL BEARINGS TO DIESELS) |
| 7. | EXTREME CHEMICAL STABILITY | 7. | CORROSION PROTECTION |

# APPLICATIONS

- MECHANICAL
    - Cutting tools
    - Knives
        - medical
        - wood cutting
    - bearings
    - optical scanners
    - nozzles
    - 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
    - Electroluminescent Light Emitters

Victor JVC

日本ビクター株式会社

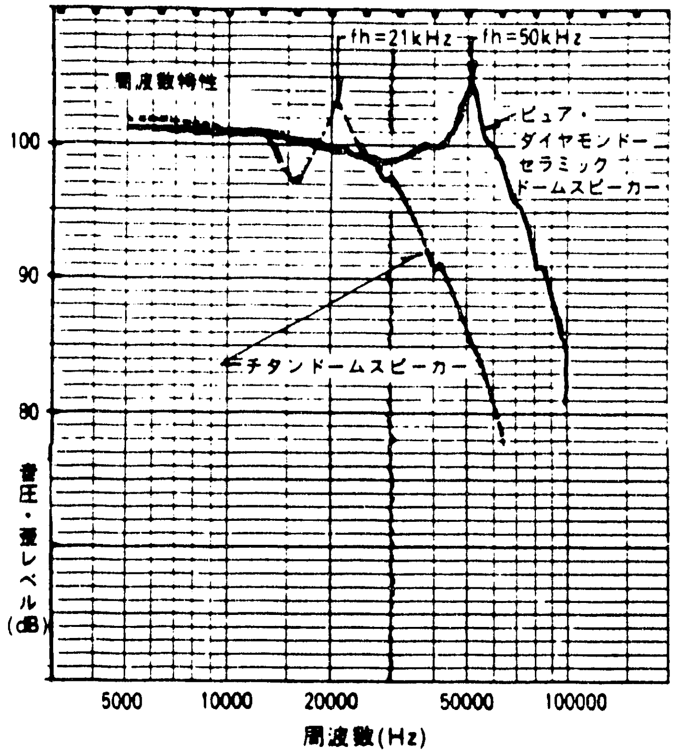


図8　直径25mmピュア・ダイヤモンドーセラミックス ドーム試作ツィータの特性

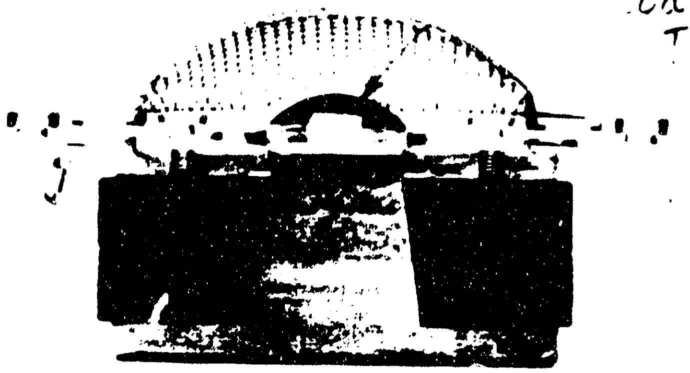
SX-1000

"Component of the year of 1987"

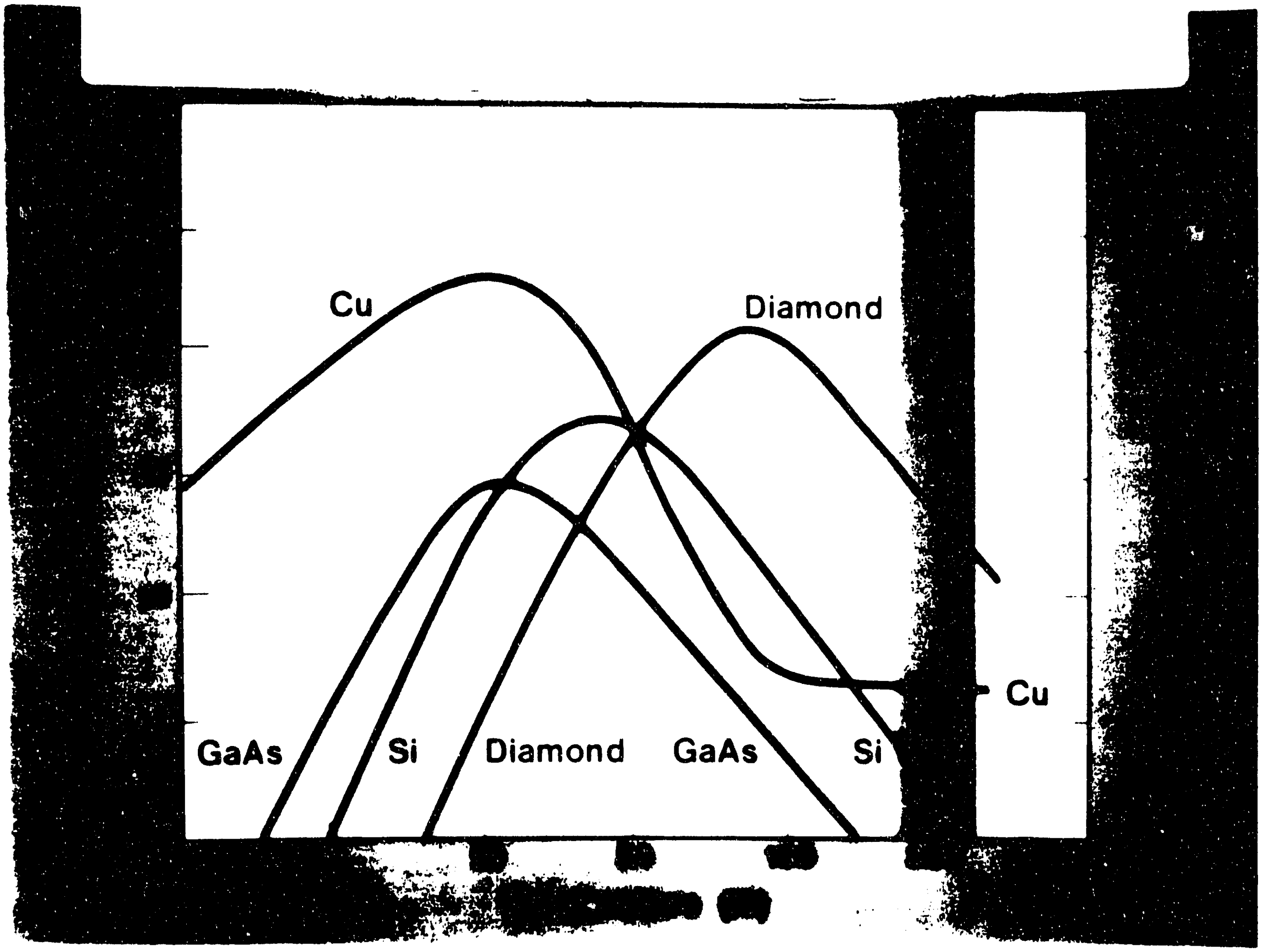
Stereo Sound

Japanese audio Magazine

Diamond Coated Tweeter

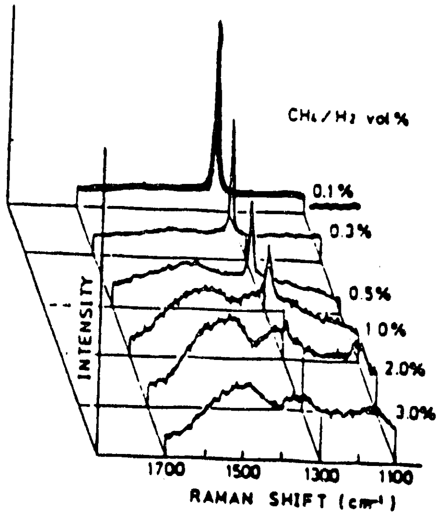


# THERMAL CONDUCTIVITY

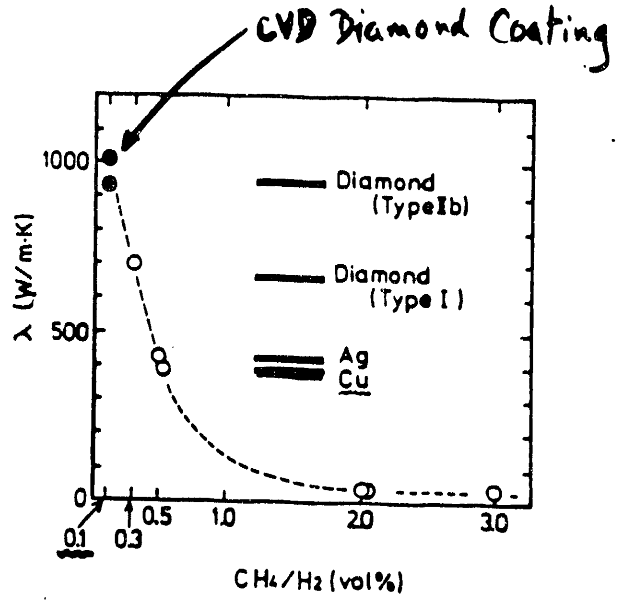


from Mike Geis

# 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

# THERMAL CONDUCTIVITY

## Crystallite Size Dependence

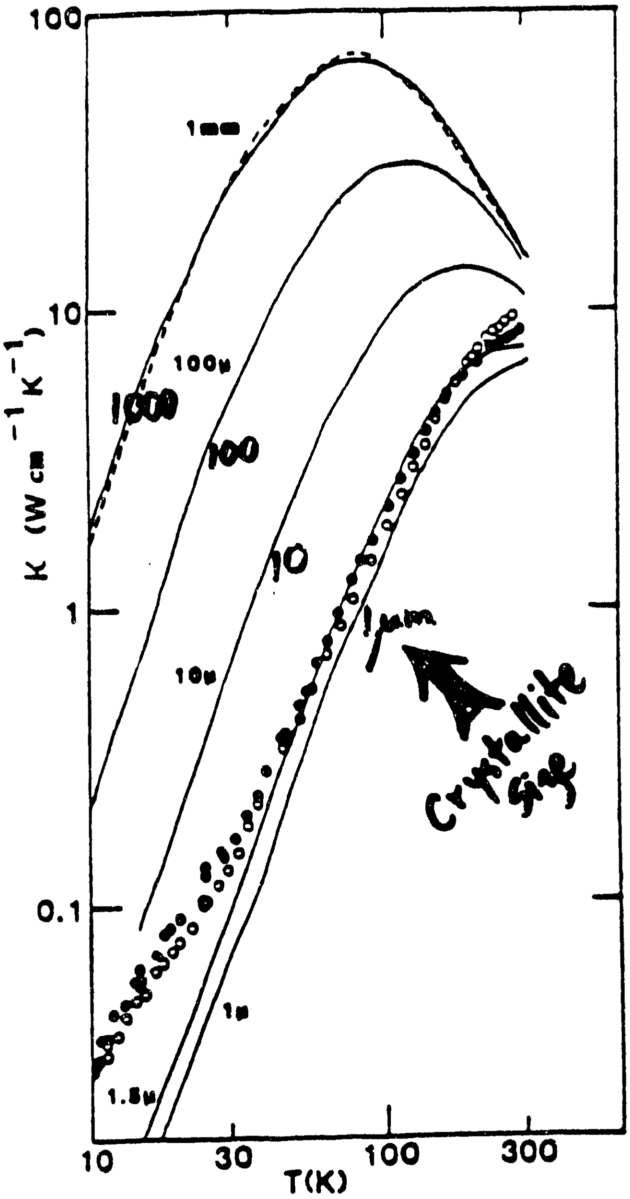
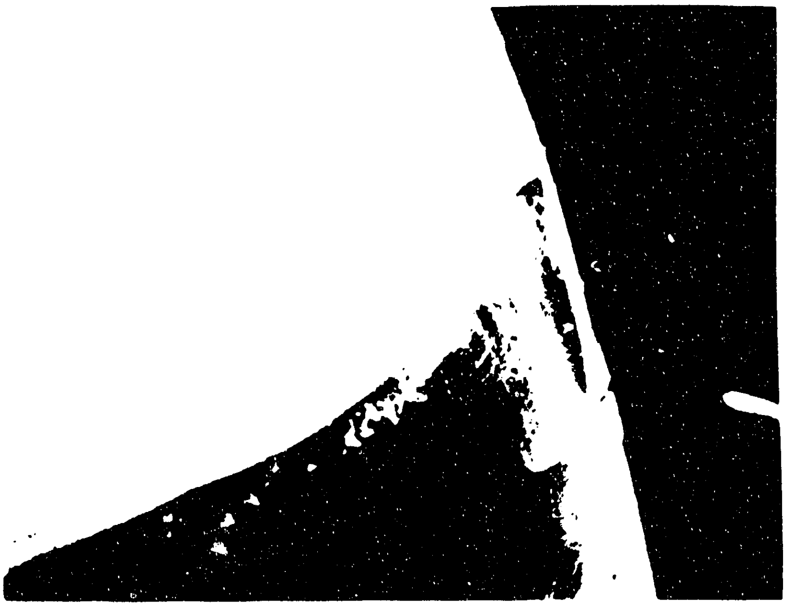


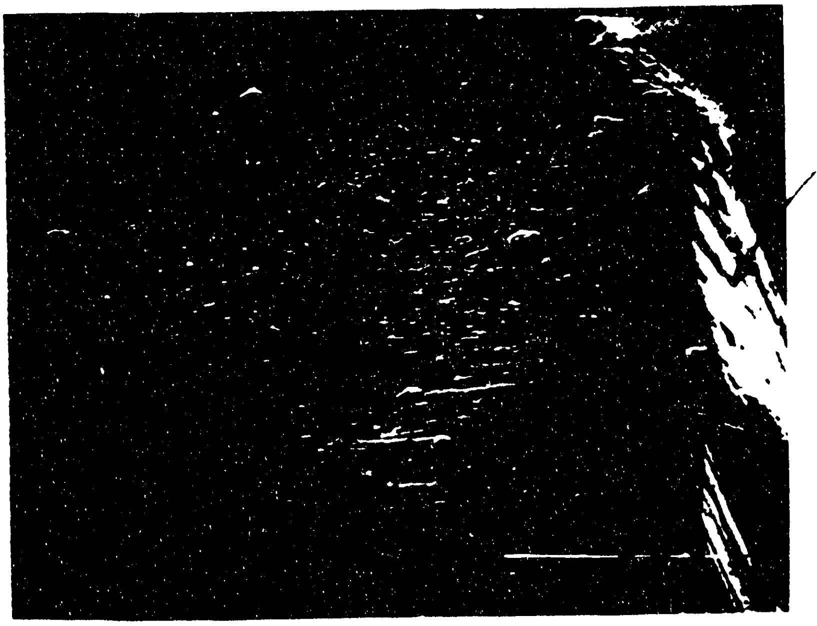
FIG. 3. Thermal conductivity of two diamond films (open circles: DT-13; full circles: DT-15). Bold lines are fits using different crystallite sizes $L$. Dashed line indicates data of Berman, Foster, and Ziman (Ref. 3) on a single crystal of lateral dimension of 1.1 mm.

J. Appl. Phys. 64, 3063- (1988)

# DIAMOND COATINGS ON SIALON CERAMIC CUTTING TOOLS



uncoated (std)



flank wear

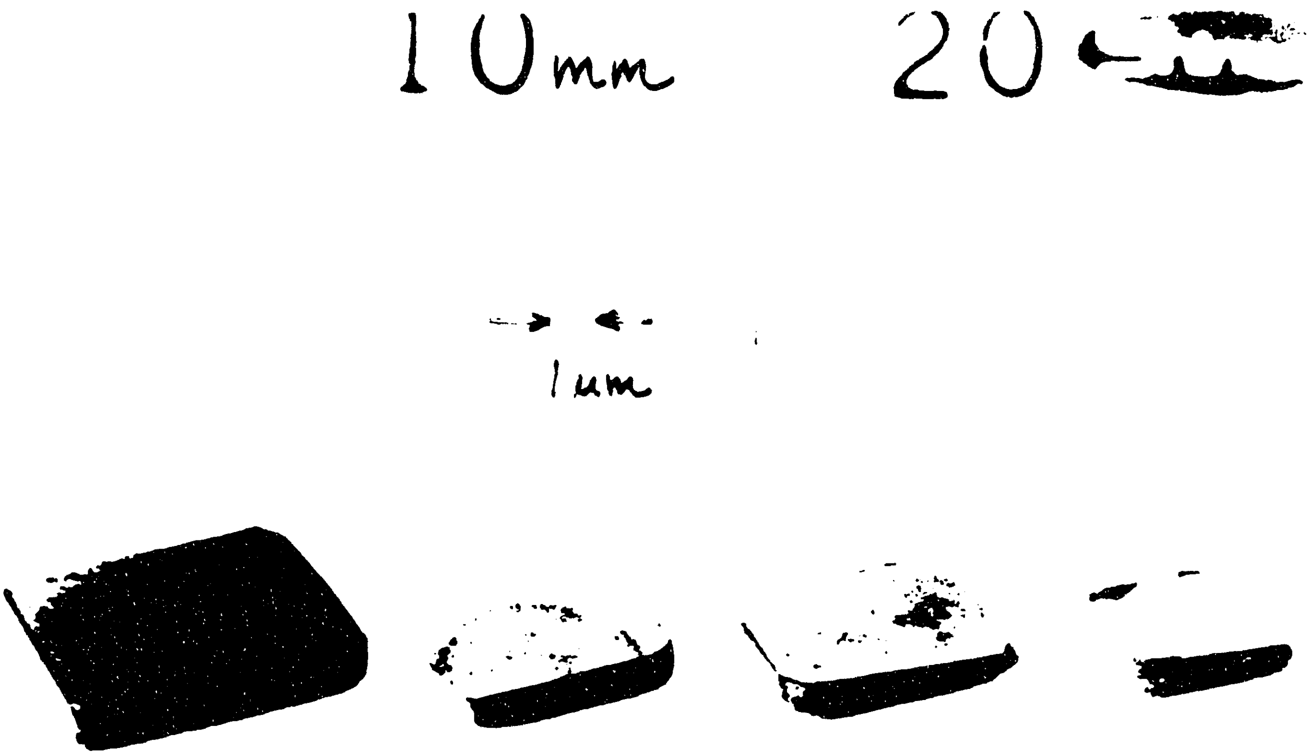
~5 um diamond coating

AL. 390 (16-18% Si)

1500 ft/min. speed
0.0051"/rev feed
0.020" depth.

from Bill Drawl

# HEAT DIFFUSERS



DC plasma torch deposition

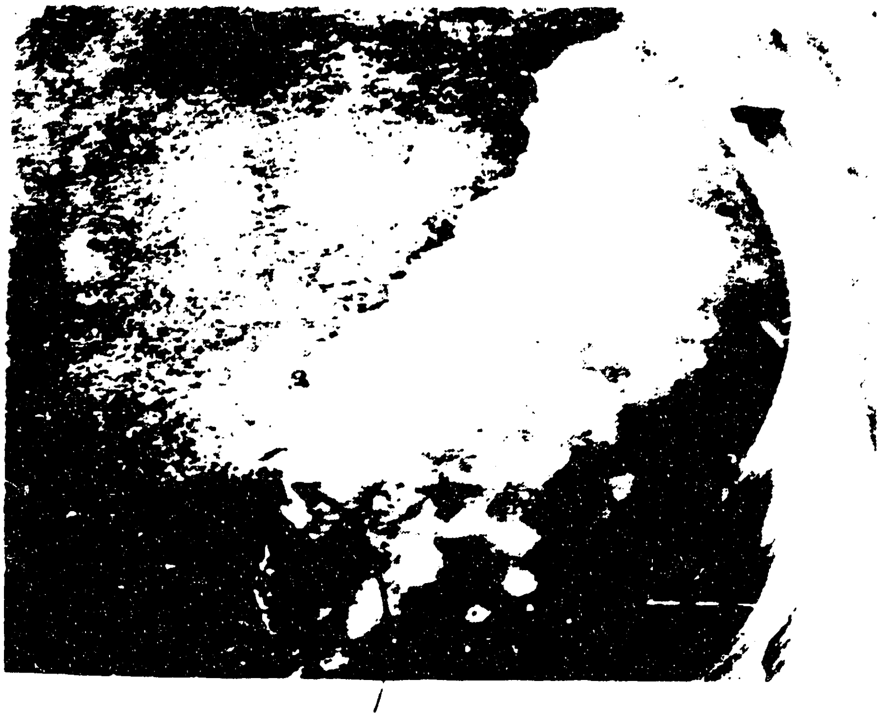
Koshino (1988)
[Fujitsu]

- Metal Build-up

M-3-R3

- Some flank wear

M-3-R4



Adhesion failure

from Bill Draw!

# X-Ray Lithography

## TABLE III

## MATERIALS FOR X-RAY MASK SUBSTRATES

| | μm | W/cm°K | $10^{-6}$ | Kg/mm² | $10^{12}$ dynes/cm² | | | |
|---|---|---|---|---|---|---|---|---|
| | $t_{50\%}$ | $\kappa$ | $\alpha$ | Kn.H | UTS | Y.M. | O.T. | FM |
| Si | 5.5 | 1.6 | 2.3 | 800 | .007* | 1.3 | Poor | 1 |
| $Si_3N_4$ | 2.3 | 0.2 | 1.8 | 2200 | .05 | 3.36 | Good | 0.54 |
| $B_4C$ | 6 | 4.9 | 2.9 | 2750 | .0015 | 3.9 | Unk. | 2.7 |
| BN | 3.3 | 0.8 | 2.9 | 2500 | .10 | 1.8 | Good | 5.42 |
| B | 7.5 | 0.65 | 4.2 | 2900 | .023 | 4.5 | Unk. | 7.6 |
| SiC | 3.6 | 0.41 | 2.3 | 2540 | .20 | 3.8 | Good | 10.6 |
| C(Diam. | 3.0 | 6.55 | 1.2 | 8000 | .02 | 11.2 | Good | 37 |

Figure of Merit

* Maximum measured value [26]

$FM_{mat} = t^{2/3} \times (t \times \kappa) \times UTS \times Y.M.$

$FM = FM_{mat}/FM_{Si}$

- $t_{50\%}$ : Thickness for 50% x-ray transmission at 8.33 Å
- $\kappa$: Thermal Conductivity
- $\alpha$: Thermal Expansion
- Kn.H: Knoops Hardness
- UTS: Ultimate Tensile Strength
- Y.M.: Young's Modulus
- O.T.:Relative Optical Transparency
- FM: Figure of Merit

TABLE III

from J.R. Maldonado
J. Electrochem Soc.
(1990)

# Table I

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

| Material | $t_0$, thickness [μm] | Stiffness Factor $S = t_0E/(1-\nu)$ [GPa-μm] |
|---|---|---|
| Polyimide | > 5 | 43 |
| Mylar | > 5 | 42 |
| Ti | Opaque | --- |
| Be | Opaque | --- |
| Si | 1 | 181 |
| BN | 3 | 330 |
| $SiO_2$ | 5 | 444 |
| $Al_2O_3$ | 1 | 448 |
| $Si_3N_4$ | 6 | 728 |
| SiC | 3 | 1,590 |
| Diamond | 2 | 2,340 |

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

from H. Windischmann (1991)

# Properties of Semiconductive Materials

| Properties | Diamond | Si | GaAs | SiC |
|---|---|---|---|---|
| Band gap (eV) | 5.5 | 1.1 | 1.4 | 3.0 |
| Carrier mobility (cm²/V.sec) | | | | |
| Electron | 1,800 | 1,500 | 8,500 | 400 |
| Hole | 1,600 | 600 | 400 | 50 |
| Dielectric constant | 5.5 | 11.8 | 10.9 | 10 |
| Thermal conductivity (W/cm K) | 20 | 1.5 | 0.5 | 5 |
| Absorption edge (μm) | 0.2 | 1.4 | 1.1 | 0.4 |

# TECHNOLOGY/COMMERCILIZATION

- 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 committments 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 → lower energy
    - decrease pollution
    - economical machinging of non-ferrous metals
    - sensors in hostile locations

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

    Energy Production

    etc.

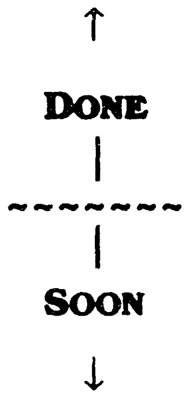
- CREATING NEW INTEREST IN NEW/OLD RELATED MATERIALS

# 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.



↑

DONE

~~~~~~~

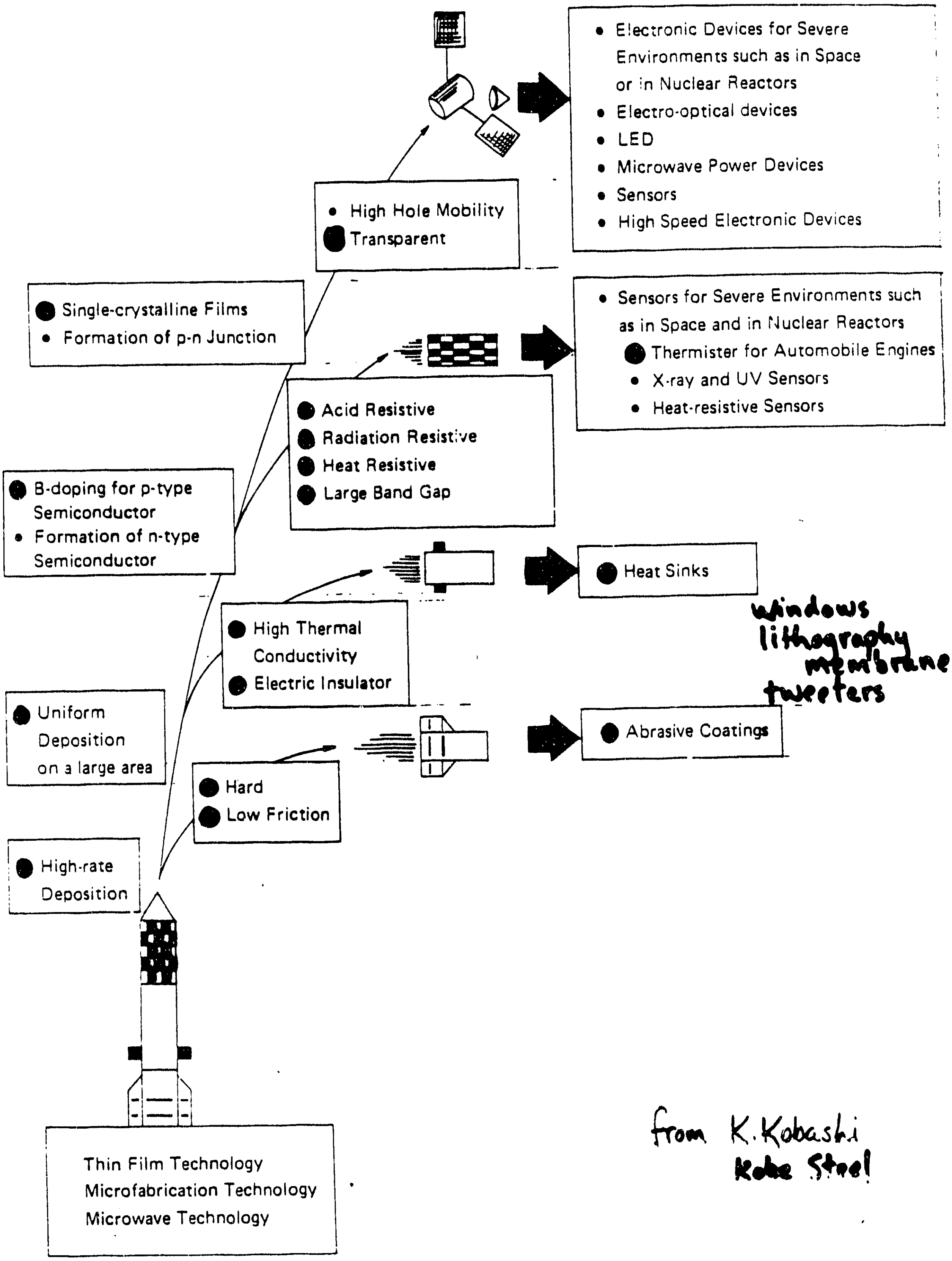
SOON

↓
~~~~~~~

# R&D on CVD DIAMONDS

KOBELCO

Trademark of Kobe Steel, Ltd.



- 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

- High Hole Mobility
- Transparent

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

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

- Acid Resistive
- Radiation Resistive
- Heat Resistive
- Large Band Gap

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

- Heat Sinks

windows
lithography
membranes
tweeters

- High Thermal Conductivity
- Electric Insulator

- Abrasive Coatings

- Uniform Deposition on a large area

- Hard
- Low Friction

- High-rate Deposition

Thin Film Technology
Microfabrication Technology
Microwave Technology

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!**

PENNSTATE

University Park
Campus

# 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

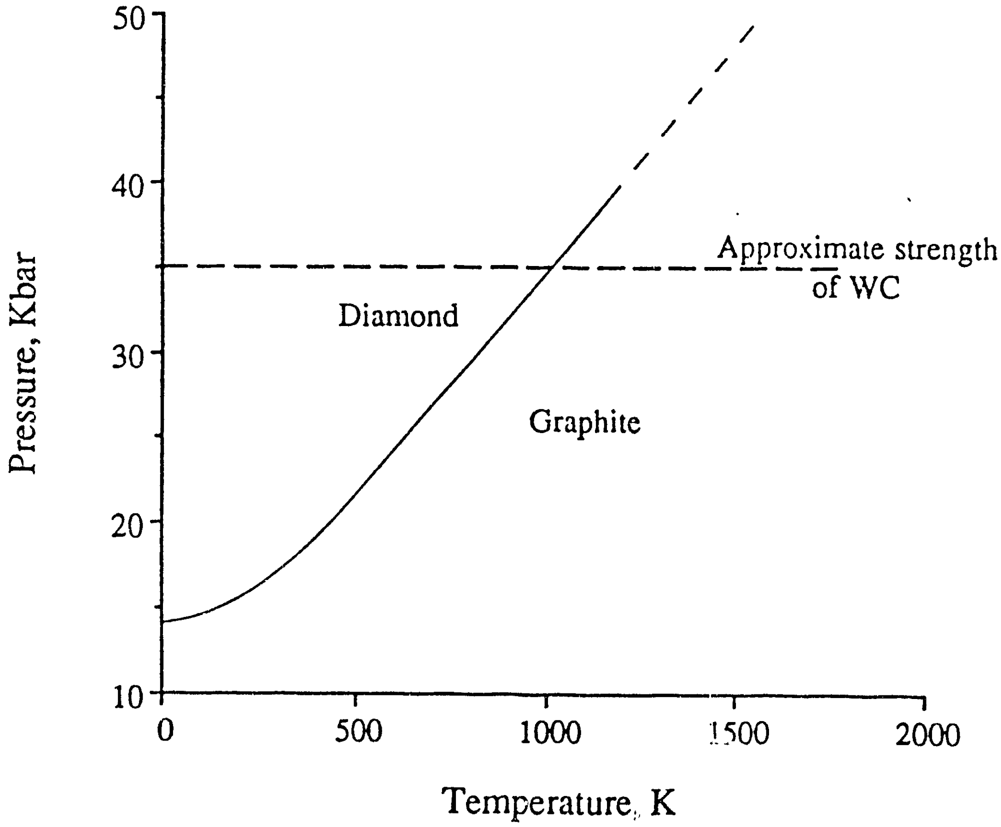
# Graphite/Diamond Equilibrium

$$dG = Vdp - SdT$$

$$\left(\frac{\partial(\Delta G)}{\partial p}\right)_T = \Delta V \qquad \left(\frac{\partial(\Delta G)}{\partial T}\right)_p = -\Delta S$$

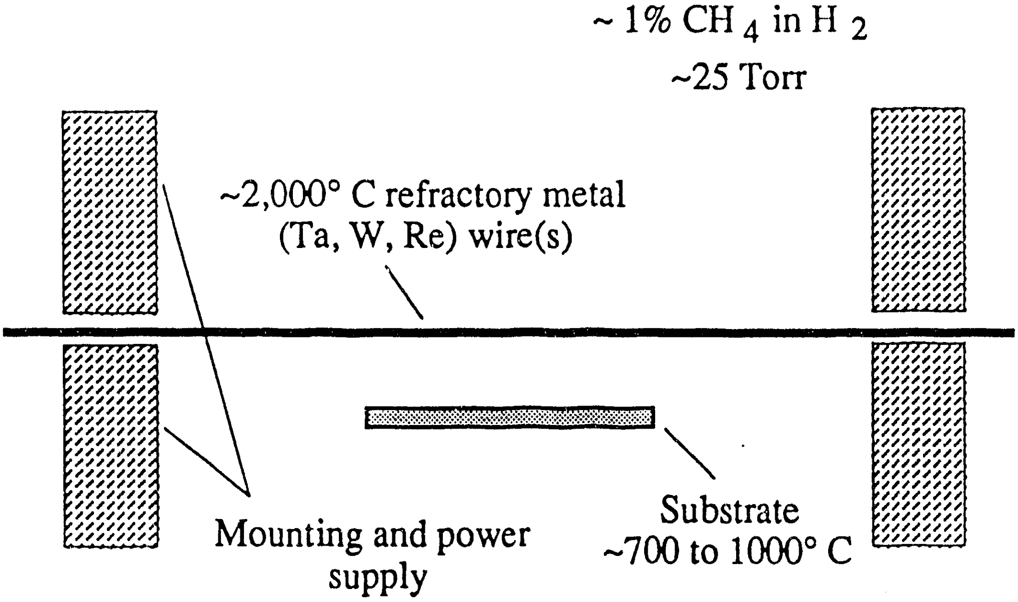
For diamond:
$\overline{V} = 3.42\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$
$\overline{S} = 2.38\ \mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}$

For graphite:
$\overline{V} = 5.34\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$
$\overline{S} = 5.74\ \mathrm{J\ mol}^{-1}\ \mathrm{K}^{-1}$

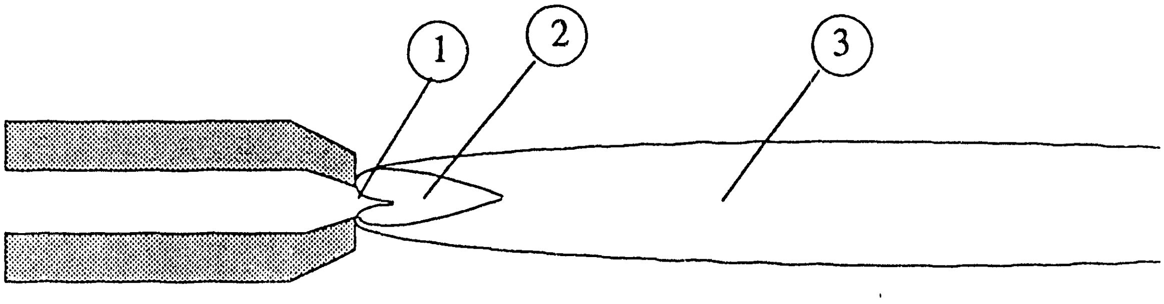


After: J. Bassett, *J. Phys. Radium*, 10, 217 (1939).

# Hot Filament Assisted CVD



# Combustion Synthesis of Diamond

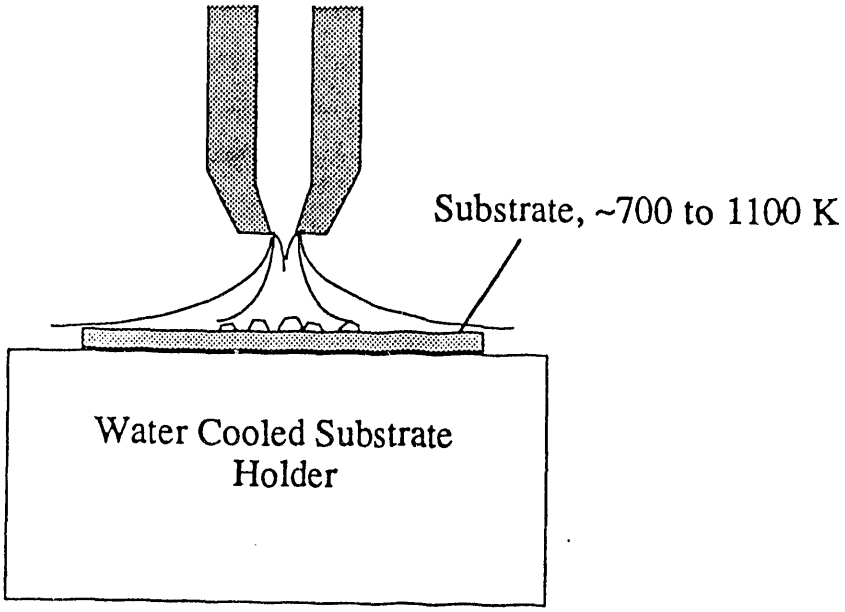


Various "zones" in an oxyacetylene brazing torch (~1:1 O/C or less)

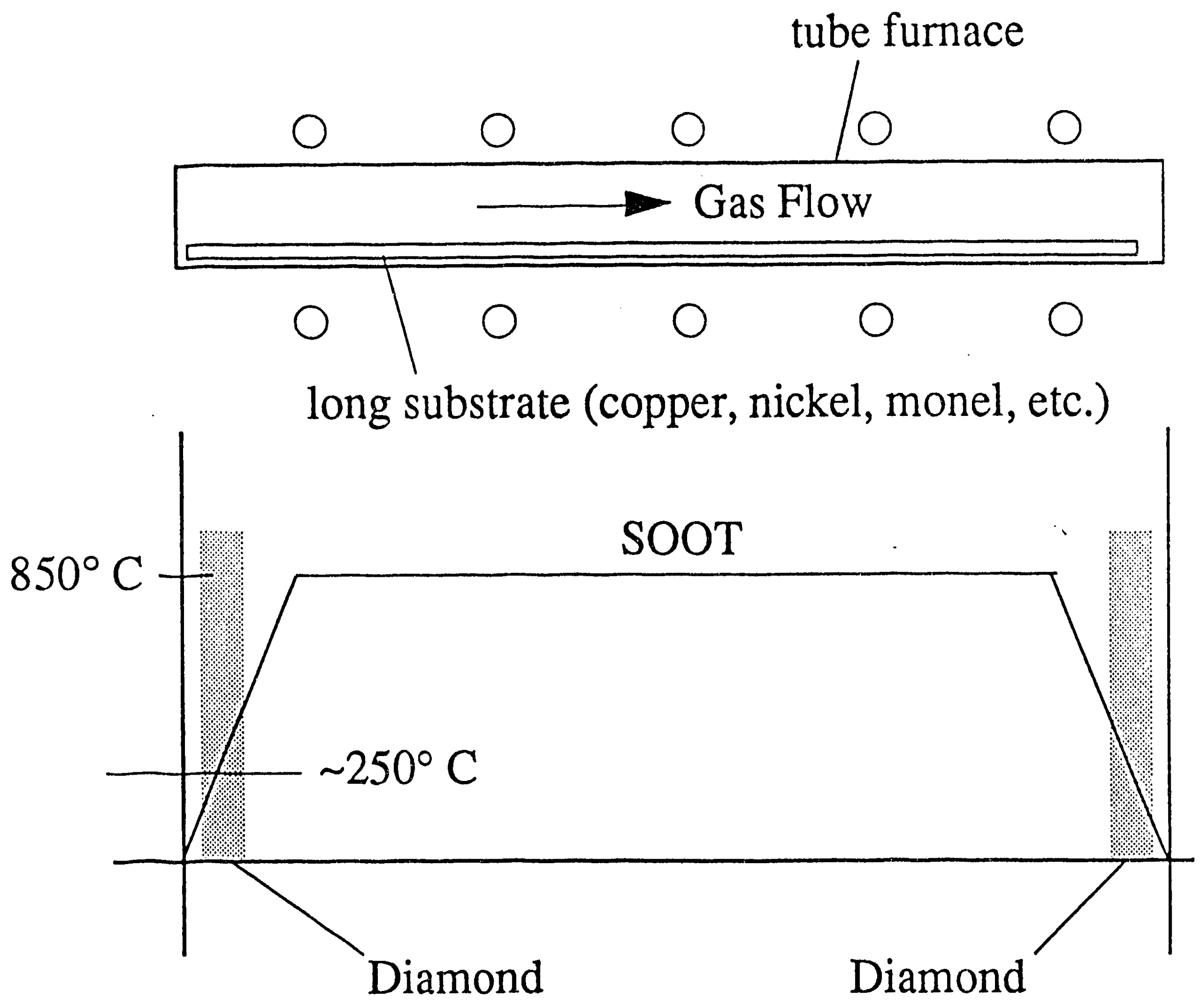
1. Transparent, colorless. Preheat zone. Premixed gas at high velocity is heated to combustion.

2. Bright incandescent white. Primary combustion. Premixed acetylene and oxygen burns to produce primarily CO and $H_2$. Adiabatic combustion temperature (1:1 $C_2H_2$ - $O_2$) 3300 K. Much $H_2$ expected to be atomic. Diamond growth observed here.

3. Blue, transparent. Secondary combustion. Combustion of the CO and $H_2$ produced in primary combustion in the surrounding air.



# Deposition of Diamond from Fluorocarbons



# Observations

- Diamond can be grown without hydrogen

$$CS_2 + 6F_2 \rightarrow C_{(dia)} + 2SF_6$$

- 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.

W. G. Eversole, "Synthesis of Diamond," U. S. Pat. no. 3,030,188, April 17, 1962.
John C. Angus, H. A. Will and W. S. Stanko, *J. Appl. Phys.*, 39, 2915 (1968).

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

H. B. Vakil, 1989.

# Kinetic Theory:

## *Competitive Growth Model -*

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

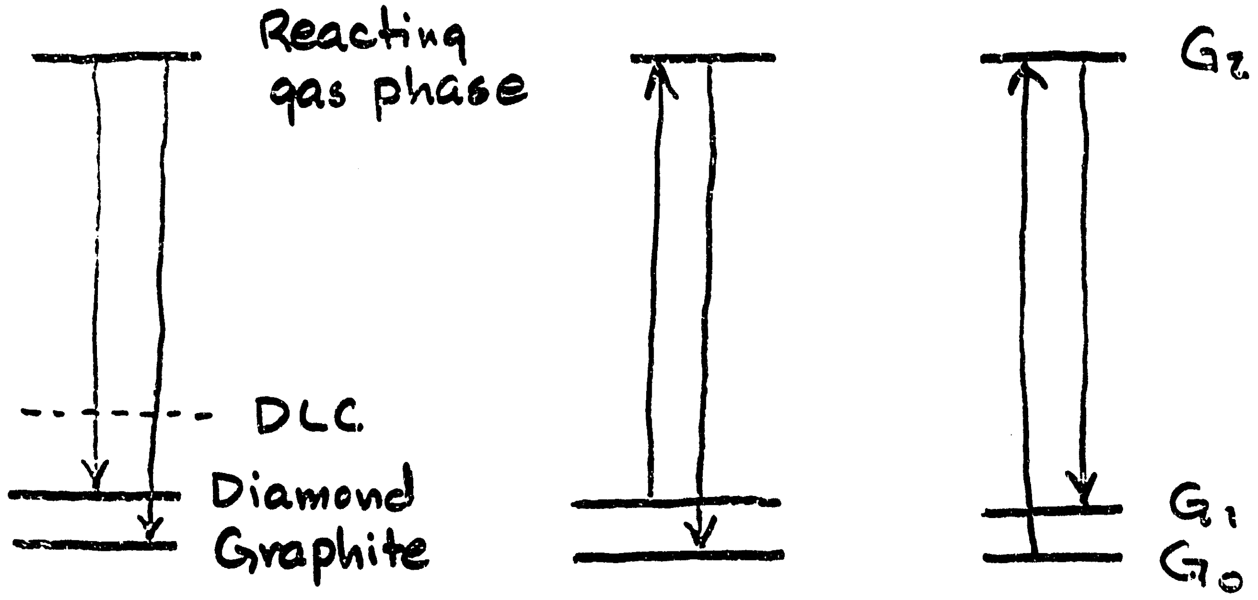
B. V. Derjaguin and D. V. Fedoseev, *Growth of Diamond and Graphite from the Gas Phase,* Nauka, Moscow (1977). (in Russian)

B. V. Spitsyn, L. L. Bouilov and B. V. Derjaguin, *J. Crystal Growth,* 52, 219 (1981).

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

M. Sommer, K. Mui and F. W. Smith, "Thermodynamic Analysis of the Chemical Vapor Deposition of Diamod Films," *Solid State Comm.,* 69 (7), 775 (1989).

# What is the synthetic Paradigm ?



Bridgman,
Eversole, etc.

$C_xH_y \rightarrow xC + H_{y/2}$

$\Delta G \ll 0$

$C_d \xrightarrow{O_2, H_2, etc.} C_g$

$\Delta G < 0$

$C_g \xrightarrow{H} C_d$

$\Delta G > 0$

## Questions

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.

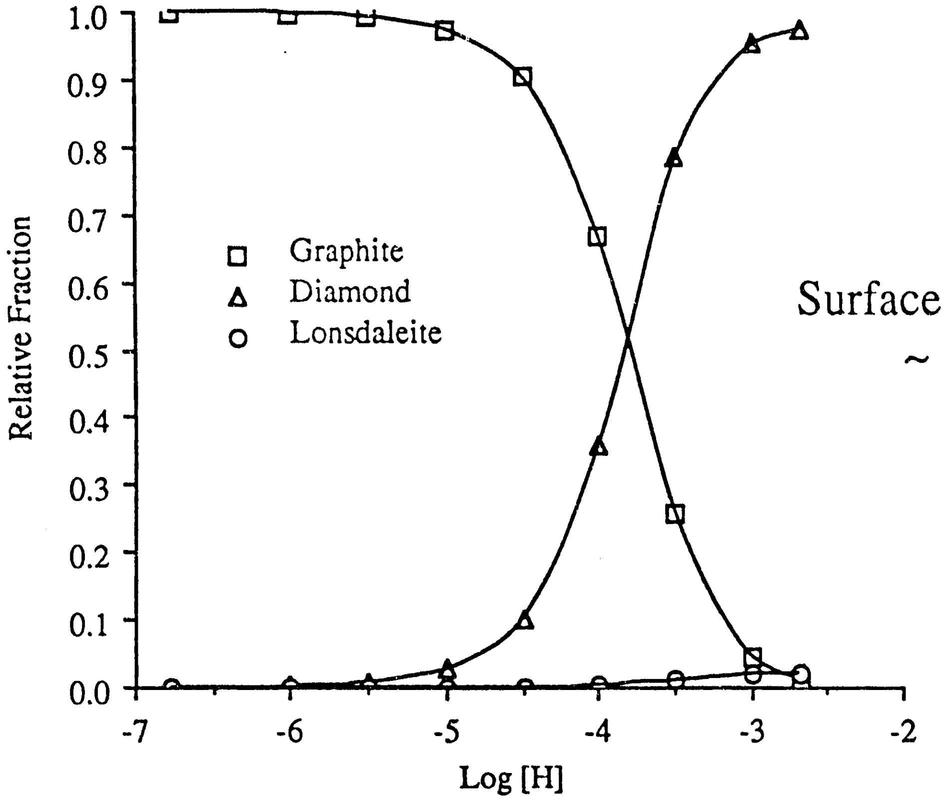
R. Roy, R. Messier and K. E. Spear, *Microwave Plasma Synthesis of Diamonds and Diamond Coatings*, Final Technical Report, ONR Contract N00014-84-K-0749, January, 1986.

B. B. Pate, *Surface Science*, 165, 83 (1986).

K. E. Spear, *Earth and Miner. Sci.*, The Pennsylvania State University, 46(4), 53-59 (1987).

W. A. Yarbrough, "Thermodynamics and the CVD of Diamond," *Diamond, Silicon Carbide and Related Wide Band Gap Semiconductors*, J. T. Glass, et. al., eds., MRS Proceedings, Vol. 162, Pittsburgh, PA (1990), pp. 75-84.

# Variation of Predicted Phase with Atomic Hydrogen Partial Pressure



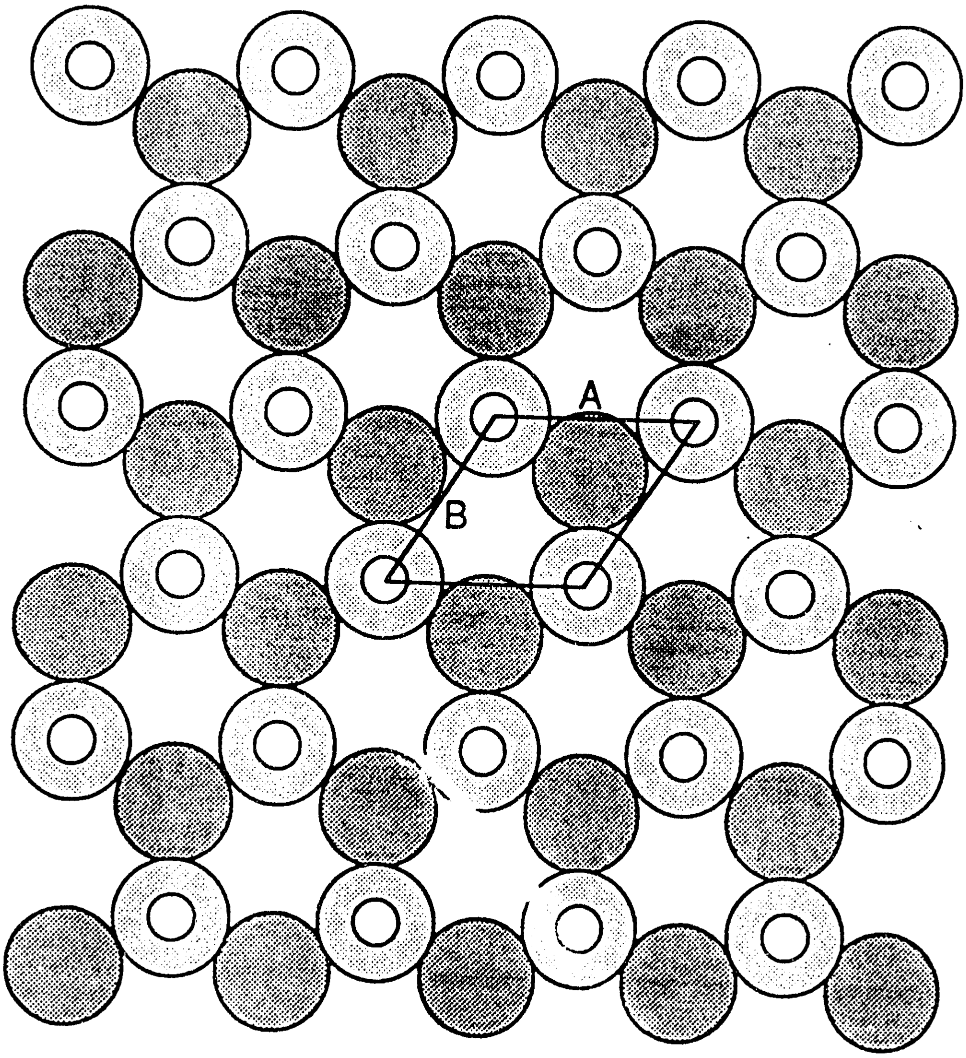
Surface temperature:
~ 1000° C

At thermostatic equilibrium:
Log [H°] = - 6.78
*Graphite* is predicted

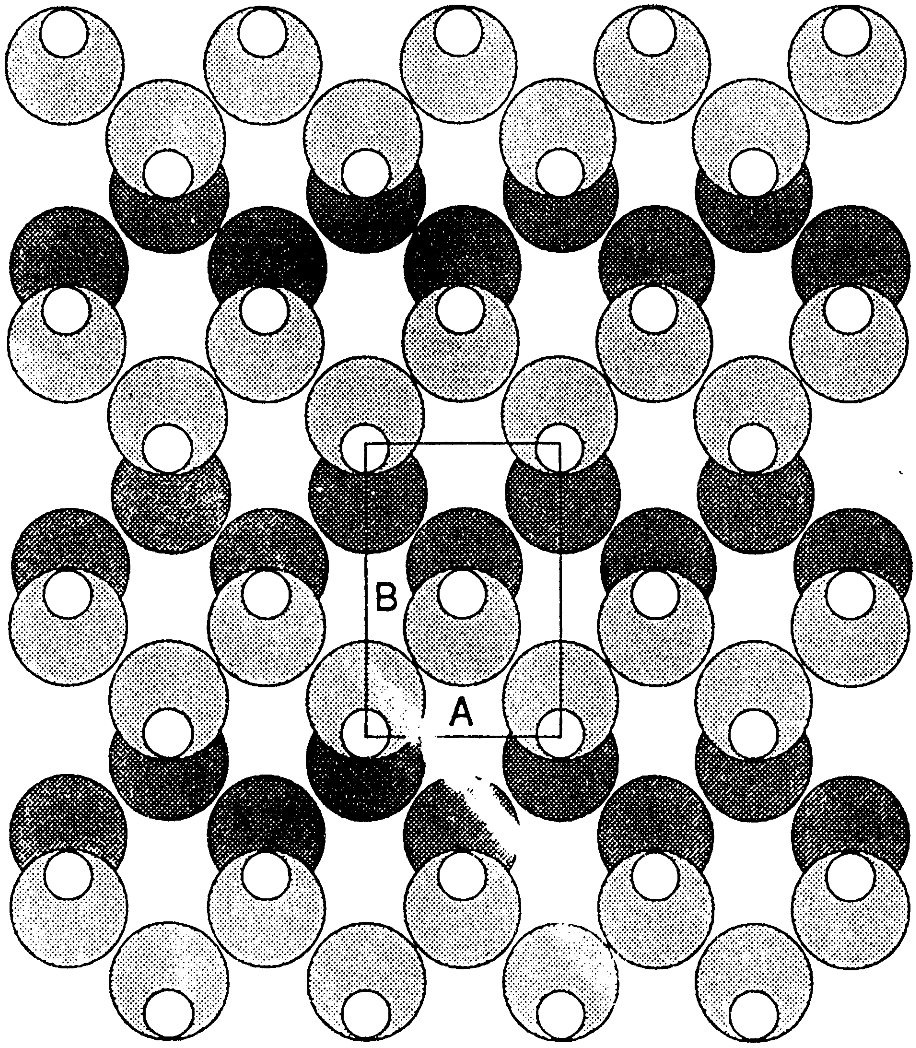
For filament at 2000°C (50 Torr):
Log [H°] = - 2.68
*Diamond* is predicted

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

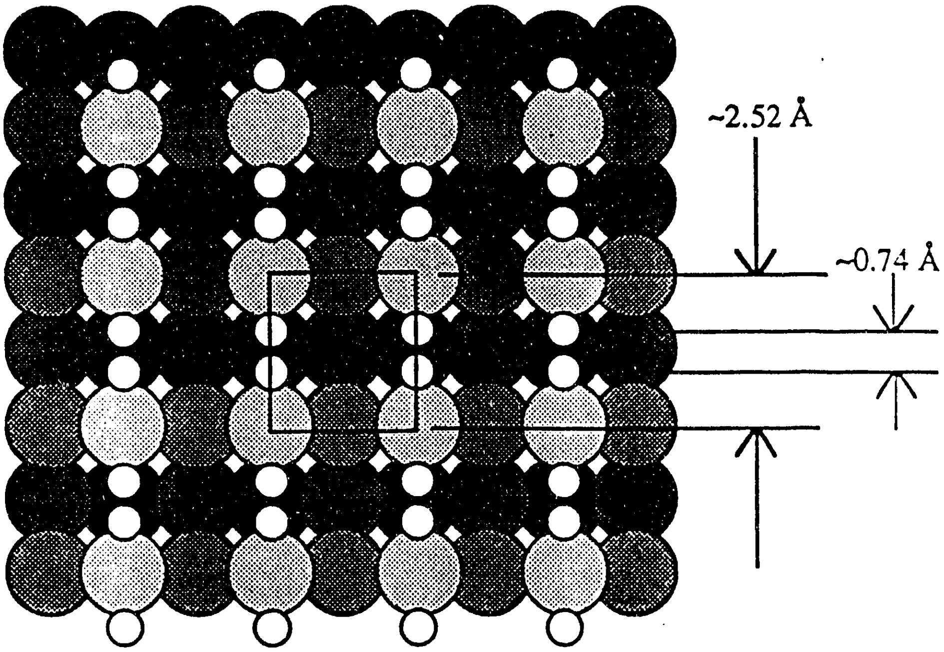
# Hydrogenated, Unreconstructed (111) Surface of Diamond



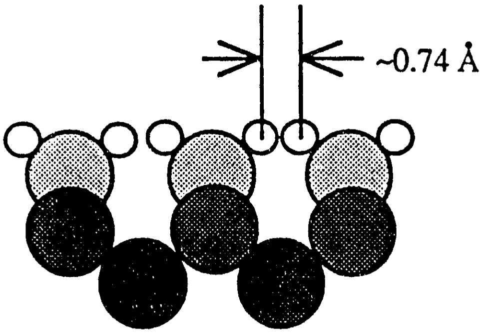
# Hydrogenated, Unreconstructed (110) Surface of Diamond



# Hydrogenated, Unreconstructed (100) Surface



Plan View



Side View

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

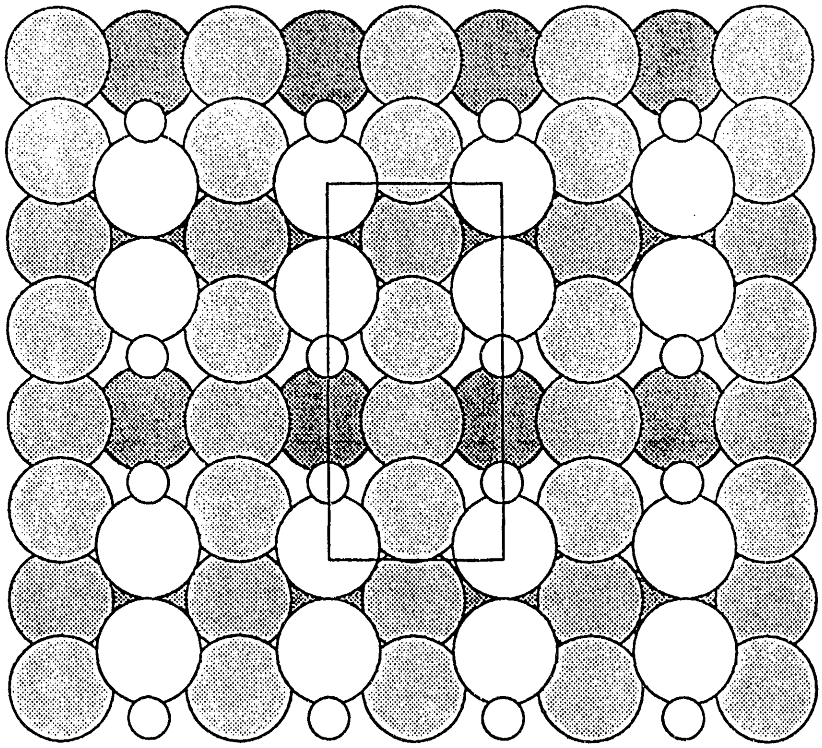
Simple hydrocarbon (cyclooctane) model, $\Delta H \sim 2.5$ kcal/mole

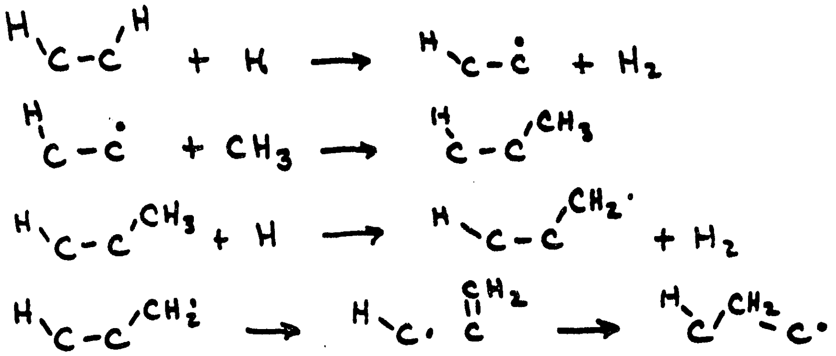
Molecular mechanical modeling, $\Delta H \sim 40$ kcal/mole

(Yang and D'Evelyn, 1991)

See: W. A. Yarbrough, in *Diamond, Silicon Carbide and Related Wide Band Gap Semiconductors*, pp. 75-84, MRS Proc., Vol. 162, Pittsburgh, PA (1990).
A. V. Hamza, et al., *Surf. Sci.*, 237, 35 (1990).
S. J. Harris, *Appl. Phys. Lett.*, 56 (23), 2298 (1990).

# Hydrogenated, Reconstructed (100) Surface of Diamond





B. Garrison (Penn State)
ė D. Brenner (NRL), 1991

# A Methyl Radical Mechanism

Gas Phase Activation

$$H_2 \rightarrow H\bullet + H\bullet \qquad (1)$$

$$CH_4 + H\bullet \rightarrow CH_3\bullet + H_2 \qquad (2)$$

Surface Activation

$$C_{(s)}H + H\bullet \rightarrow C_{(s)}\bullet + H_2 \qquad (3a)$$

$$2\,C_{(s)}H \rightarrow 2\,C_{(s)}\bullet + H_2 \qquad (3b)$$

Addition

$$C_{(s)}\bullet + CH_3\bullet \rightarrow C_{(s)}CH_3 \qquad (4)$$

Incorporation

$$C_{(s)}CH_2\bullet + C_{(s)}CH_2\bullet \rightarrow C_{(s)}CH_2CH_2C_{(s} \qquad (5)$$

$$C_{(s)}CH_2\bullet + C_{(s)}\bullet \rightarrow C_{(s)}CH_2C_{(s} \qquad (6)$$

# Unresolved Questions

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

$$2\,C_{(s)}H \leftrightarrow 2\,C_{(s)}\bullet + H_2$$

Is it possible? important?

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

$$C_2H_4 + H_2 \leftrightarrow C_2H_6$$

does not happen.

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

Can carbon species (R-$CH_3$, R=$CH_2$, etc.) diffuse on diamond?

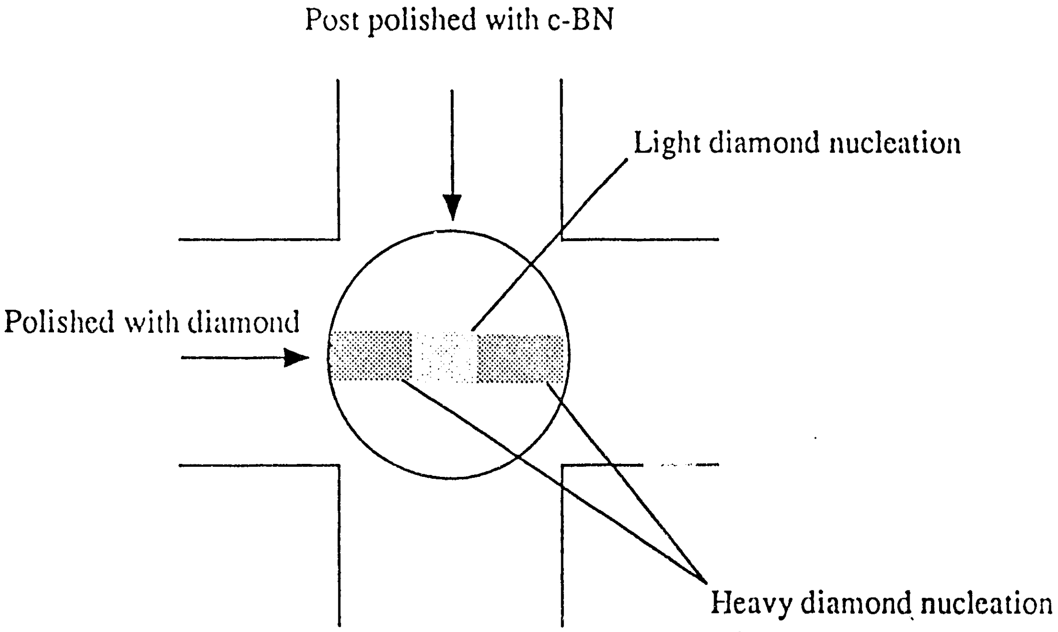
Dissociative chemisorption of $H_2$ on diamond is known at low temperature.

Y. Ishikawa, et al., in *The Chemistry and Physics of Carbon*, P. L. Walker and P. A. Thrower, eds., Vol. 12, (Marcel Dekker, New York, 1975), pp. 39-108.

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

If associative desorption does not happen - what is the mechanism?

# Polishing to enhance diamond nucleation

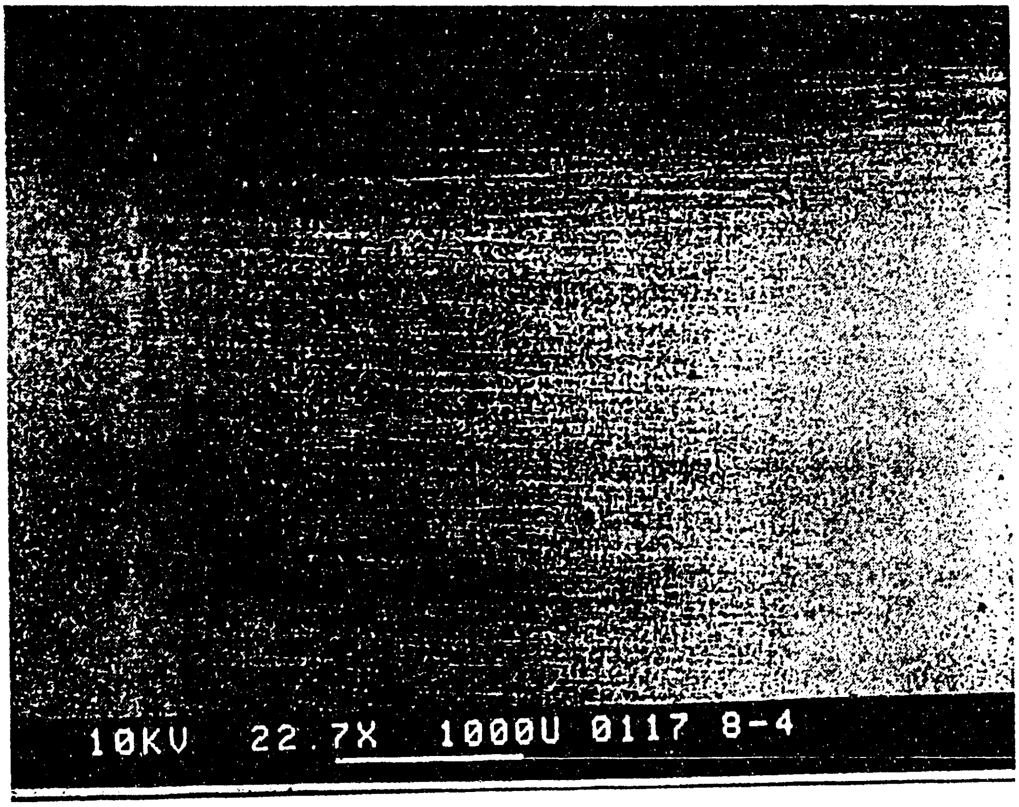


Post polished with c-BN

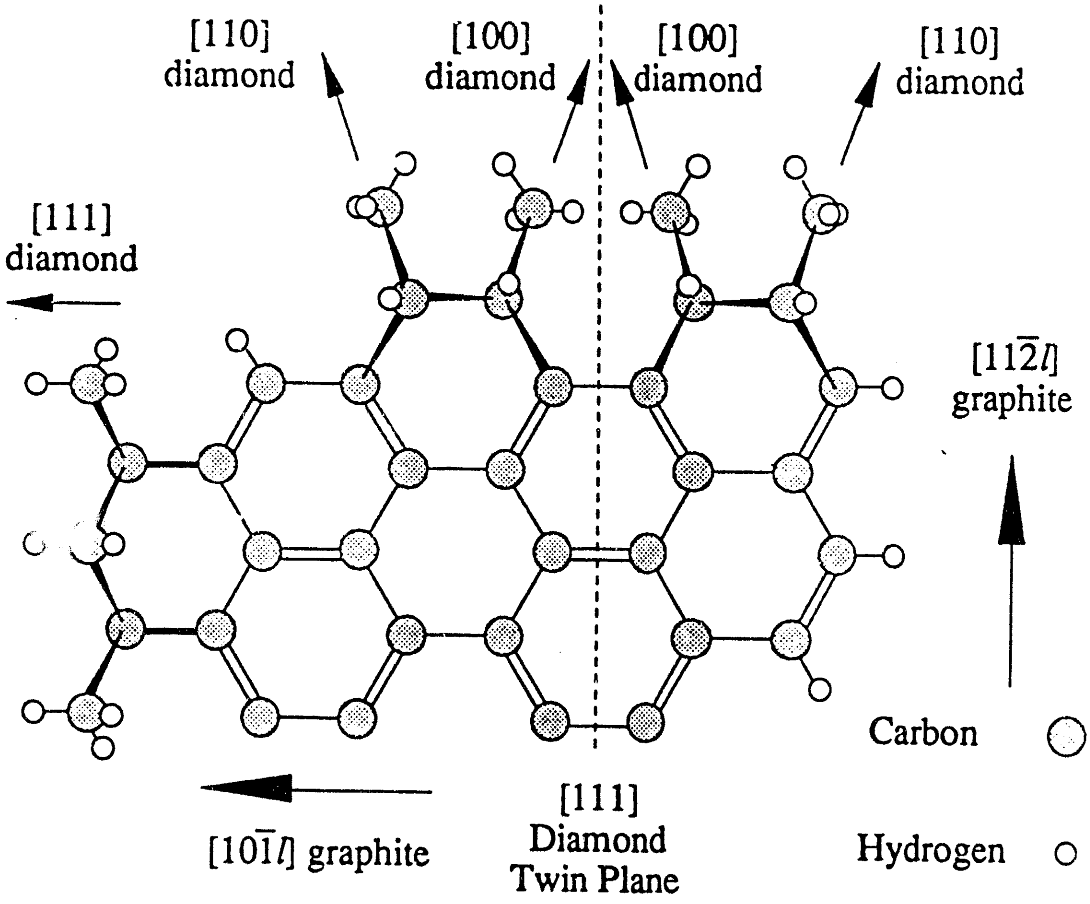
Light diamond nucleation

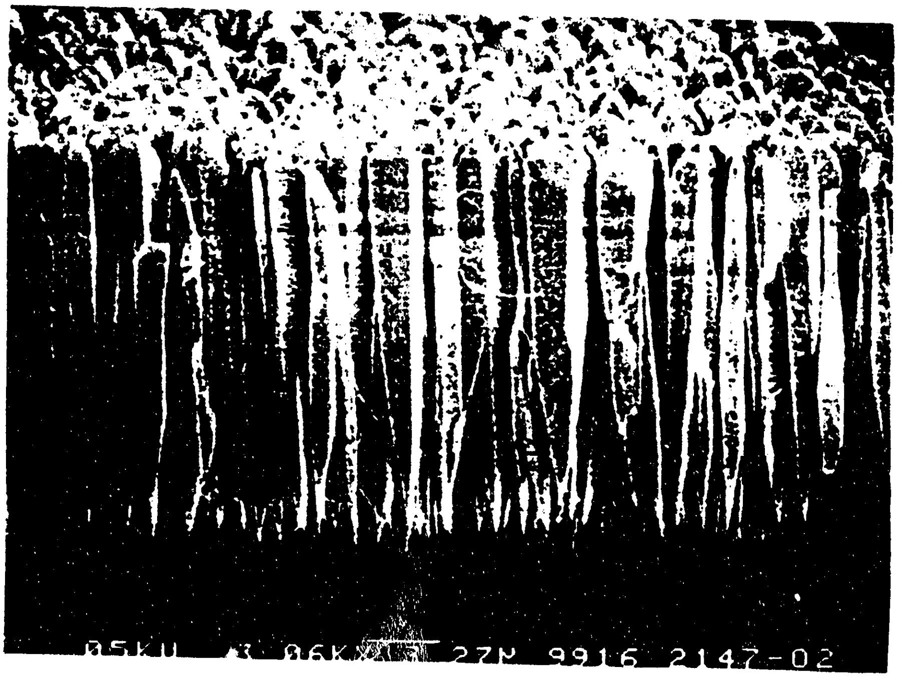
Polished with diamond

Heavy diamond nucleation



# Nucleation of Diamond on Graphite





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

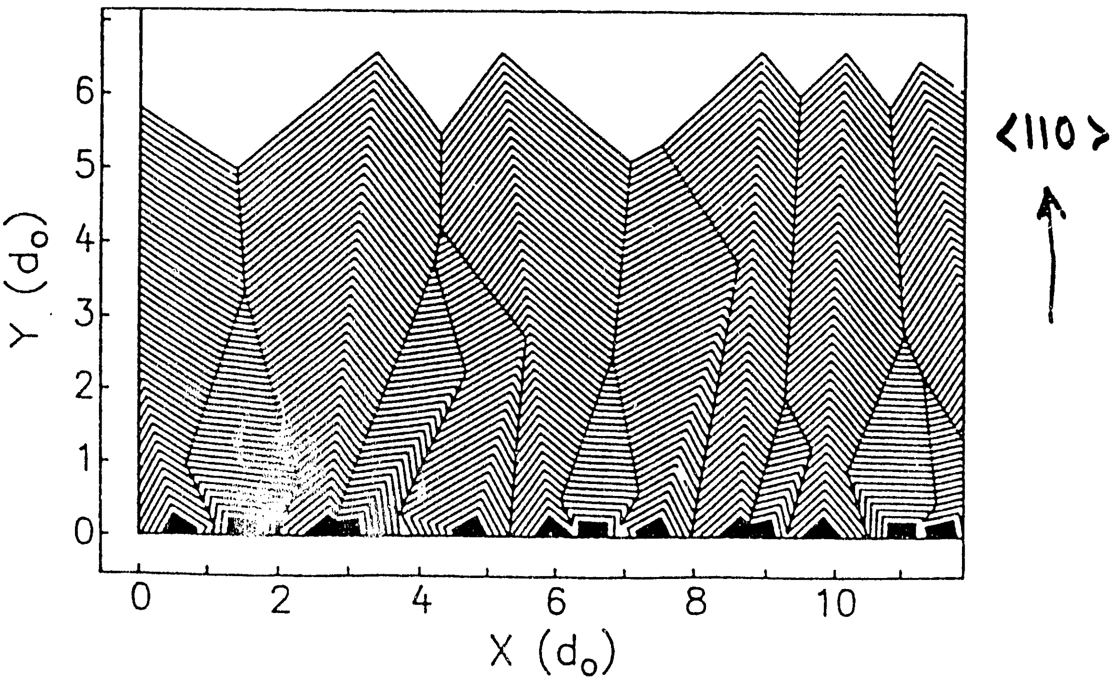


Fig 8 Computer simulation of the growth of a polycrystalline film. The X and Y axis are normalized with respect to the mean nuclei distance $d_0$

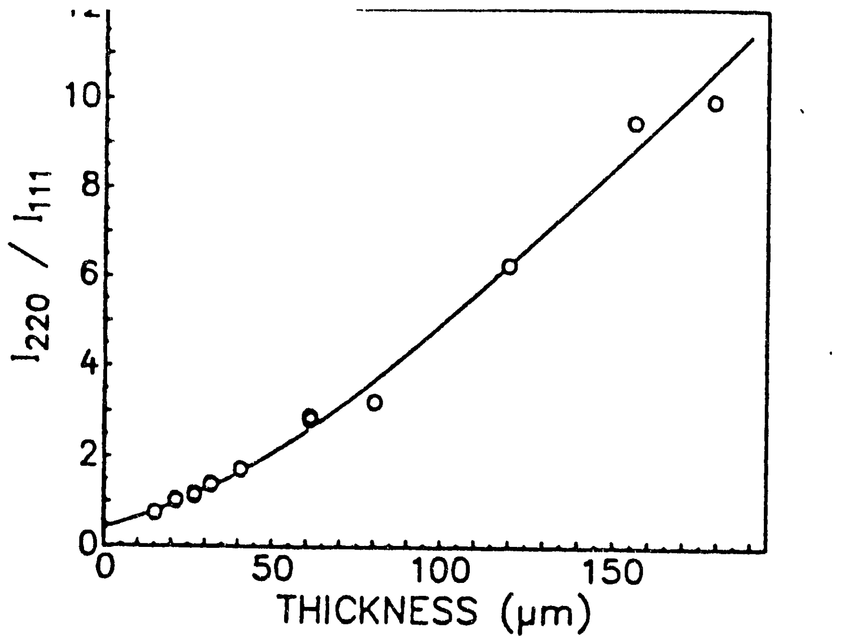
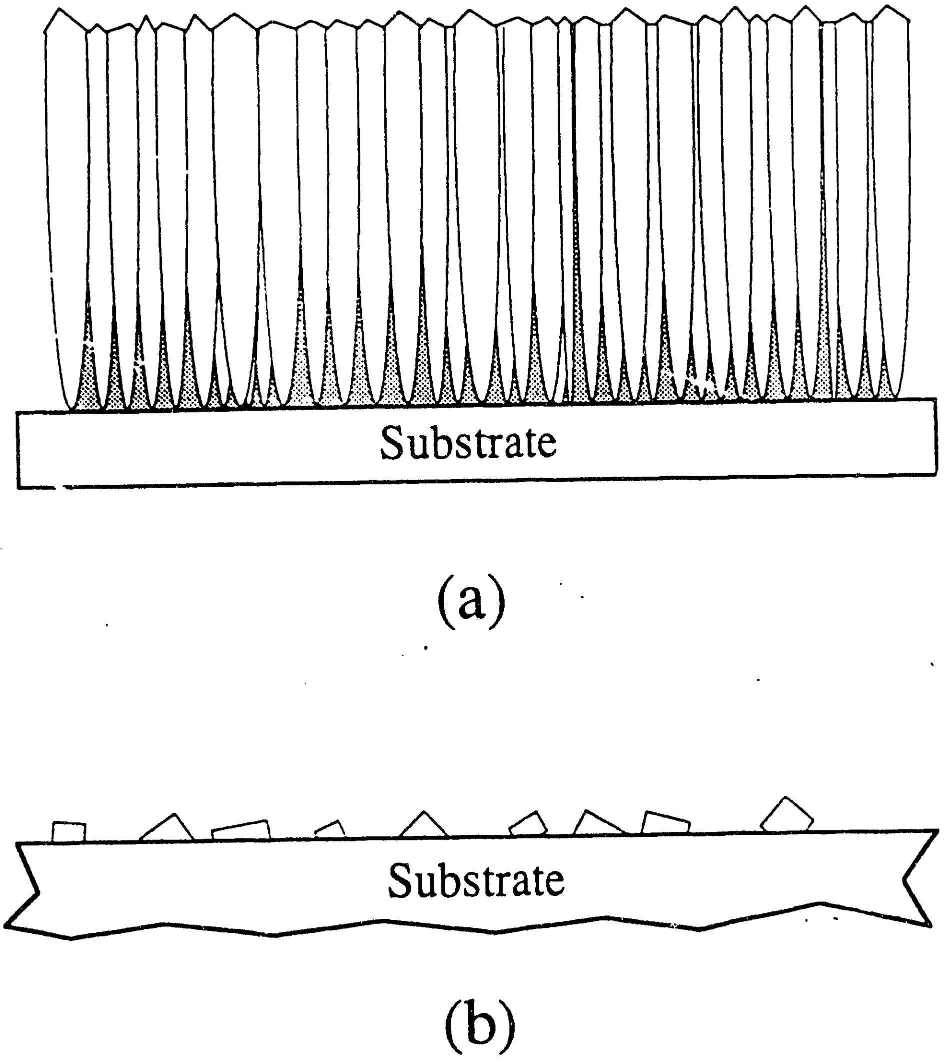


**FIG. 5. Intensity ratio of the 220 peak to the 111 peak as a function thickness.**

# Modeling of Texture Development in Polycrystalline Films

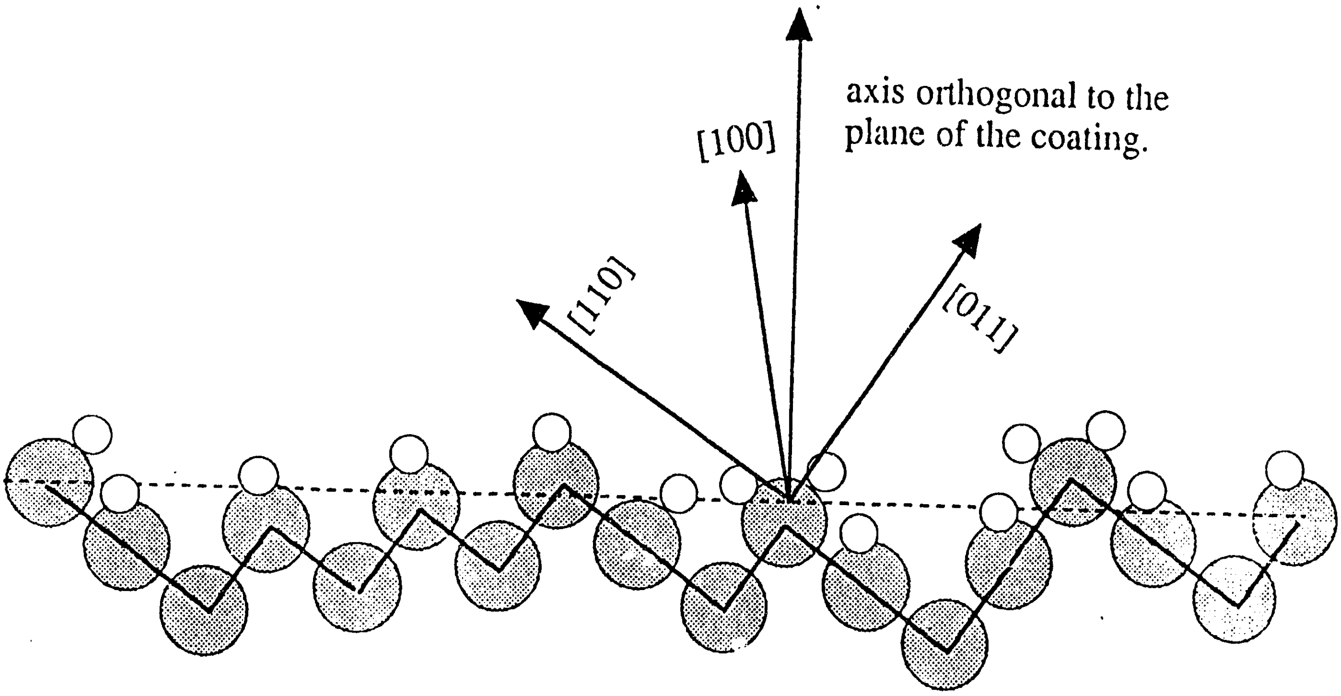
Ch. Wild, N. Herres and P. Koidl, "Texture Formation in Polycrystalline Diamond Films," *J. Appl. Phys.*, 68 (3), 973-978 (1990).

# Model for Microstructural Development



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



FOR VICINAL <100> TEXTURE SEE:

E.D. SPRECHT, R.E. CLAUSING AND L. HEATHERLY

J. MATER. RES., <u>5</u> (11), 2351 (1990).

# Requirement for Elastic Isotropy in Cubic Materials

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

*Values for diamond*

from: M. H. Grimsditch and A. K. Ramdas, *Phys. Rev.*, B11, 3139 (1975)

$$c_{11} = 10.76, \quad c_{12} = 1.25, \quad c_{44} = 5.77 \quad \times 10^{11}\ \mathrm{Nm}^{-2}$$

or

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

Conclusion: Diamond is elastically anisotropic.

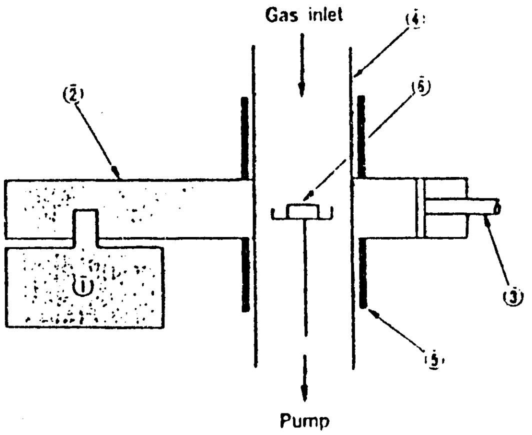


Fig. 4 Schematic diagram for synthesis equipment of microwave plasma CVD method. (1) magnetron (2.45 GHz), (2) wave guide, (3) plunger, (4) quartz tube, (5) sleeve, (6) substrate.

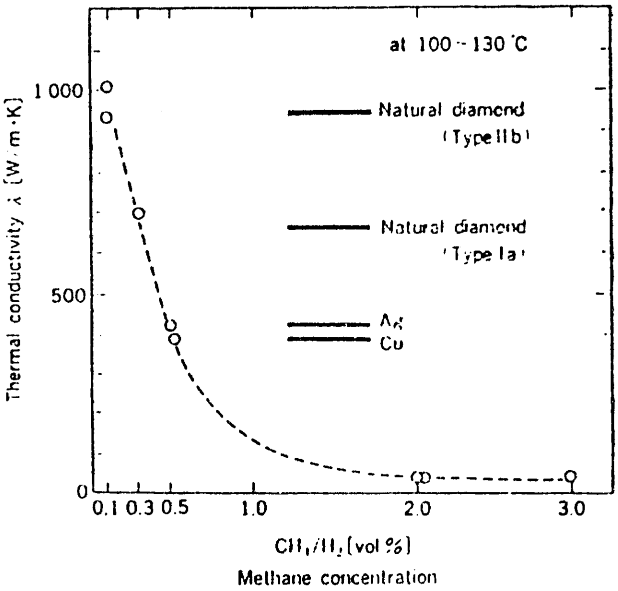


Fig. 5 Thermal conductivity of diamond films for different methane concentrations.

Table 1 Deposition condition of diamond films.

| | |
|---|---|
| Method | MicroWave Plasma CVD |
| Reaction gas | $CH_4+H_2$ |
| $CH_4$ concentration($CH_4/H_2$) | 0.1~3.0 vol% |
| Total gas pressure | 4kPa |
| Flow rate | 300SCCM |
| Microwave power(2.45GHz) | 500W |
| Temperature(on sub.) | ~800 C |
| Substrate | Si(100) |
| Substrate dimensions | 30× 5×0.6mm |
| Thickness of diamond films | 7~30μm |

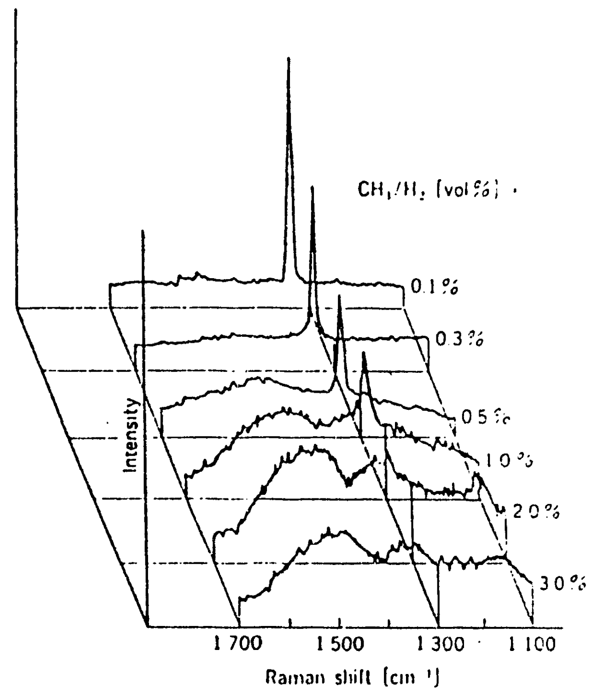
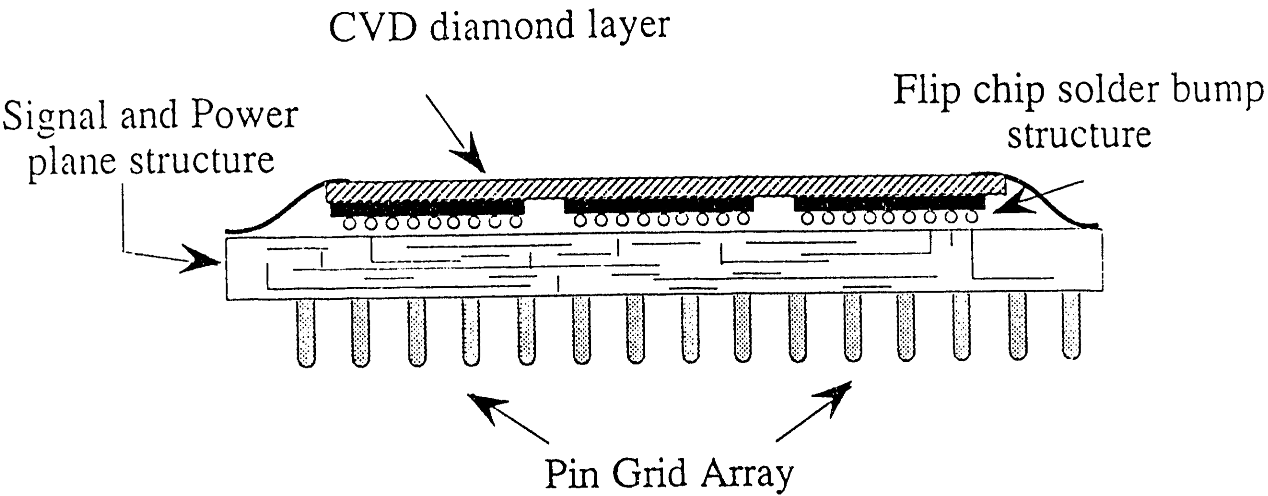
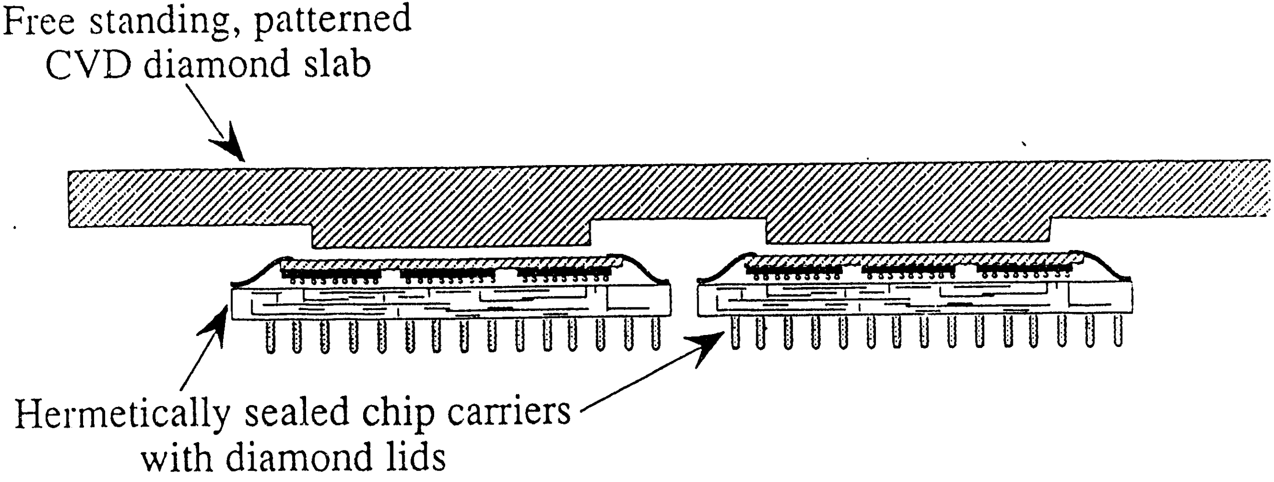


Fig. 6 Raman spectra of diamond films for different methane concentrations.

A. Nishikawa, "Measurement for Thermal Conductivity of Diamond Films," *New Diamond 1990*, Japan New Diamond Forum, through Ohmsha, Ltd., Tokyo, Japan.

# Chip Carrier Possibilities





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.

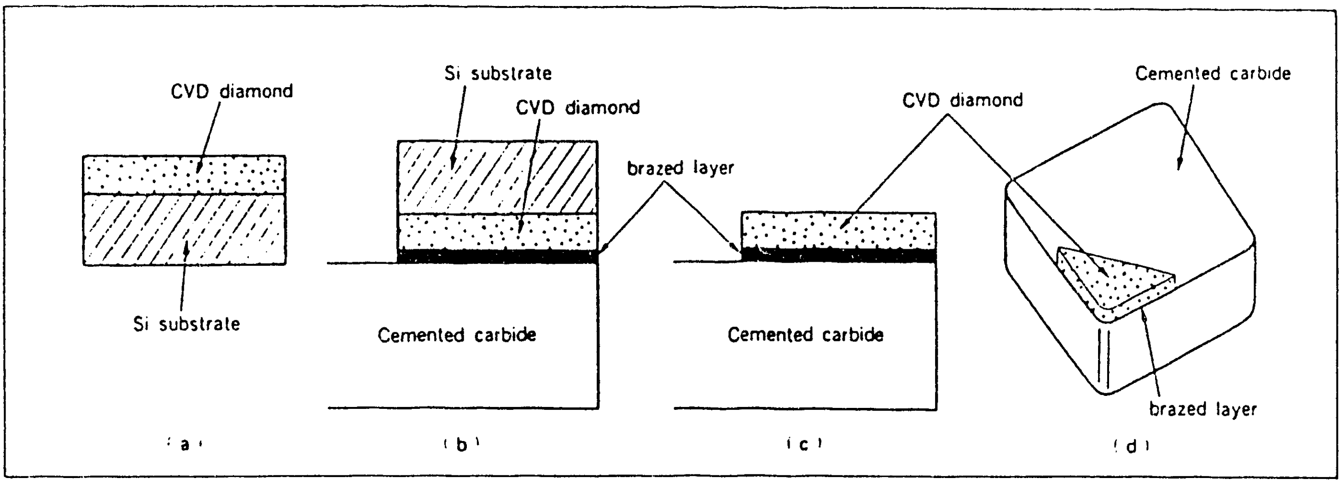


Fig. 2 Manufacturing method for a CVD poly-crystalline diamond tool.

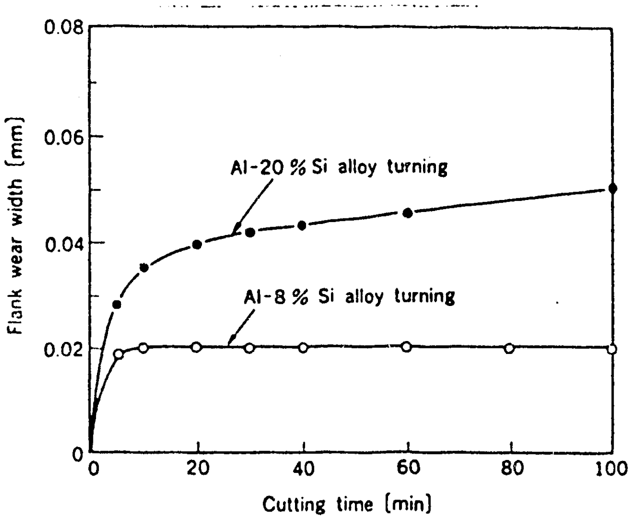


Fig. 4 Flank wear curve diagram of CVD poly-crystalline diamond tips in Al-8%Si and Al-20%Si alloy turning.

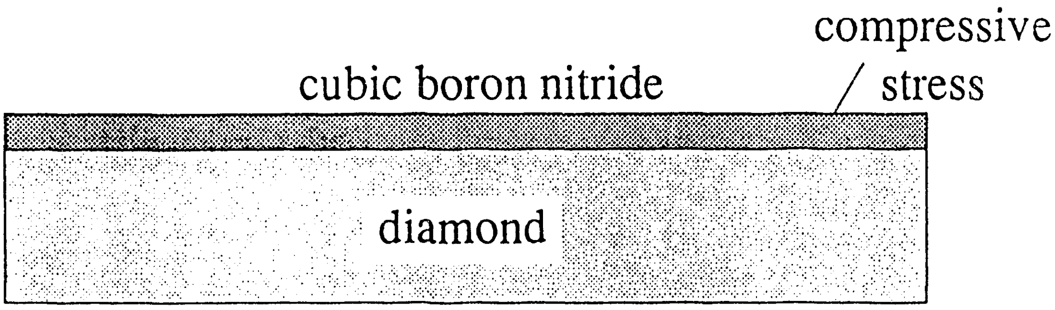
# Brazed Diamond Cutting Tool and its performance

Asahi Industrial Diamond Co., Ltd.
Osaka, Japan

F. Okuzumi, "Gaseous Phase Synthesis Poly-crystalline Diamond Tool," *New Diamond 1990,* Japan New Diamond Forum, Ohmsha, Ltd., Tokyo, 1990.

# Future Possibilities

- Composite designs, e.g. consider



- 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 it 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 pyrolysized 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.

$$CH_4 \xrightarrow{\text{Heat}} \text{Deposit (Diamond \& Graphite)} + 2\,H_2 \qquad (1)$$

$$H_2 + \text{Deposit} \xrightarrow{\text{Heat}} \text{Diamond} + CH_4 \qquad (2).$$

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.

$$CH_4 \xrightarrow{\text{Heat \& Atomic Hydrogen}} \text{Diamond} + 2\,H_2 \qquad (3)$$

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).

$$H_2 \text{ ---> } 2\,H \quad ; \quad \Delta H = +104{,}000 \text{ kcal/mole} \qquad (4)$$

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 $W_2C$ 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 $M_2C$ forming first followed by MC where M is one of the refractory metals(Fig 3). Under typical hot-filament CVD diamond growth, $M_2C$ 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]:

$$\mathbf{H + H + M \text{------>} H_2 + M} \qquad (5)$$

where H is atomic hydrogen and 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 K and P = 10 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 growth. 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.

## IIC. 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 exists 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 diamond[47]. These experiment 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 CH4/H2 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-$H_2$-$CH_4$ 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, ie 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 $sp^3$ bond to the diamond surface. The exothermic chemistry drives the reaction while the $sp^3$ 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 form low to high. Some fluorocholorohydrocarbons 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 dicholordifluorocarbon 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 wide-spread 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 $CF_4$ and $CH_4$:

$$CH_4 + \text{Diamond-F} \text{ -----> } \text{Diamond-C-H} + HF \qquad (6a)$$

$$CF_4 + \text{Diamond-H} \text{ -----> } \text{Diamond-C-F} + HF \qquad (6b)$$

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 $C_NX_M$ and $C_LZ_P$:

$$C_NX_M + \text{Diamond-Z} \text{ ------> } \text{Diamond-C-X} + ZX \qquad (7\ a)$$

$$C_LZ_P + \text{Diamond-X} \text{ ------> } \text{Diamond-C-Z} + ZX \qquad (7b)$$

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 $C_NX_M$ and $C_LZ_P$ 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:

$$C_NX_M + C_LZ_P + \text{X-Diamond-Z} \text{ ------> } \text{Diamond} + ZX \quad (8)$$

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].

## IIIE. 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 [redacted] 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 hydroxl 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.

## IIIF. 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.

## LIST OF REFERENCES

1. W.G. Eversole, U.S. Patent No. 3030188, Apr 17, 1962.
2. J.C. Angus, H.A. Will, and W.S. Stanko, J.Appl.Phys, 39, 2915 (1968)
3. D.J. Poferi, N.C. Gardner and J.C. Angus, J.Appl.Phys, 44, 1428 (1973)
4. K.E. Spear, J. Am. Ceramic Soc, 72, 171 (1989)
5. B.V.Spitsyn, L.L.Bouilov and B.V. Deryagin, J.Cryst.Growth, 52, 219 (1981)
6. T.R.Anthony,"Synthesis of Metastable Diamond" in "Diamond, Boron, Nitride, Silicon Carbide and Related Wide Band Gap Semiconductors", edited by J.F.Glass, R.F.Messier and N.Fujimori, Proc MRS 162, in press (1990)
7. W.E. Jones, S.D. Macknight and L. Teng, Chemical Revs, 73, 407 (1973)
8. I. Langmuir, J.Amer.Chem.Soc, 34,860 (1912)
9. I. Langmuir, J.Amer.Chem.Soc, 34,1310 (1912)
10. I. Langmuir and G.M.J. Mackay, J.Amer.Chem.Soc, 36,1708 (1914)
11. I. Langmuir, J.Amer.Chem.Soc, 37,417 (1915)
12. M.Kamo, Y. Sato, S. Matsumoto and N. Setaka, J. Crystal Growth, 62,642 (1983)
13. S. Matsumoto, Y. Sato, M. Kamo and N. Setaka, Japn.J.Appl.Phys, 21, L183 (1982)
14. H.J. Grabke,Berichte der Bunsengesellschaft, 69, 409 (1965)
15. H.J Grabke, Metallurgical Transactions, 1, 2972 (1970)
16. F.G. Celii, P.E.Peterson, P.E.Wang and J.E.Butler, Appl Phys Letters 52, 2043 (1988)
17. F.G. Celii and J.E.Butler, Appl Phys Letters 54, 1031 (1989)
18. T.R.Anthony, MRS Fall Meeting, Nov30-Dec3 (1987) Boston

19. B.Singh, Y.Arie, A.W.Levine and R.O.Mesker, Appl Phys Letters 52, 451 (1988)
20. T.D. Moustakas, Solid State Ionics 32, 861 (1989)
21. H.B.Vakil, Am Chem Soc Meeting, Mar (1989) Dallas
22. H.Aikyo and K.Kondo, Jap Jour Appl Phys 28, L1631 (1989)
23. Benno Lux and R. Haubner, Proceedings 12th Int Plansee Seminar,C16, 461, (1989)
24. T.R.Anthony, p 555, "Diamond and Diamond-like Films", Proceedings of the NATO Conference on Diamond and Diamond-like Films, July, 1990, Castelvecchio, Pascoli, Italy, edited by J.C.Angus, R.E.Clausing, L.L.Horton and P.Koidl, Plenum Press (NY, 1991)
25. Y.Hirose, J Jpn Soc Precis Eng 53, 1507 (1987)
26. H.J.Hinneberg, M.Eck and K.Schmidt, Proceedings of the Second European Conference on Diamond, Diamond-like and Related Coatings, Sept 2-6, Nice,France (Elsevier, Lausanne, 1992)
27. A.Sawabe and T.Inuzuka, Thin Solid Films 137, 89 (1986)
28. J.T. Glass, NATO Meeting on Boride, Carbides and Hard Materials, Manchester, UK (July, 1989)
29. K. Kobashi, NATO Meeting on Boride, Carbides and Hard Materials, Manchester, UK (July, 1989)
30. W.F.Banholzer, Proceedings of the First European Conference on Diamond, Diamond-like and Related Coatings, Sept Crans-Montana, Switzerland (Elsevier, Lausanne, 1991)
31. R.W. Wood, Proc Roy Soc, Ser A, 102, 1 (1923)
32. J. Suzuki, H. Kawarada, K.Mar, J.Wei, Y.Yokota and A. Hiraki, Jap Journ Appl Phys, 28, L281 (1989)
33. I.Watanabe and K Sugata, Jap Journ.Appl.Phys., 27, 1397 (1988)
34. O. Matsumoto, H.Toshima and Y.Kanzaki, Thin Solid Films, 128, 341 (1985)
35. Y.Mitsuda, Y.Kojima,T.Yoshida and K.Akashi., Journ Mat Sci, 22, 1557 (1987)
36. H.Kawarada, K.S. Mar and A.Hiraki, Jap.Journ.App.Phys, 26, L1032 (1987)
37. M.Kamo, Y.Sato, S. Matsumoto and N. Setaka, J.Crystal Growth, 62, 642 (1983)
38. Y.Saito, S. Matsuda and S.Nogita, Journ.Mat.Sci.Letters, 5, 565 (1986)
39. A.R.Badzian and T.Badzian, Proceedings of the Fifteenth International Conference on Metallurgical Coatings Vol 1, 283 , Elsevier Applied Science (1988)
40. Y.Liou, A.Inspektor, R.Weimer and R. Messier, Appl Phys Letters 55, 631 (1989)

41. B.E.Williams, J.T.Glass, R.F.Davis, K.Kobashi and T. Horiuchi, J. Vac Sci Technol A, Vac Surf Films 6, 1819 (1988)
42. K.Kobashi, K.Nishimura, Y.Kawate and T.Horiuchi, J. Vac Sci Technol A, Vac Surf Films 6, 1816 (1988)
43. A.R.Badzian,T.Badzian, R.Roy, R.Messier, K.E.Spear, Mater Res Bull 23, 531 (1988)
44. K.Kobashi, K.Nishimura, Y.Kawate and T.Horiuchi, Phys Rev B38, 4067 (1988)
45. Y.Saito, K.Sato, H.Tanaka and H.Miyadera, J.Mater.Sci 24, 293 (1989)
46. L.Vandenbulcke, P.Bou, R.Herbin, V.Cholet and C.Beny, Colloq Phys C-5, 177 (1989)
47. R.Martin and M.W.Hill, Appl Phys Letters 55, 2248 (1989)
48. R.Haubner and B.Lux, Int J. Refractory & Hard Metals 6, 210 (1987)
49. C.Chen, Y.C. Huang, S.Hosomi and I.Yoshida, Mater Res Bull 24, 87 (1989)
50. H.Kawarada, K.Mar, and J.Suzuki, Jap J Appl Phys 27, L683 (1988)
51. W.Hsu, D.M.Tung, E.A.Fuchs, K.F.McCarty and A.Joshi, Appl Phys Letters 55, 2739 (1989)
52. W.Zhu, C.A.Randall, A.R.Badzian and R.Messier, J.Vac.Sci.Technol A Vac Surface Films 7, 2315 (1989)
53. J.D.Jackson, "Classical Electrodynamics", John Wiley & Sons, New York (1962)
54. J.Keiser and M.Neusch, Thin Solid Films 118, 203 (1984)
55. D.K.Smith, E.Sevillano, M.Besen, V.Berkman and L. Bourget, Proceedings of the Second European Conference on Diamond, Diamond-like and Related Coatings, Sept 2-6, Nice,France (Elsevier, Lausanne, 1992)
56. S. Matsumoto, J.Mater.Sci.Letters, 4, 600 (1985)
57. D.E.Meyer, R.O.Dillon and J.A.Woollam, J Vac Sci & Technol A 7, 2325 (1989)
58. K. Akashi, T.Yoshida, S. Komatsu and Y.Mitsuda, J.Korean Inst Metals 24, 712 (1986)
59. D.E. Meyer, N.J. Ianno, J.A. Woollam, A.B. Swartzlander and A.J.Nelson, J.Maters.Res 3, 1397 (1988)
60. H.Hayashi, Y.Ohnishi, K. Kobashi, K.Nishimura, K.Miyata and Y.Kawate, Kobelco Technol Rev 6, 14 (1989)
61. D.J.Vitkavage, R.A.Rudder, G.G.Fountain and R.J.Markunas, J.Vac.Sci Technol A6, 1812 (1988)
62. S.Matsumoto, M.Hino and T.Kobayashi, Appl Phys Letters 51, 737 (1987)

63. J.L.Franklin, S.A.Studniarz and P.K.Ghosh, J.Appl.Phys 39, 2052 (1968)
64. F.H.Dorman and F.K.Taggart, J.Microwave Power 5, 4 (1970)
65. K. Yanagihara and N.Niinomi, Proc Int Conf Ion Engineering Congr, page 1475, Kyoto (1983)
66. M.M.Millard and E.Kay, J.Electrochem Soc 129, 160 (1982)

67. T. Chonan, M.Uenura, S.Futaki and S.Nishi, Jap.Journ.Appl.Phys, 28, L1058 (1989)
68. K.Suziki, A.Sawabe, H.Yasuda and T.Inuzuka, Appl.Phys.Letters,50,728 (1987)
69. F. Akatsuka, Y.Hirose and K.Komaki, Jap.Journ.Appl.Phys, 27, L1600 (1988)
70. K.Kurihara, K.Sasaki, M.Kawarada and N.Koshima, Appl Phys Letters, 52, 437 (1988)
71. K.Kurihara, K.Sasaki and M.Kawarada, Fujitsu Scientific and Technical Journal 25, 44 (1989)
72. Y. Mitsuda, T.Yoshida and K. Akashi, Rev Sci Instrum 60, 249 (1989)
73. S .Matsumoto, T.Kobayshi, M. Hino, T.Ishigaki and Y.Moriyoshi, 8th International Symposium on Plasma Chemistry, ISPC,8, Paper#S7-03, p2458,Tokyo, (1987)
74. R.R.Baldwin, D.E. Hopkins and R.W.Walker, Trans Faraday Soc., 66, 189 (1970)
75. C.P.Fenimore and G.W.Jones, J.Phys.Chem, 65, 2200 (1961)
76. C.P.Fenimore and G.W.Jones, 1962 Symp. Int. Combust.Proc.,9th, 597 (1963)
77. Y.Hirose and N.Kondo, Program and Book of Abstracts, Japan Applied Physics 1988 Spring Meeting, p434 (March 29, 1988)
78. S.Yazu, S.Sato and N.Fujimori, SPIE Proceedings (San Diego, August 16-20, 1988)
79. L..M.Hanssen, W.A.Carrington, D.B.Oakes, J.E.Butler and K.A.Snail, 1989 Diamond Technology Initiative Symposium, Paper T7, (July 11-13, 1989)
80. D.G.Goodwin, 1989 Diamond Technology Initiative Symposium, Paper T15, (July 11-13, 1989)
81. M.A. Cappelli and P.H.Paul, 1989 Diamond Technology Initiative Symposium, Paper W1, (July 11-13, 1989)
82. M.Murakawa, S.Takeuchi and Y.Hirose, Surface & Coatings Technol 39-40, 1 (1989)
83. R.G.Vardiman, C.L.Vold, K.A.Snail, J.E.Butler and C.S.Pande, Mater Letters 8, 468 (1989)

84. L.M.Hanssen, W.A.Carrington, J.E.Butler and K.A. Snail, Mater Letters 7, 289 (1989)
85. Y.Matsui, A.Yuuki, M.Sahara and Y.Hirose, J.Appl.Phys 28, 1718 (1989)
86. W.A.Carrington, L.M.Hanssen, K.A.Snail, D.B.Oakes and J.E.Butler, Metall Trans 20A, 1282 (1989)
87. Irvin Glassman, "Combustion", Academic Press, New York (1977)
88. Y.Tzeng, P.J.Kung, R.Zee, K.Legg, H.Solnick-Legg, Appl Phys Letters 53, 2326 (1988)
89. P.J.Kung and Y.Tzeng, J.Appl.Phys 66, 4676 (1988)
90. D.E.Patterson, R.H.Hauge, C.J.Chu and J.L.Margrave, US Patent 5,071,677 (Dec 10, 1991)
91. D.E.Patterson, B.J.Bai, C.J.Chu, R.H.Hauge and J.L.Margrave, Proceedings of the Second International Conference on New Diamond Science and Technology, Washington,DC, Sept 23-27, 1990 , page 433, Material Research Society, Pittsburgh, Pa (1991)
92. R.A.Rudder, J.B.Posthill and R.J.Markunas, Electronic Letters 25, 1220 (1989)
93. T.R. Anthony, Mat.Res.Soc.Symp.Proc, Vol 162, 61 (1990)
94. T.R.Anthony, "The Physics and Chemistry of Carbides, Nitrides and Borides, Editor, R.Freer, p 133, Kluwer Academic Publishers, Dordrecht, Netherlands (1990)
95. M. Yoder, personal communication
96. K.Kitahama, K.Hirata, H.Nakamatsu,S.Kawai, N.Fujumori, T.Imai, H.Yoshino and A.Doi, Appl Phys Letters 49, 634 (1986)
97. K.Kitahama, Appl Phys Letters 53, 1812 (1988)
98. J.Narayan,Proceedings of the Second European Conference on Diamond, Diamond-like and Related Coatings, Sept 2-6, Nice,France (Elsevier, Lausanne, 1992)
99. A.R.Patel and K.A.Cherian, Indian J.Pure&Appl Phys 19, 803 (1981)
100. K.A.Cherian, Proceedings of the First European Conference on Diamond, Diamond-like and Related Coatings, Sept Crans-Montana, Switzerland (Elsevier, Lausanne, 1991)
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.

Figures 15a. Addition of Carbon onto a Fluorinated Diamond Surface by Methane.

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

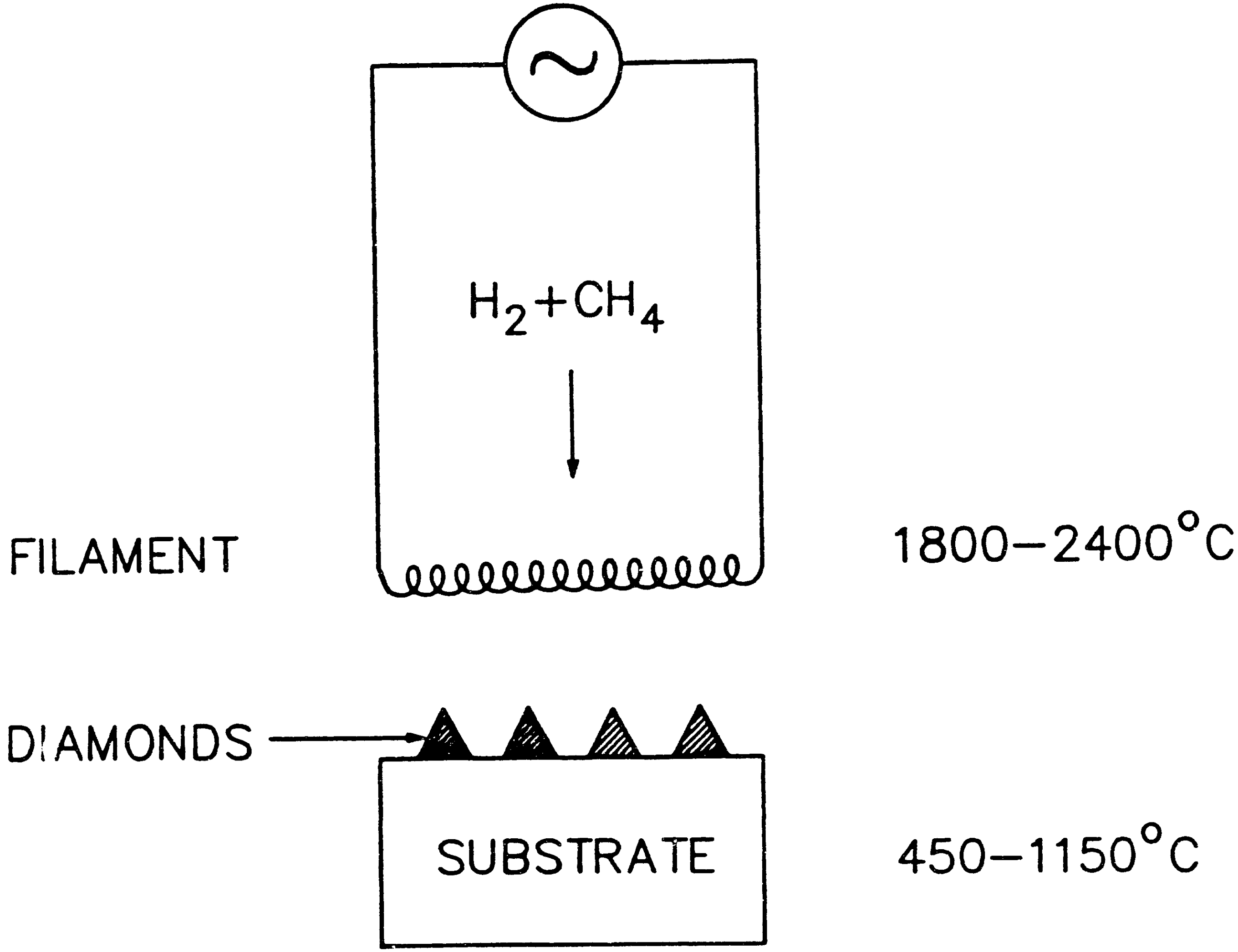
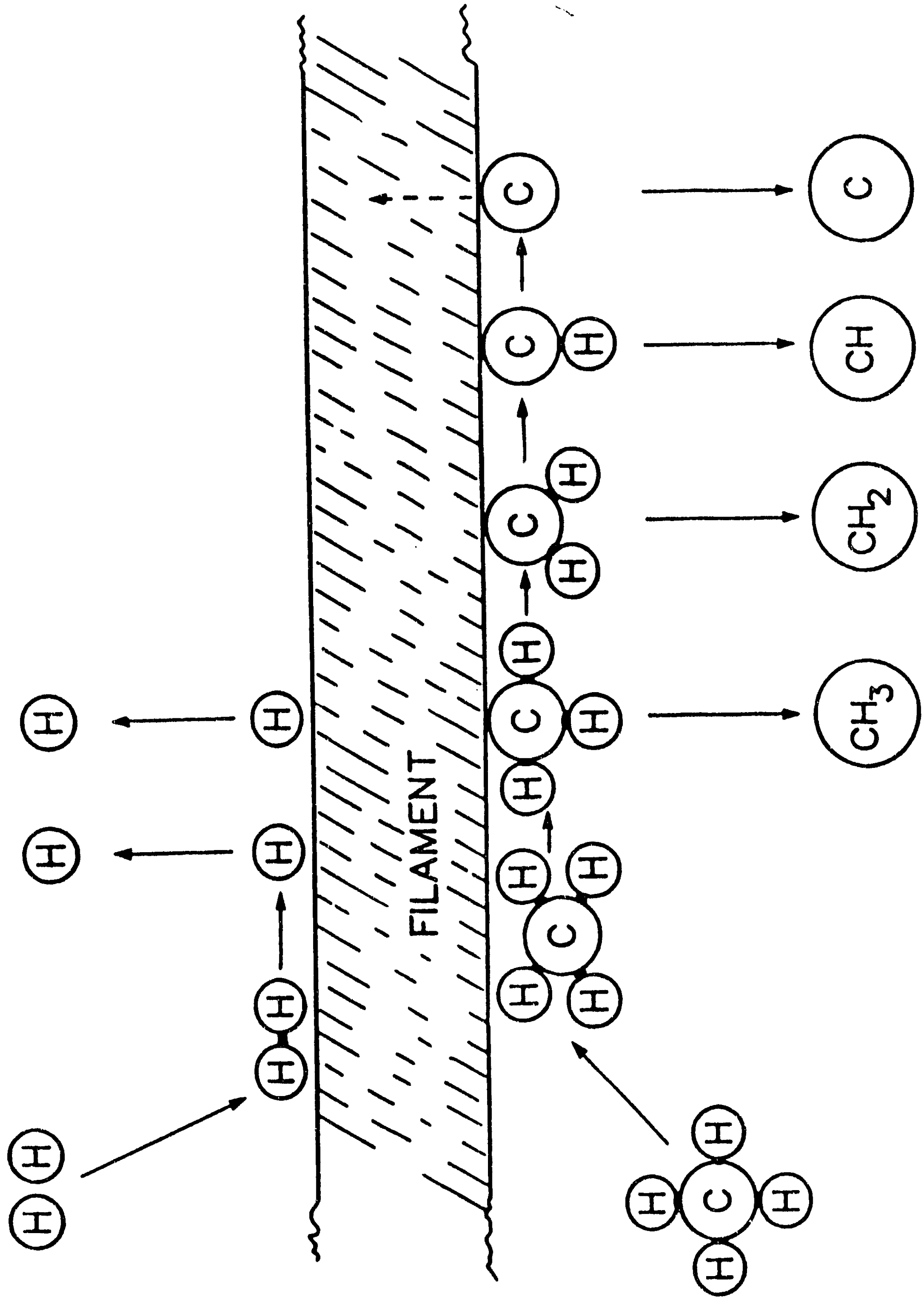
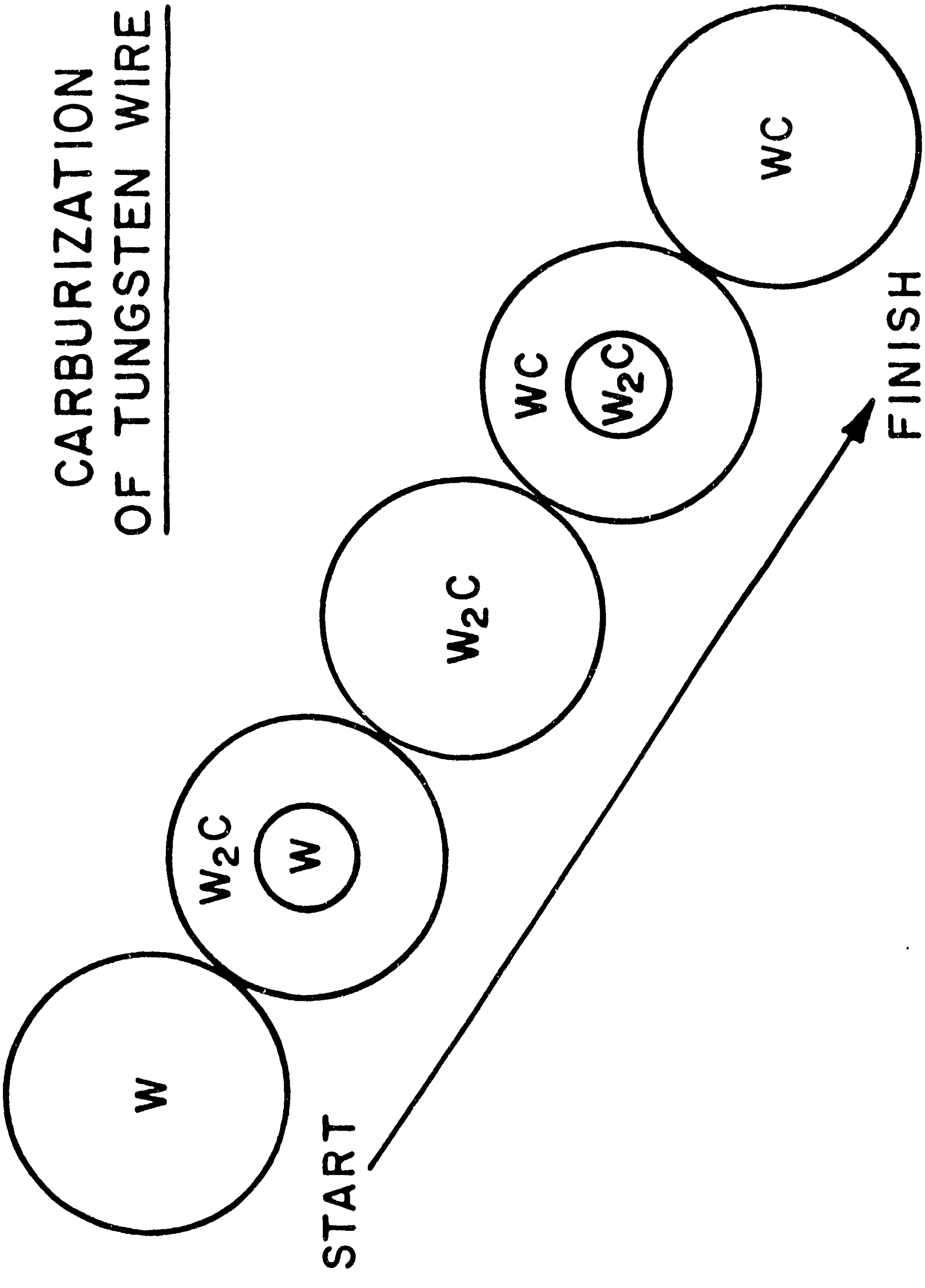


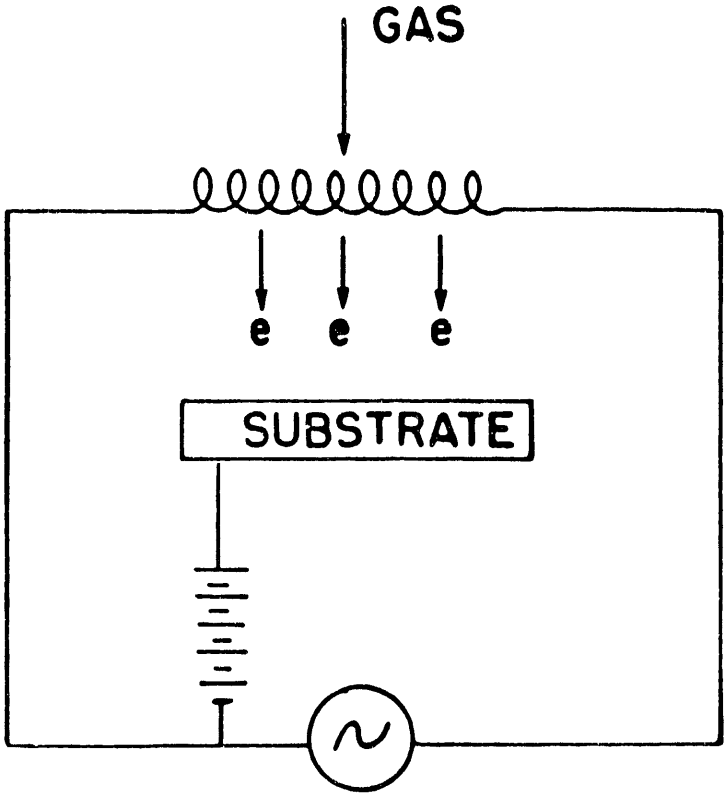
Fig. 1

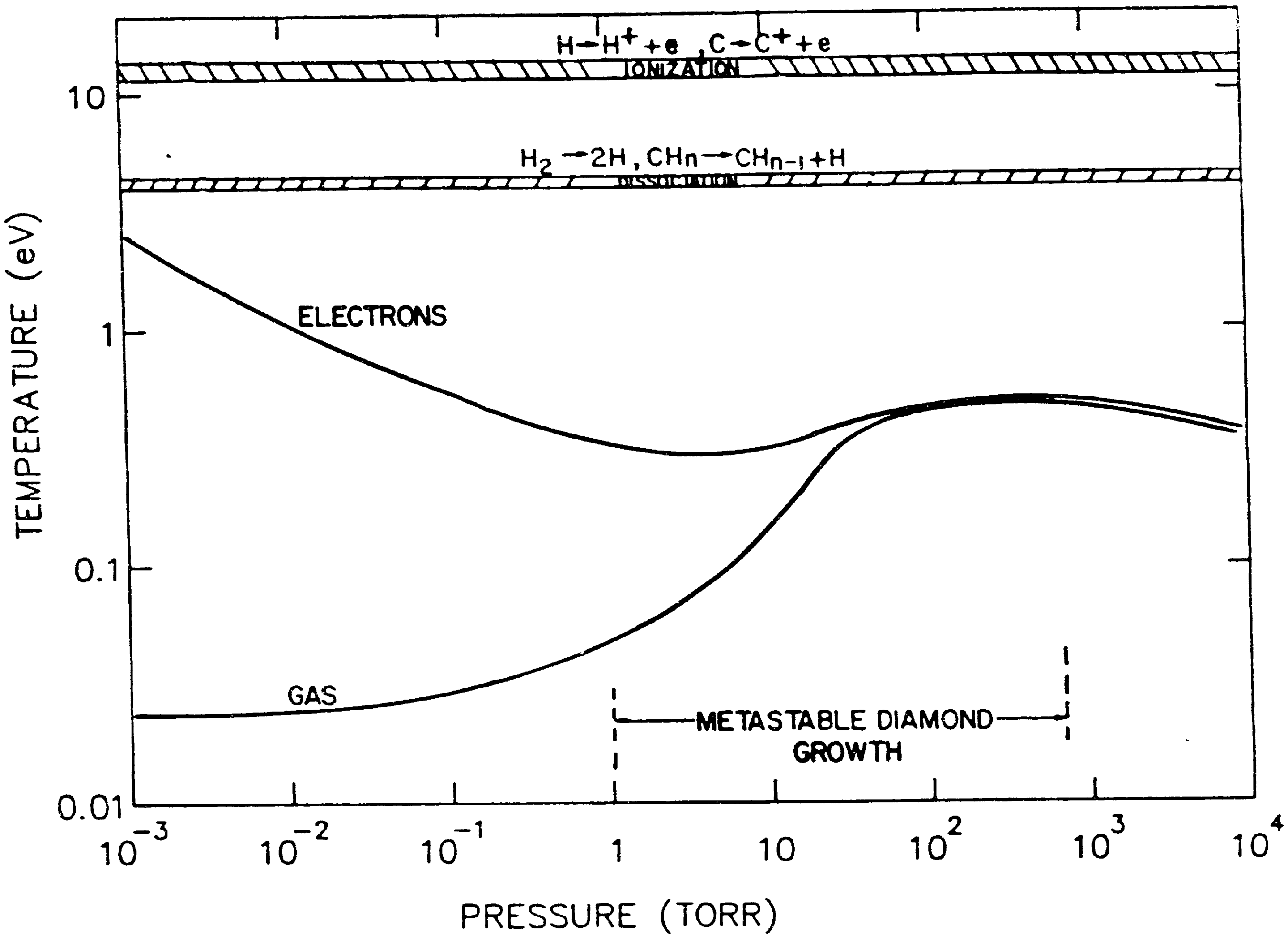
# DISSOCIATION OF GAS MOLECULES ON FILAMENT




CARBURIZATION OF TUNGSTEN WIRE

# ELECTRON ASSISTED CVD





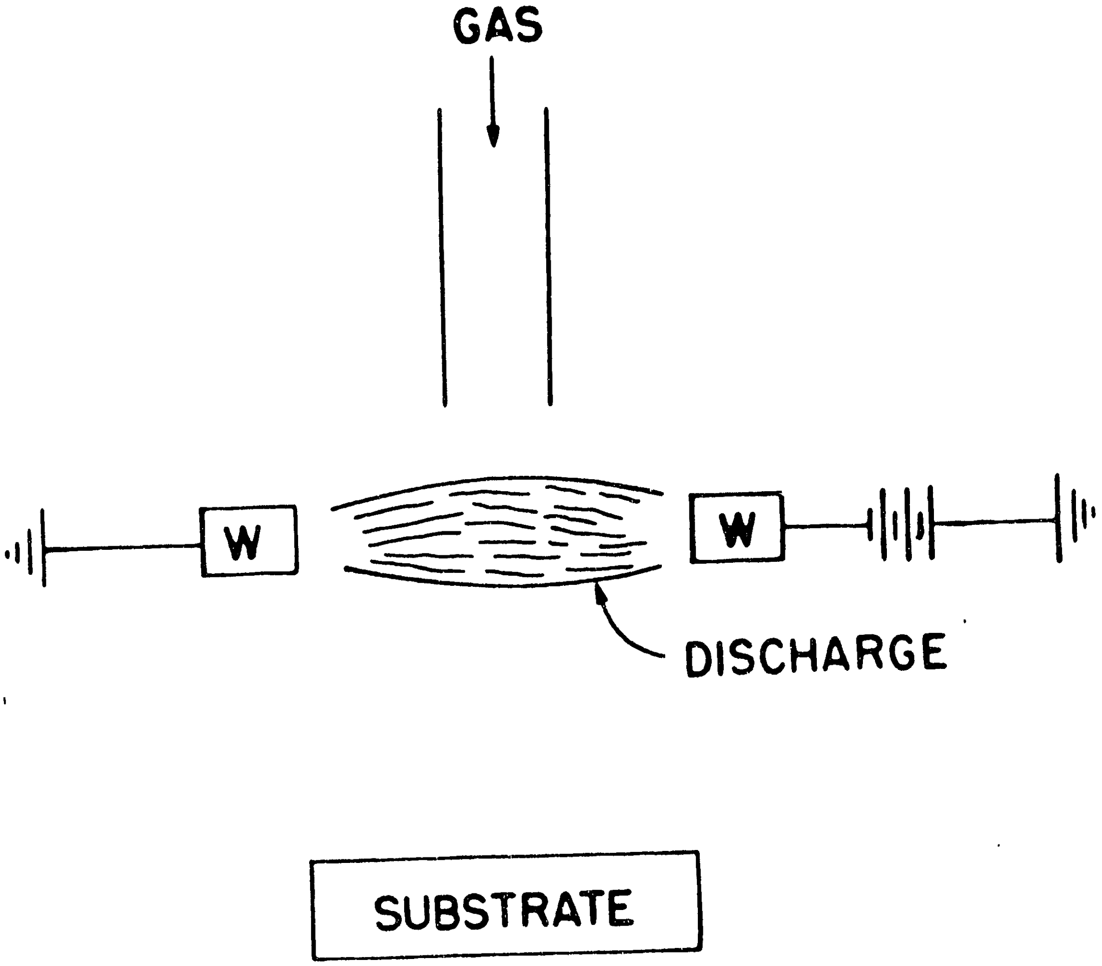
ELECTRON AND GAS TEMPERATURE VS PRESSURE IN A PLASMA

Fig 5

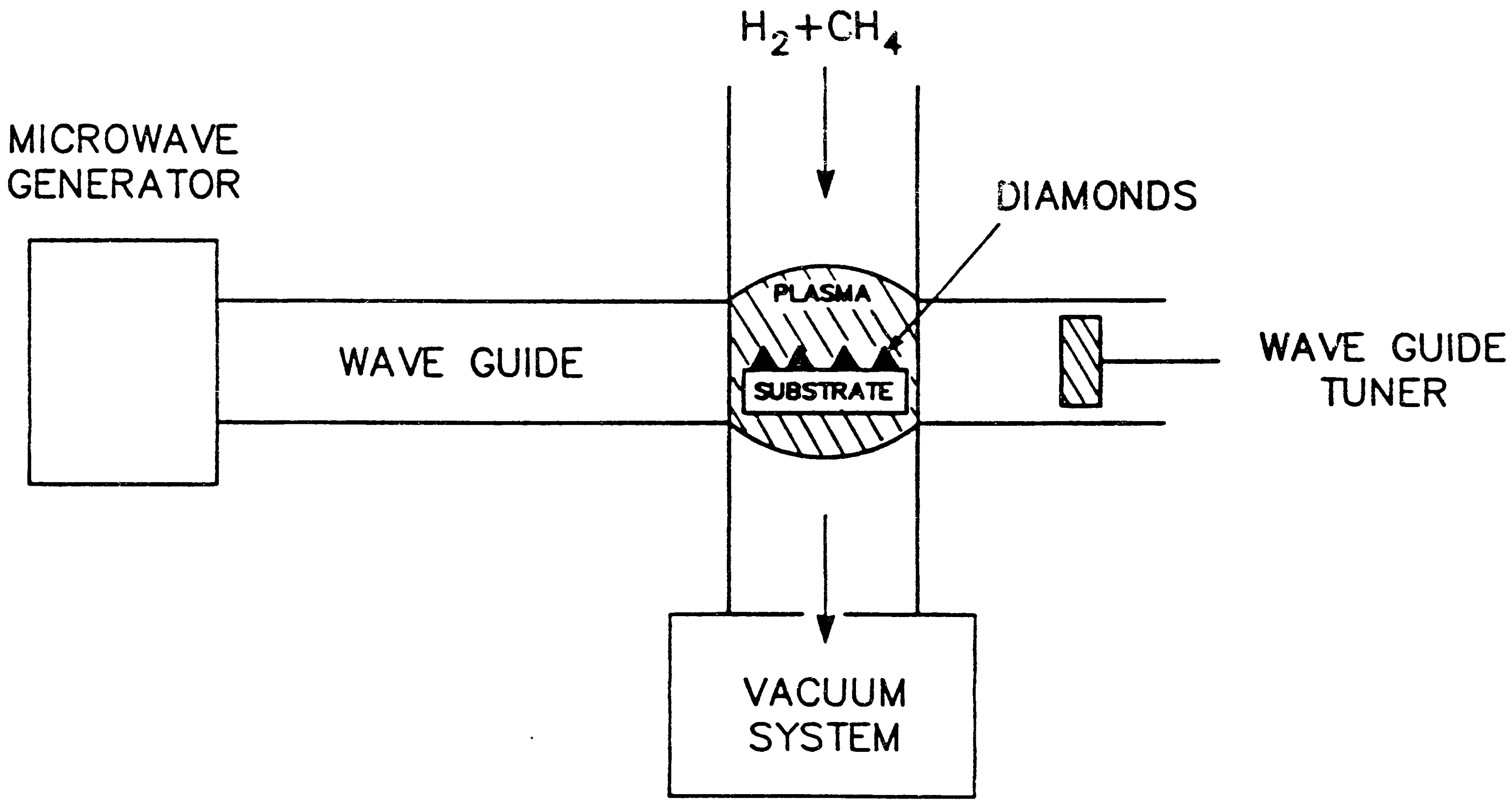
# PLASMA COMPOSITION

| SPECIES | RELATIVE CONCENTRATION | CONDENSABLE |
|---|---|---|
| MOLECULES<br>($H_2$, $CH_4$) | 10,000 | NO |
| NEUTRAL RADICALS<br>($H$, $CH_3$, $CH_2$, $CH$, ⋯) | 100 | YES |
| IONS<br>($H_2^+$, $CH_4^+$, $H^+$, ⋯) | 1 | YES |

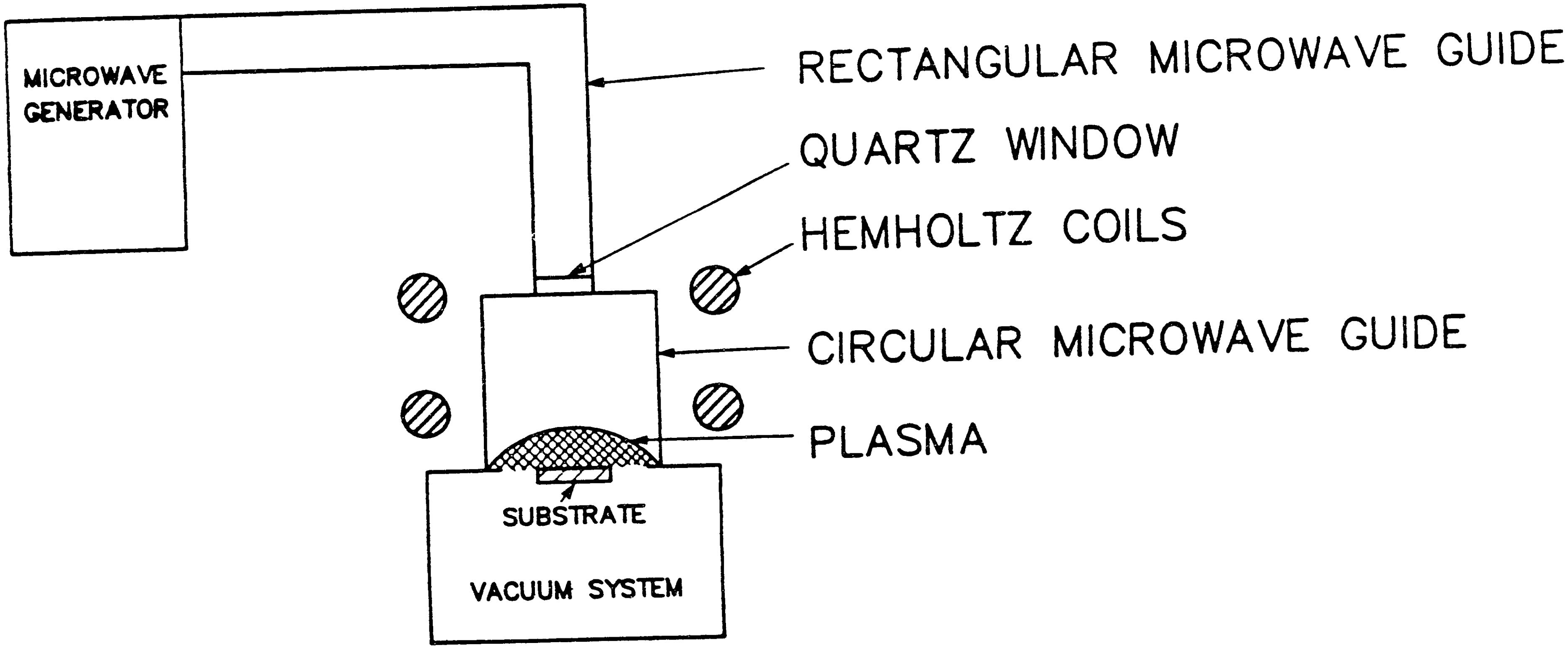
## ARC DISCHARGE



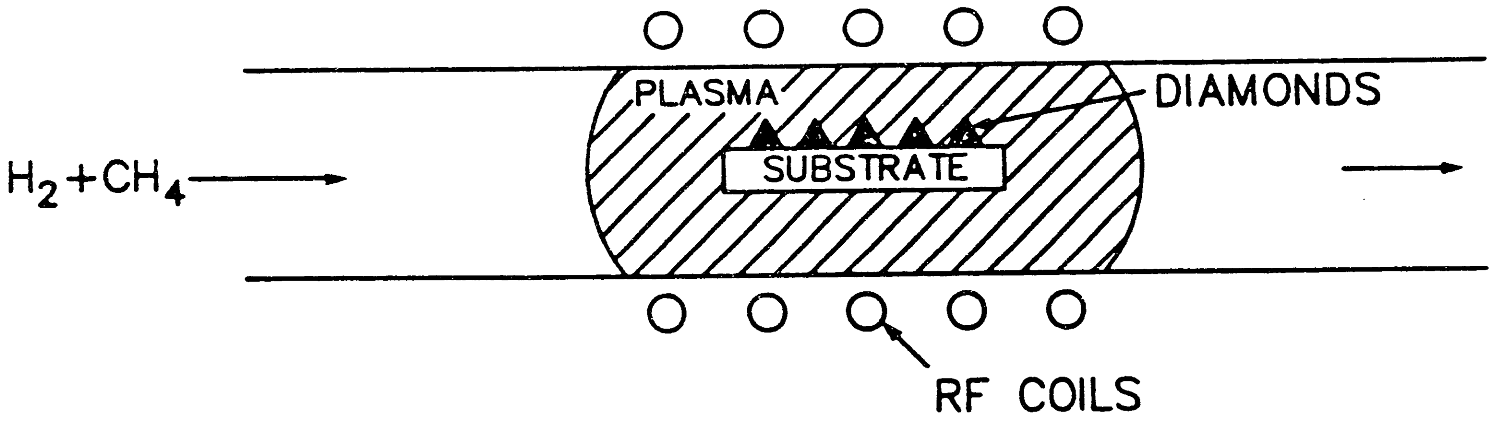
# MICROWAVE–ASSISTED DIAMOND CVD



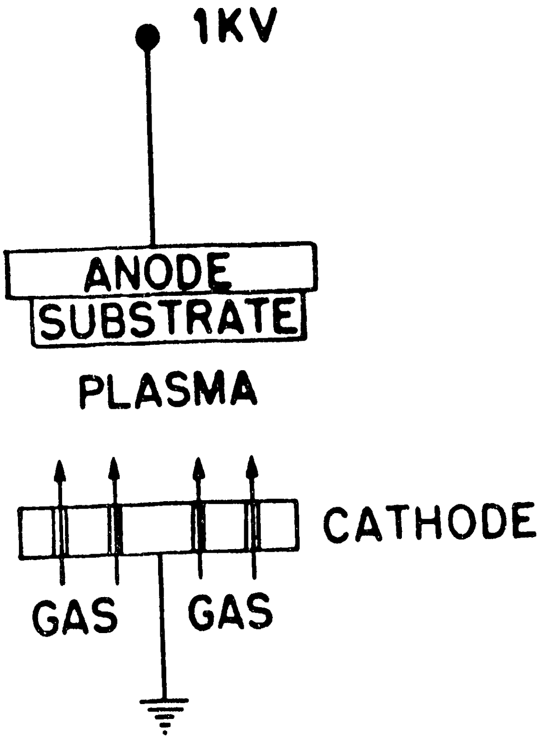
## ECR PCVD DIAMOND GROWTH



# RF – ASSISTED DIAMOND CVD



# DC PLASMA CVD



# RF THERMAL PLASMA

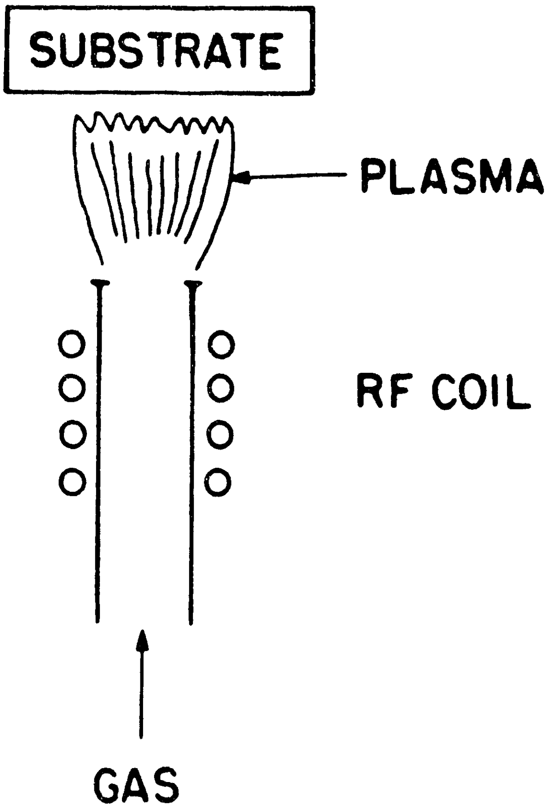
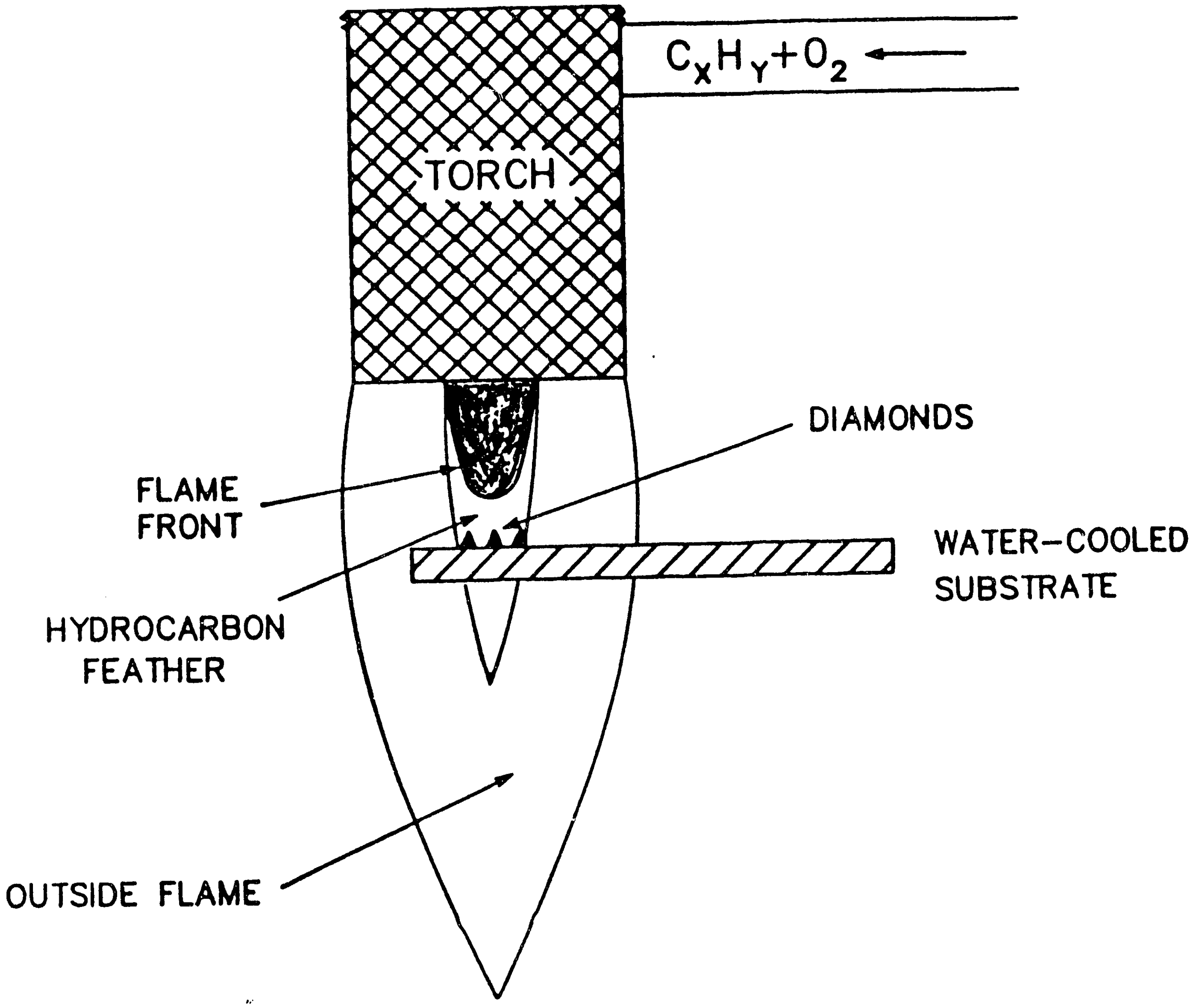


Fig 12

# FLAME DIAMONDS

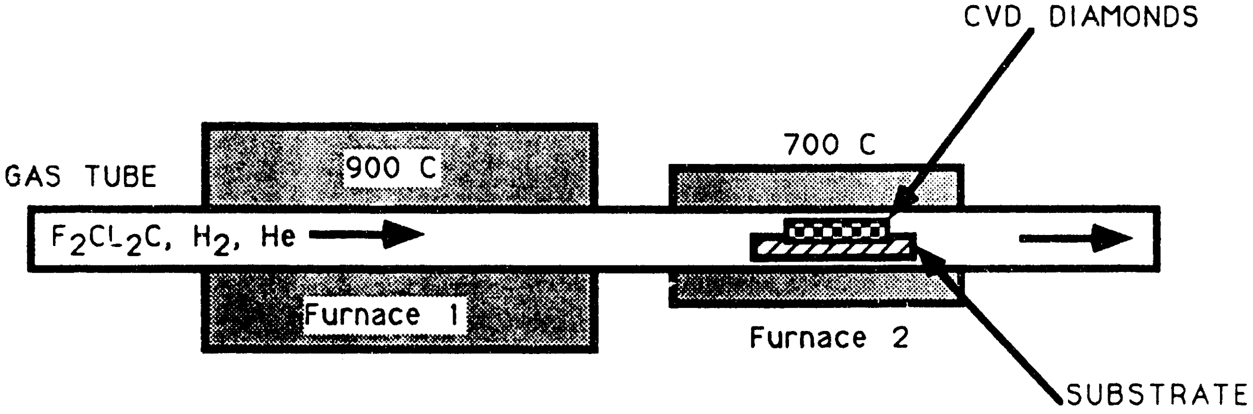


FLAME FRONT: $C+\frac{1}{2}O_2 \rightarrow CO$ (3000°C)

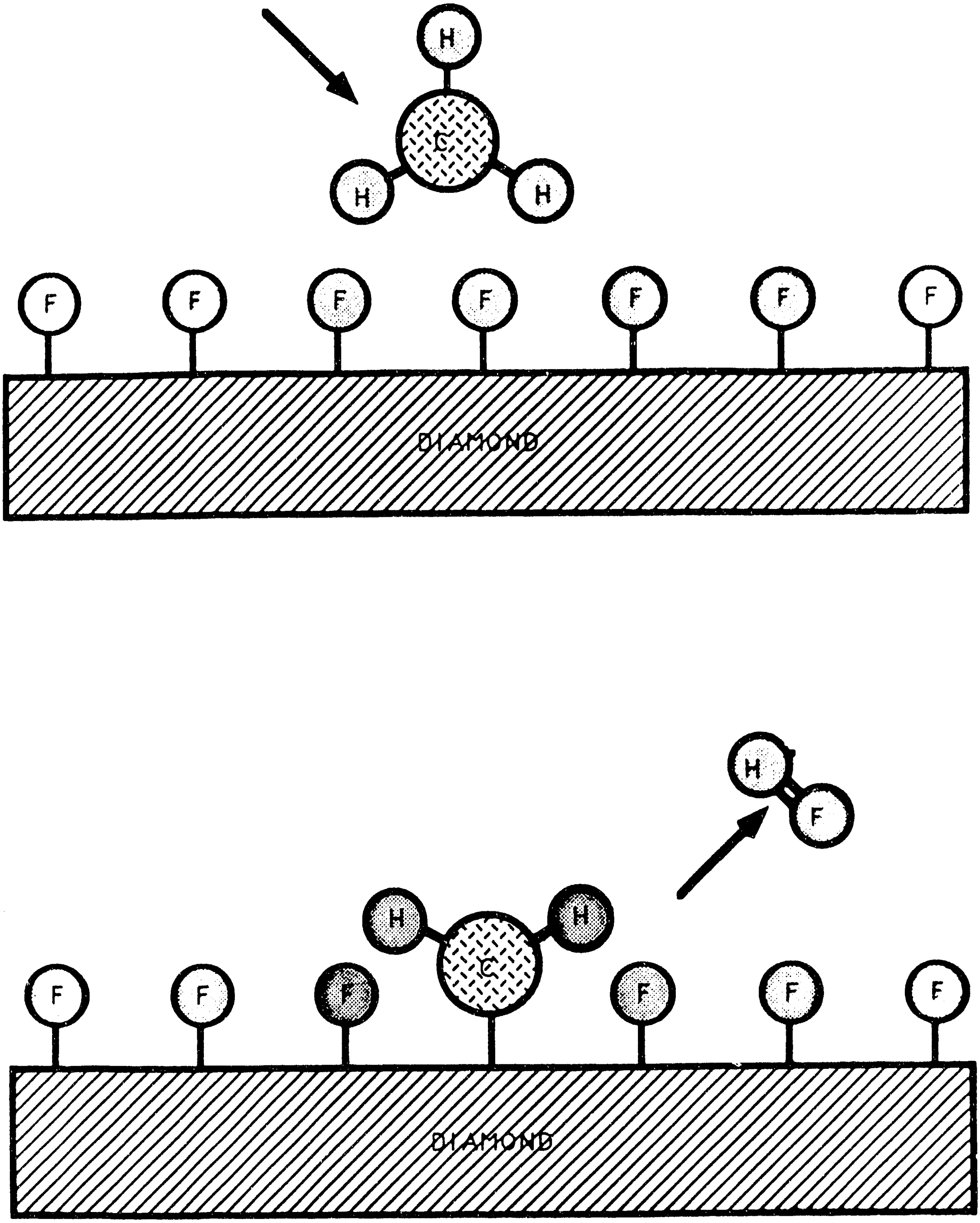
HYDROCARBON: $C+\frac{1}{2}O_2$ (EXTERNAL) $\rightarrow CO$

OUTSIDE FLAME: $CO+\frac{1}{2}O_2$ (EXTERNAL) $\rightarrow CO_2$

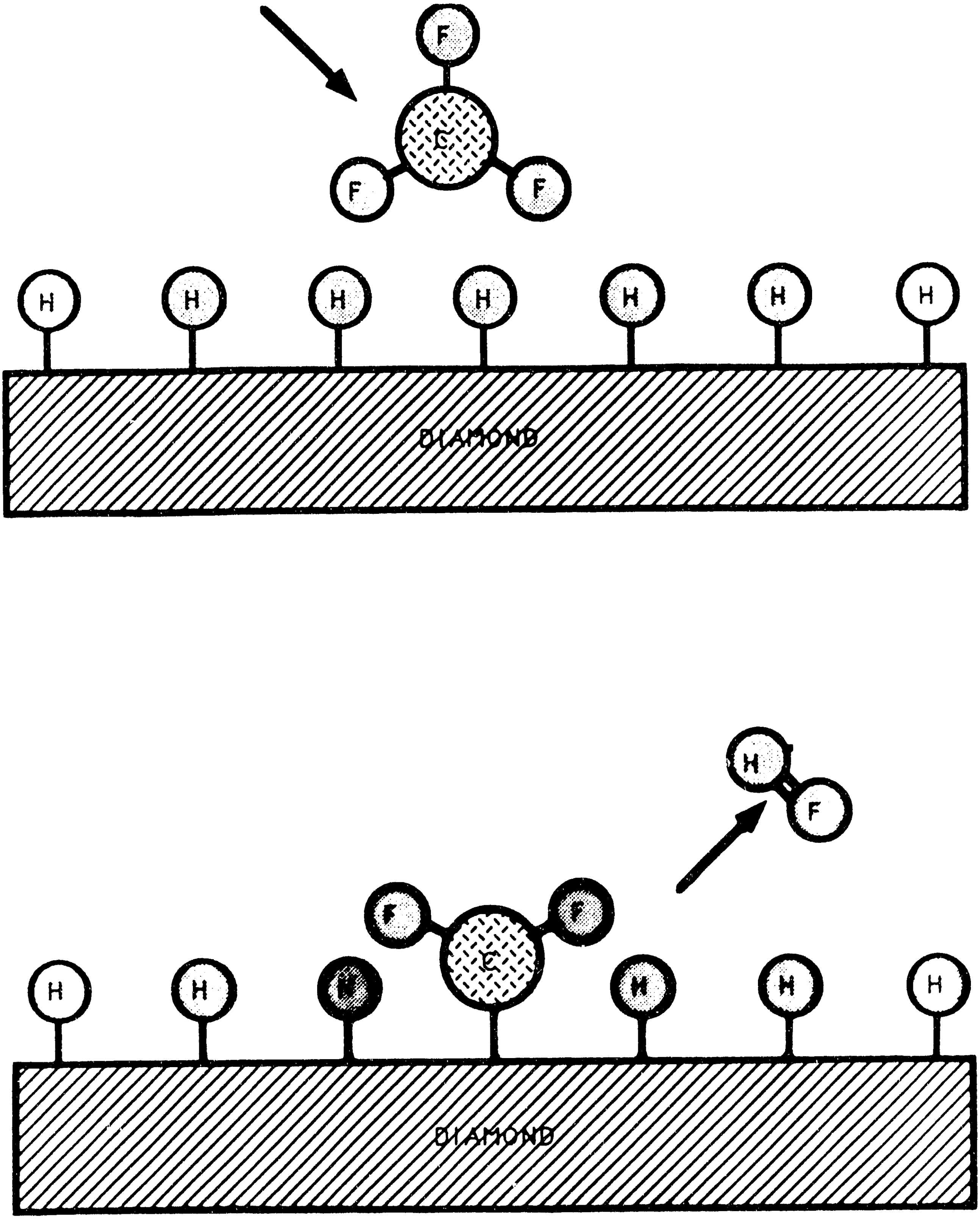
# HALOGEN-ASSISTED THERMAL GROWTH OF CVD DIAMOND



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

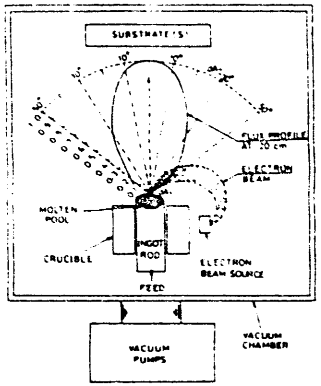
- Review/description of deposition processes
  - CVD
  - PVD
  - IBD/IAD
- Properties of IBD/IAD
- Tribological performance of IBD/IAD Coatings
- Issues

# Deposition Techniques

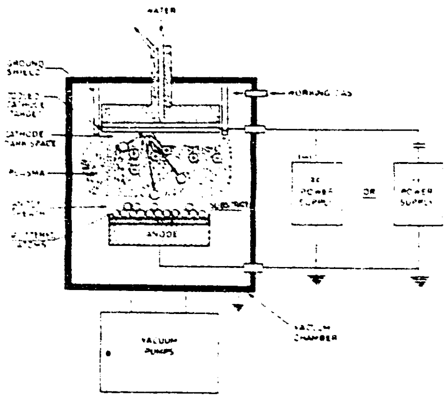
- CVD (e.g., HFCVD, PACVD, etc.)
- PVD (plasma sputtering, ion beam sputtering, evaporation, etc.)
- IBD (low–energy ion implantation)
- Hybrid processes (biased sputtering, IBAD, biased HFCVD, etc.)

# PVD Deposition Processes

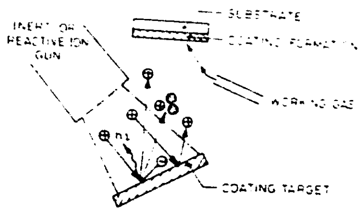
- Evaporation (e.g., electron beam evaporation)
- Cathodic arc discharge
- Sputtering
- Ion beam sputtering
- Laser evaporation



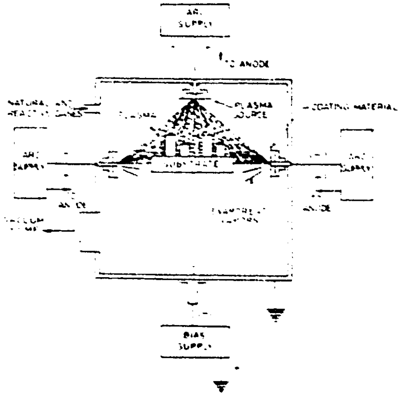
Electron Beam
Evaporation



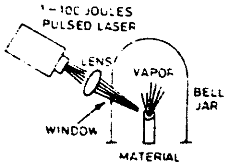
Plasma Sputtering



Ion–Beam Sputtering

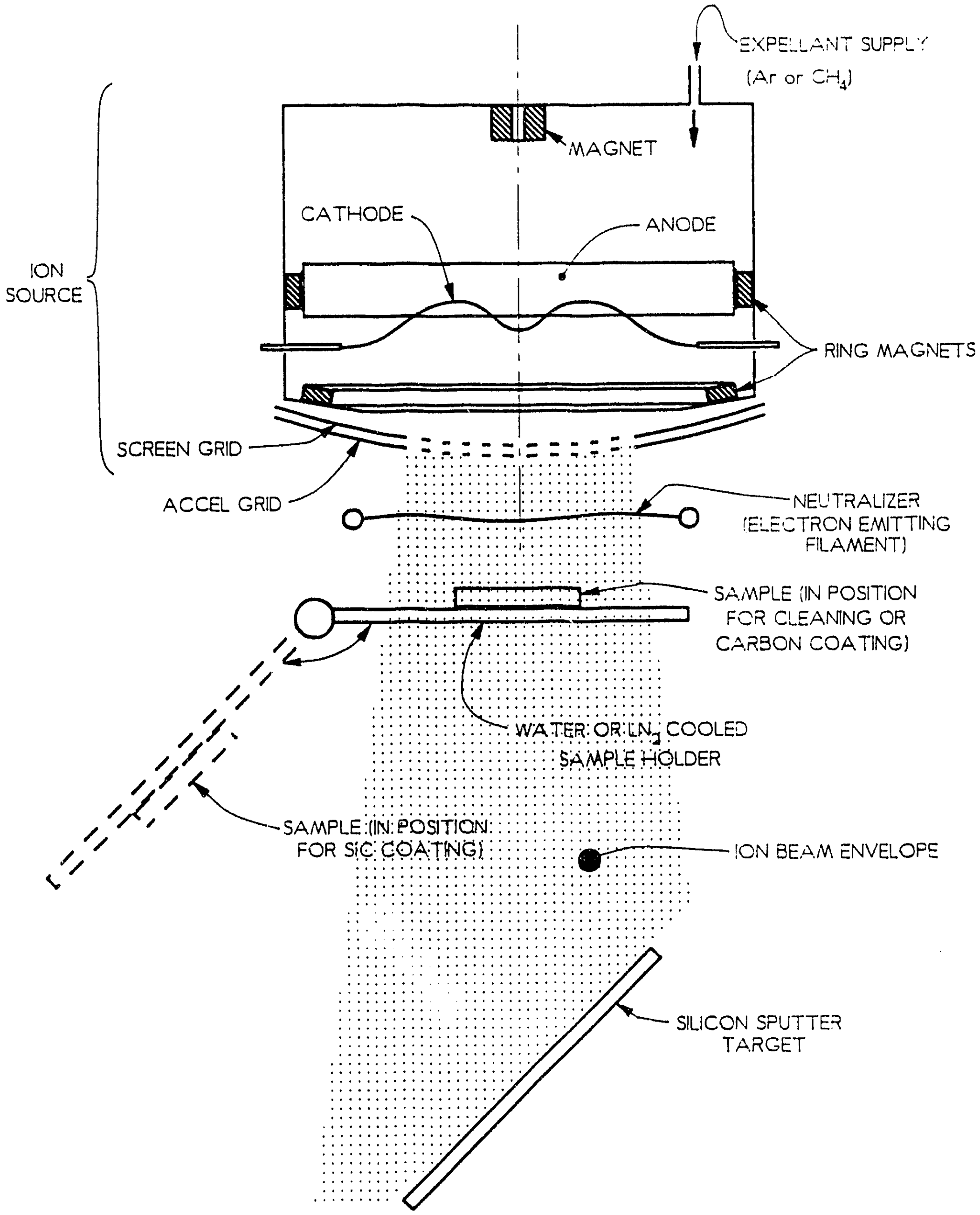


Cathodic Arc Deposition



Laser Evaporation

**DOE OTM Tribology Program**

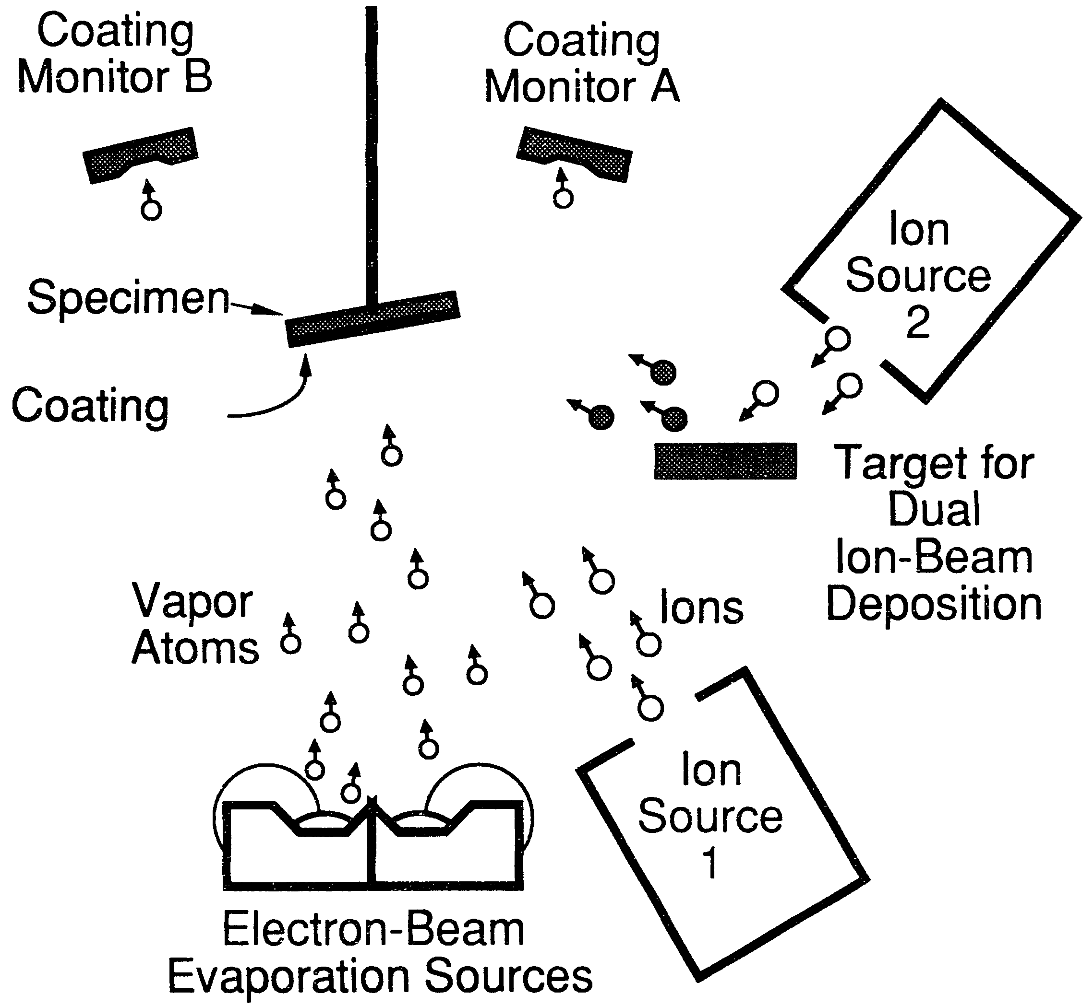


**Paul Wilbur:**
**Colorado State University**

**DOE OTM Tribology Program**

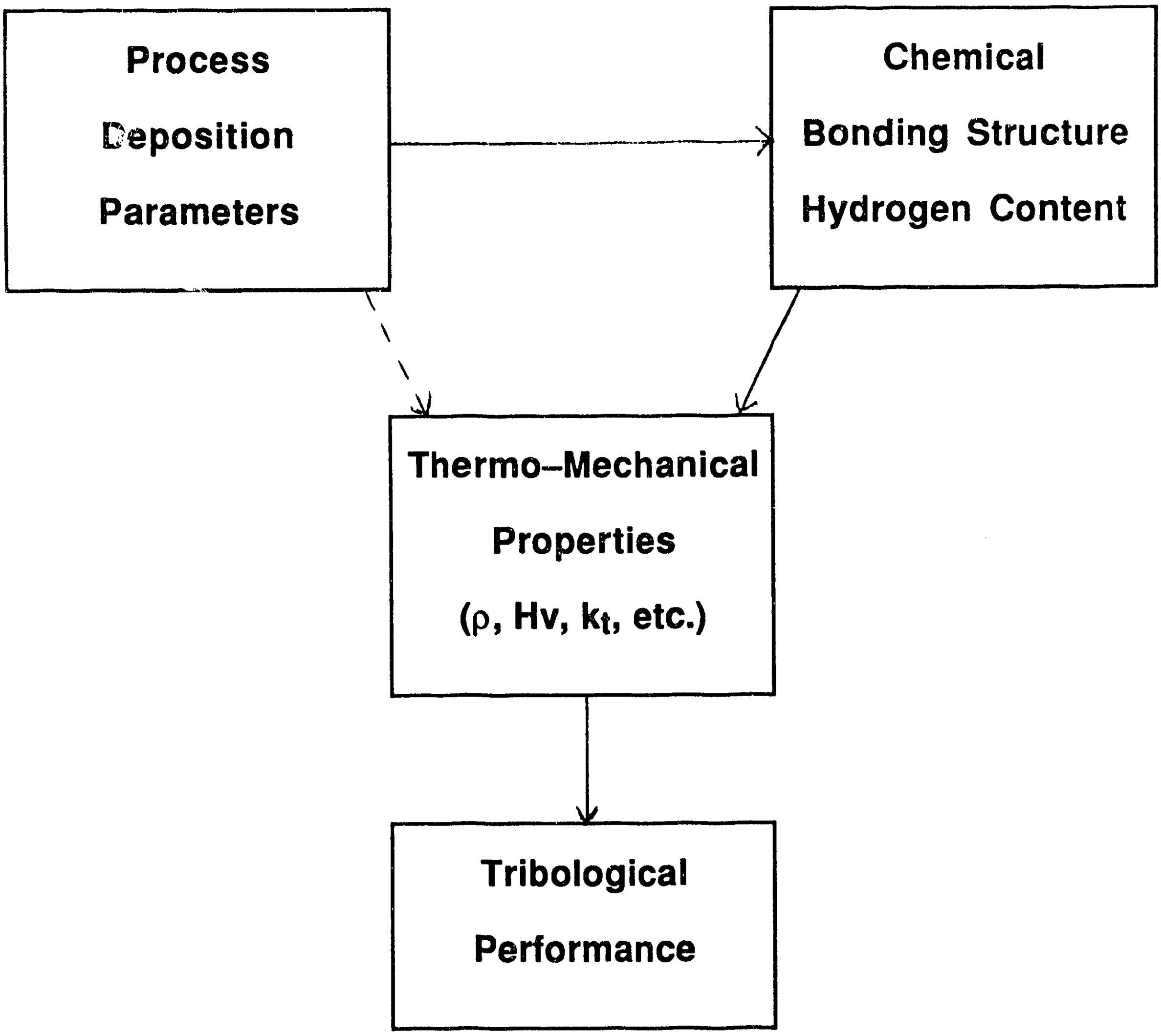
# Hybrid Process

- <u>Simultaneous</u>
  - Ion Beam Assisted Deposition
    - e–beam evaporation
    - ion–beam sputtering
  - Biased Sputtering
  - Biased PECVD (Chang)
  - Ion Plating (hollow cathode, laser)
- <u>Sequential</u>
  - Laser/HFCVD
  - IBS/IBD


Coating
Monitor B
Coating
Monitor A
Ion
Source
2
Specimen
Coating
Target for
Dual
Ion-Beam
Deposition
Vapor
Atoms
Ions
Ion
Source
1
Electron-Beam
Evaporation Sources

# Comparison of Typical Deposition Conditions

| Process | Carbon Source | Particle Energy (eV) | Substrate Temperature °C | Film Characteristics |
|---|---|---|---|---|
| CVD | Dilute hydrocarbon gas in hydrogen | 0.1–1 eV | Typical 800–1100°C (<500°C possible) | Polycrystalline diamond & DLC/DLHC |
| PVD | Solid carbon | 0.1–10 eV | R.T. and higher | DLC/DLHC |
| IBD | Gas ($CH_4$, $H_2$, etc.) (solid carbon) | 0.1–100 keV | R.T. and higher | DLC/DLHC |
| Hybrid | Gas solid | 0.1–10 keV | R.T. and higher | DLC/DLHC |



Process Deposition Parameters

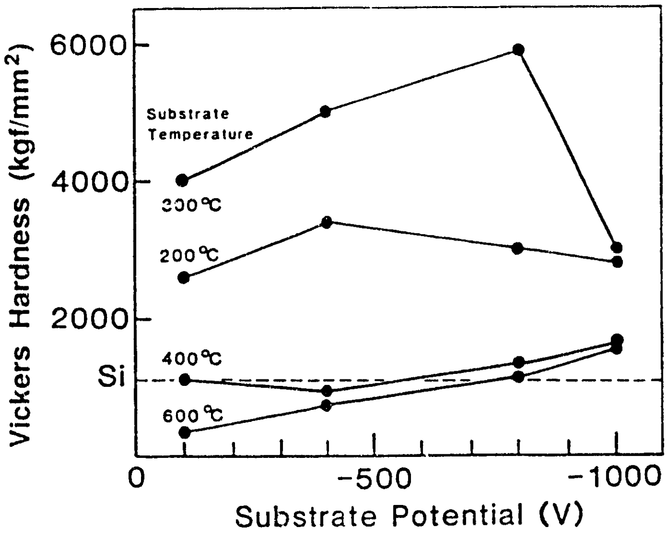
Chemical Bonding Structure Hydrogen Content

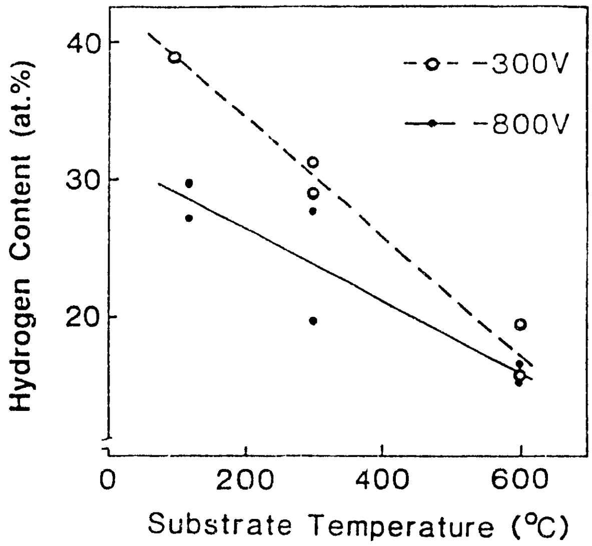
Thermo–Mechanical Properties ($\rho$, Hv, $k_t$, etc.)

Tribological Performance

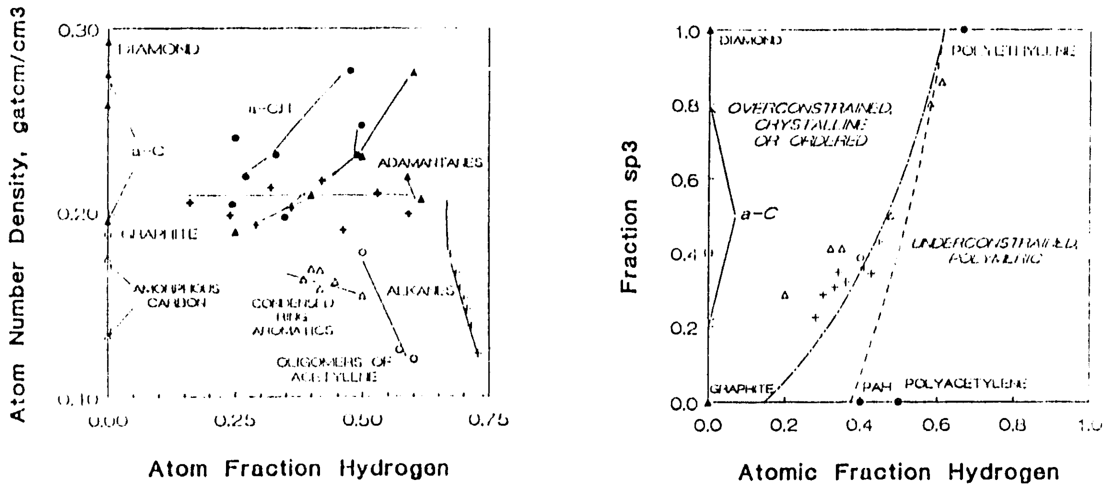
DOE OTM Tribology Program

# Effect of Process Process Parameters on DLHC Properties





**Okada et al.**

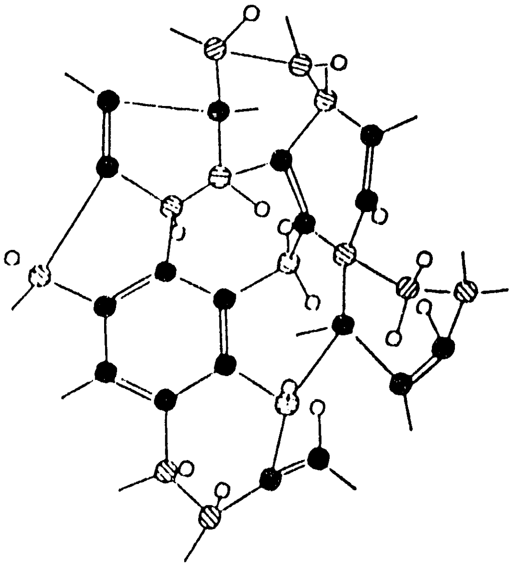


**(Angus)**

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

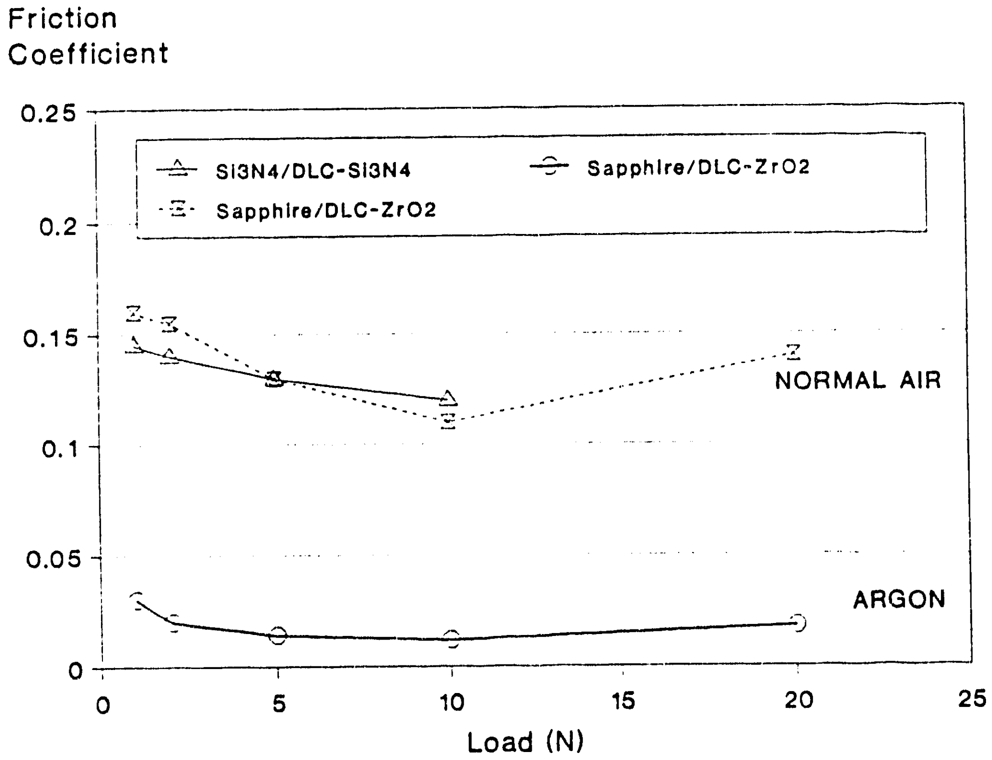
- amorphous (small crystallites)
- hydrogen content – $\rho$, $sp^3$ bonding

# Structure of Amorphous Carbon Films (Angus et al.)

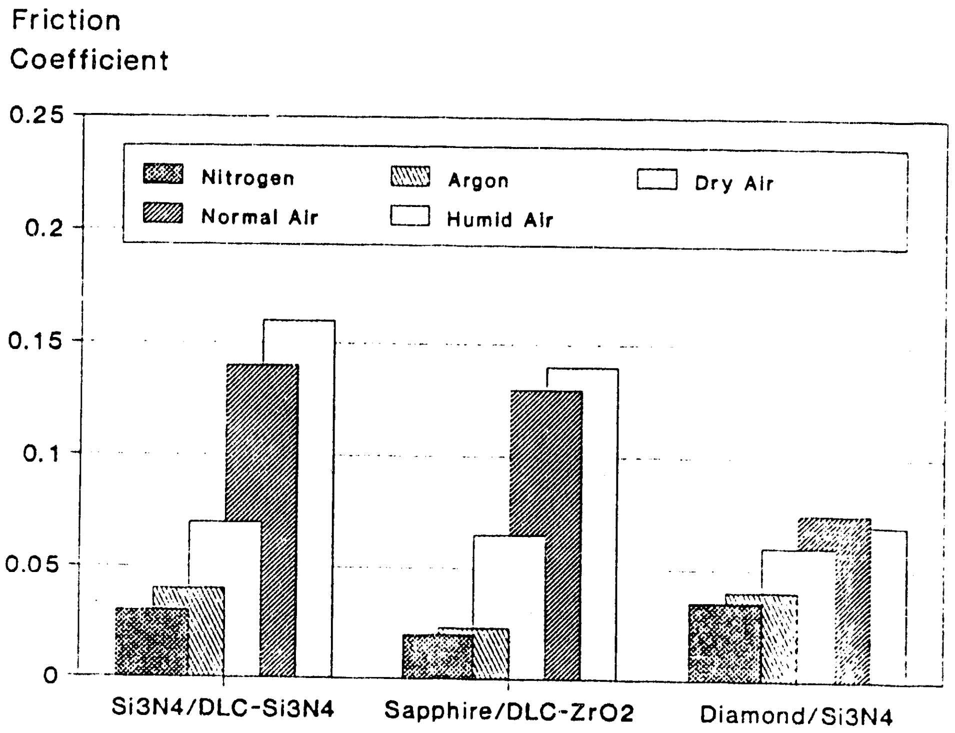


- Short range $sp^2/sp^3$ bonding
- No long–range order

# Friction Coefficient of DLHC Films on Ceramics (Erdemir, Wei, and Wilbur)

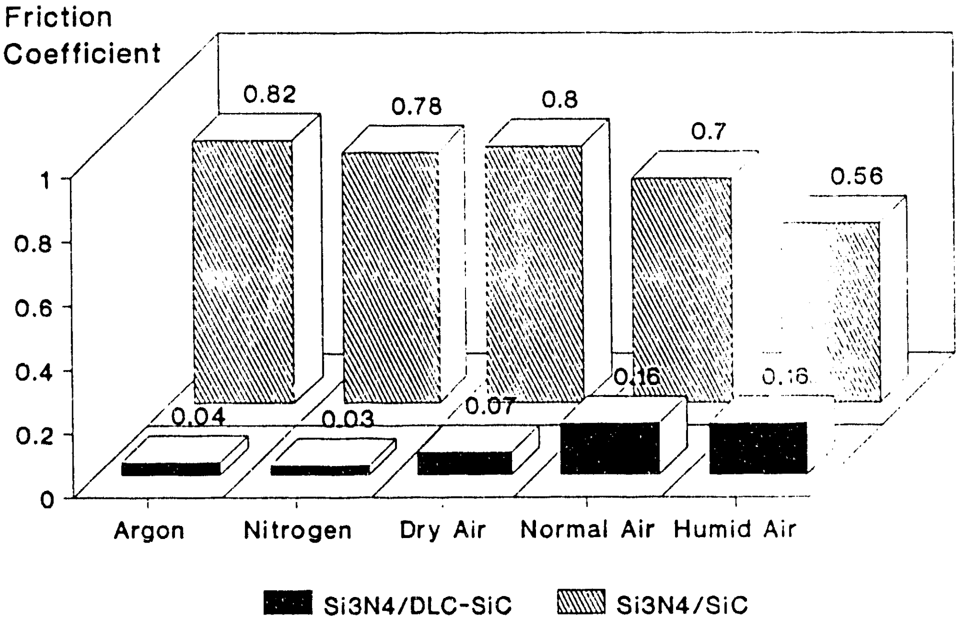


# Friction Coefficient of DLHC Films on Ceramics (Erdemir, Wei, and Wilbur)

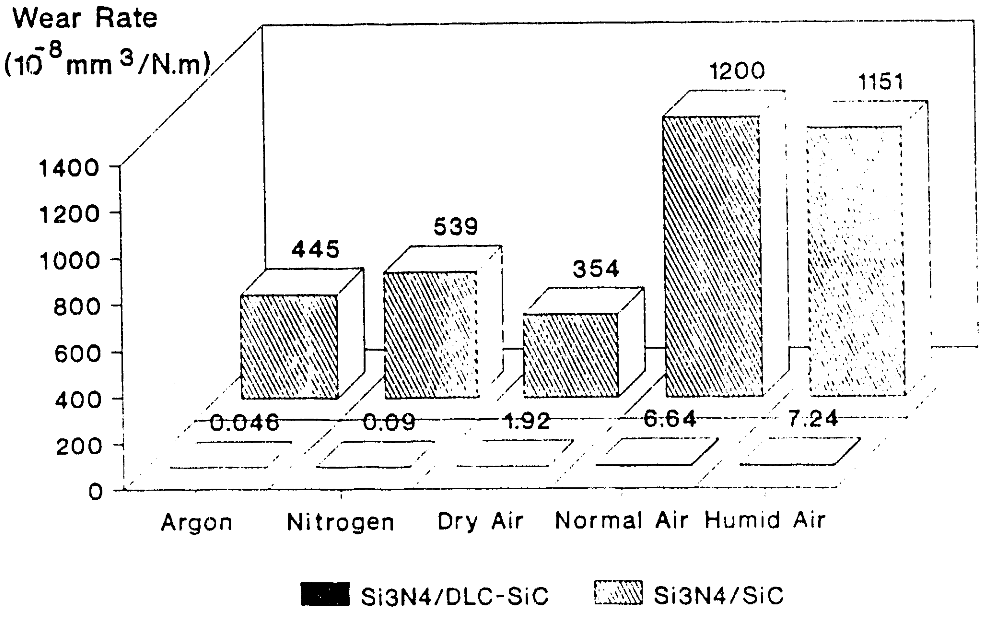


**DOE OTM Tribology Program**

# Friction and Wear of DLHC Films on Ceramics (Erdemir, Wei, and Wilbur)

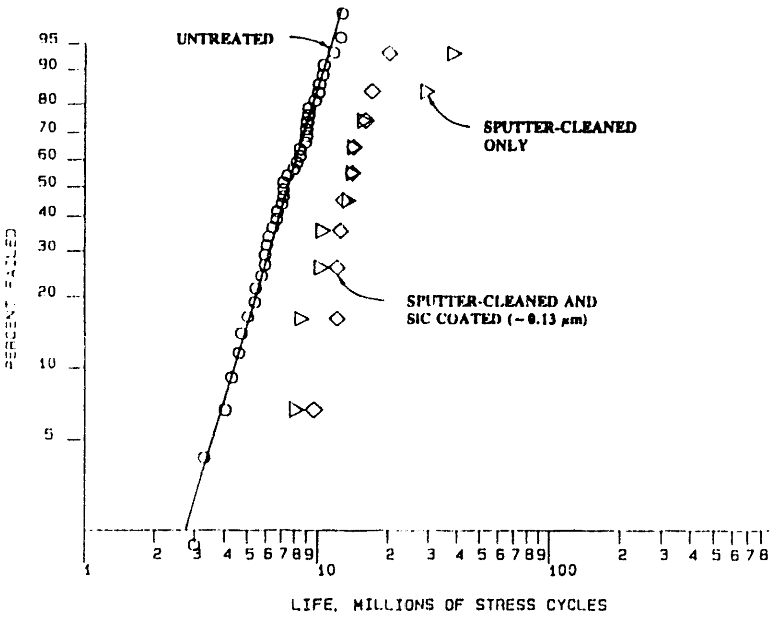


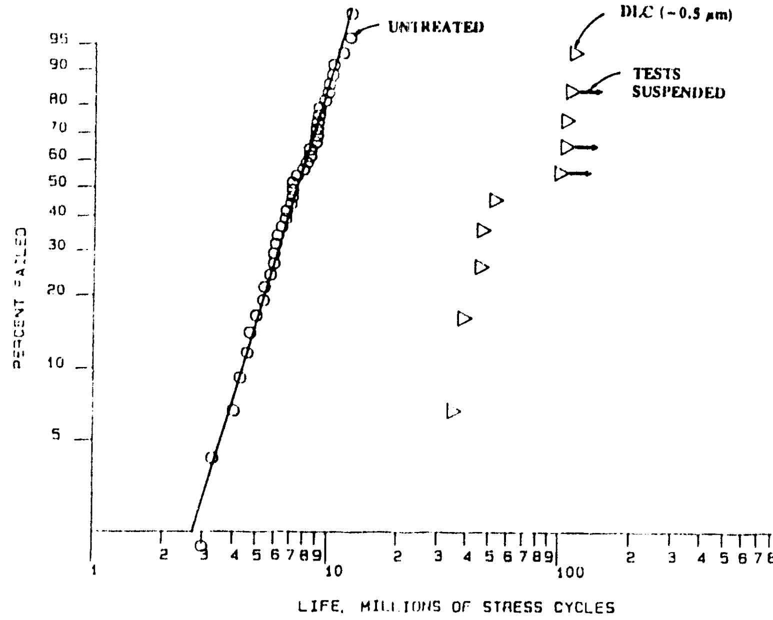
(a)



(b)

# Rolling Contact Fatigue Tests of Thin DLC Films on M50 Steel (Wilbur, et al.)





# 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
Argonne National Lab

J.T. Glass
Materials Sci. & Eng.
North Carolina State Univ.

# Acknowledgements

## NCSU Diamond Group:

M. Ma
M. McClure
B. Stoner
T. Tachibana
D. Tucker
M. Veil
J. von Windheim
X. H. Wang
B. Williams *
S. Wolter
W. Zhu
F. Sivaslian

## Collaborators:

K. Kobashi
R. Nemanich
K. Bachmann
R. Davis
R. Trew
Y. VanderWeide
L. Bergman
K. Turner
A. Freedman
H. Das

Sponsorship from SDIO/IST through the Office of Naval Research, MITI/NEDO, Kobe Steel, Ltd., Oak Ridge Associated Universities SHaRE Program (DOE) is gratefully acknowledged. Other sponsors include NSF, ARO, and Aerodyne.

* Current Employer: GE Superabrasives

# Outline

Introduction

Raman Spectroscopy

SEM

TEM

Surface Analysis

Comparison of Techniques

In-vacuo Analysis

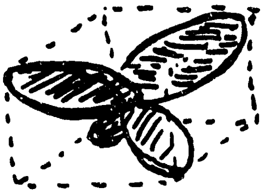
In-situ Analysis

Summary

NORTH CAROLINA STATE UNIVERSITY

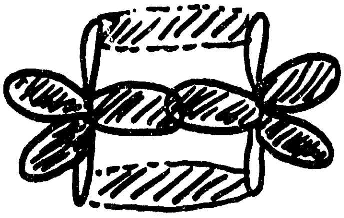
# Carbon Bonding

C — C
$(sp^3)$



$(1s^2)$ $\underline{2s^1p^3}$ $(4\sigma$'s$)$
Diamond
Tetrahedral

C = C
$(sp^2)$



$$\begin{array}{ccc}(1s^2) & 2p^1 & 2sp^2 \\ & \Uparrow & \Uparrow \\ & 1\pi & 3\sigma\text{'s}\end{array}$$

Graphitic
Planar

C ≡ C
$(sp^1)$

$$\begin{array}{ccc}(1s^2) & 2p^2 & 2sp^1 \\ & \Uparrow & \Uparrow \\ & 2\pi & 2\sigma\text{'s}\end{array}$$

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 Difraction

## C. Bonding (sp$^3$, tetrahedral)

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

# II. Defects in Diamond Films

## A. Scanning Electron Microscopy

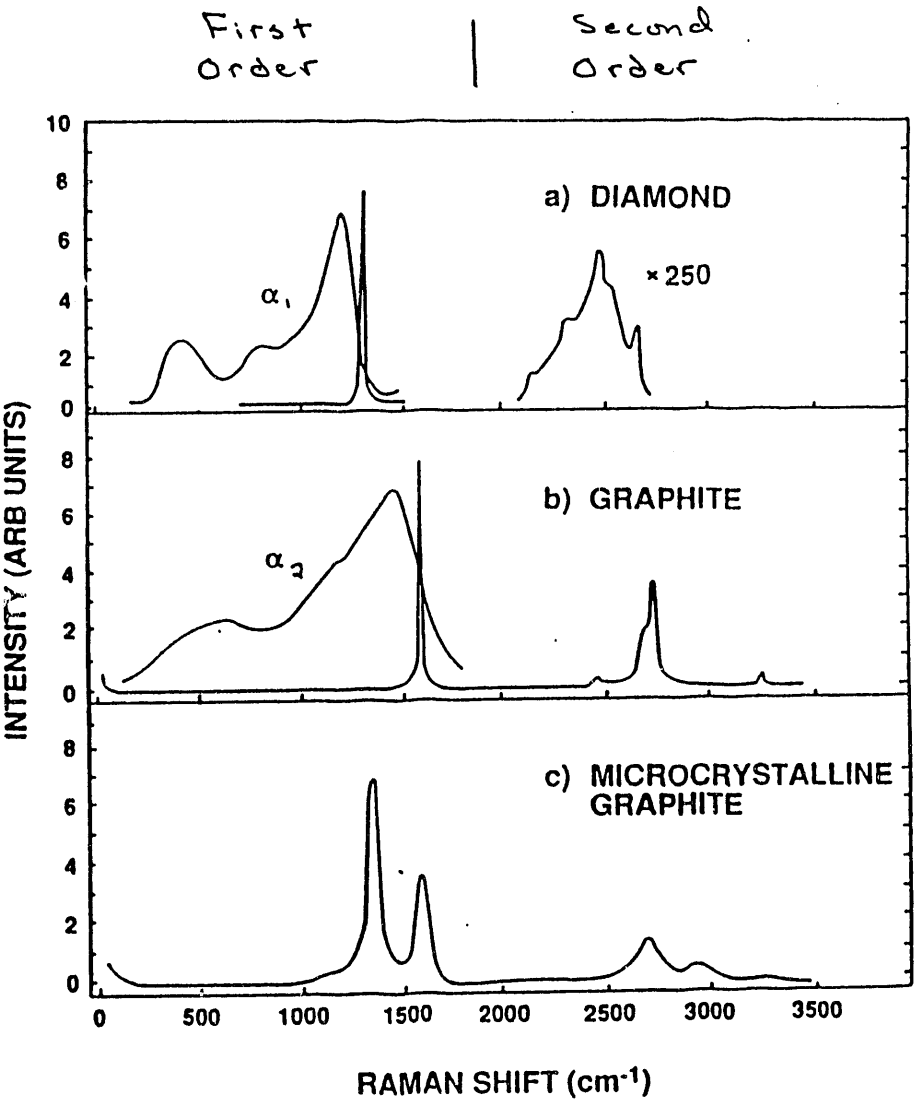
Grain Boundaries
Particle Morphology
Secondary Nucleation

## B. Transmission Electron Microscopy

Dislocations
Stacking Faults
Twins
Grain Boundaries

## C. Electrical Measurements

Impurities
Electrically Active Defects



(Nemanich, et al. (1988))

1332 $cm^{-1}$ - primary 1st order diamond peak

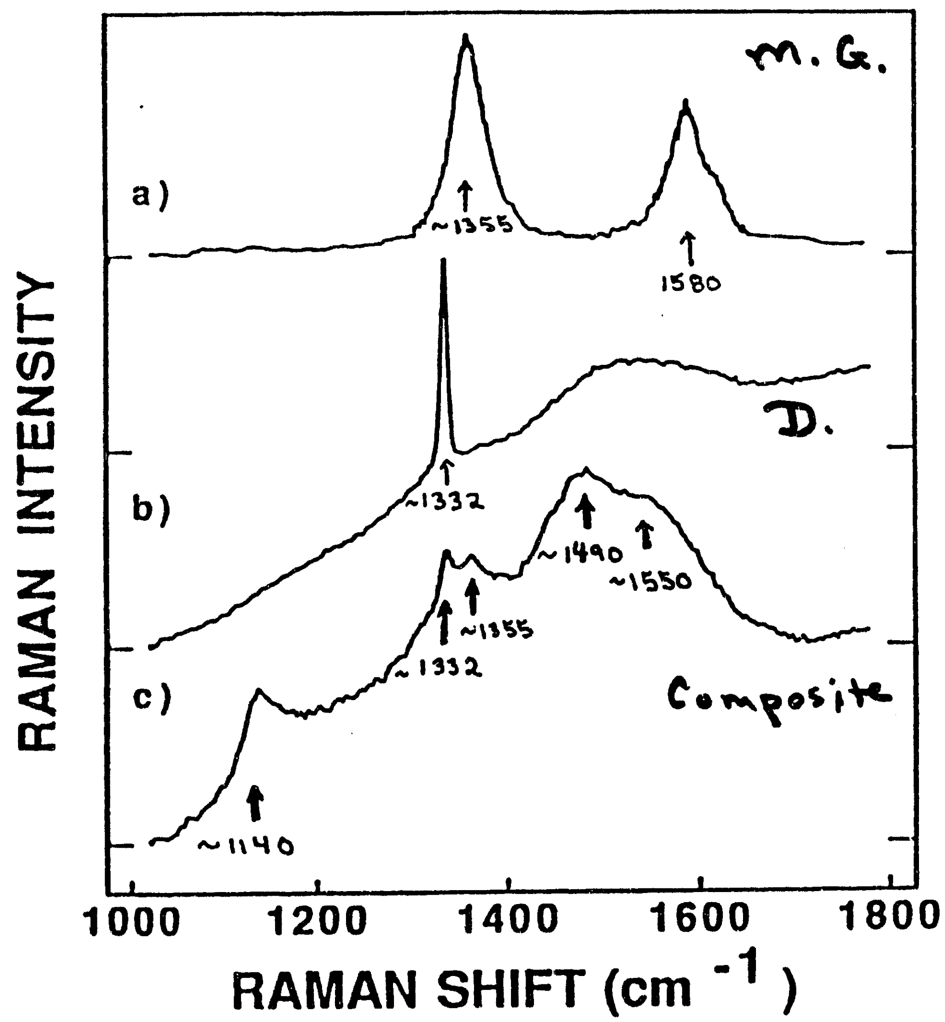
1580 $cm^{-1}$ - primary 1st order graphite peak

1355 $cm^{-1}$ and 1590 $cm^{-1}$ - primary, 1st 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" ⇒ 3-fold coordinated, $sp^2$ bonded
carbon with no long range order
Amorphous "diamond" ⇒ 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 1322cm$^{-1}$ is indicative of crystalline diamond while features between 1350 and 1600cm$^{-1}$ are attributed to sp$^2$ bonded carbon. (Shroder (1988)).

1332 cm$^{-1}$ – Diamond

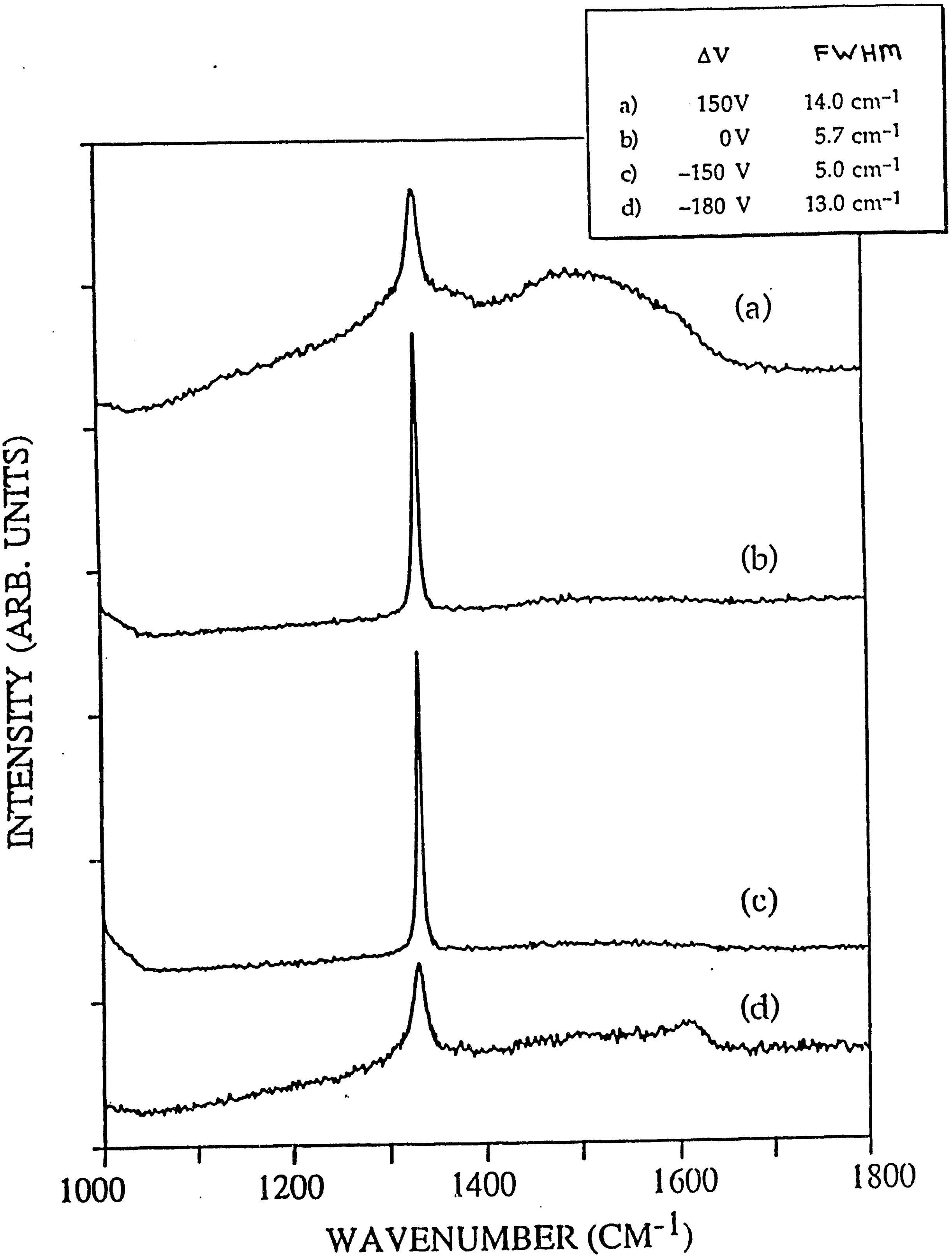
1355 & 1580 cm$^{-1}$ – Microcrystalline Graphite

1490 cm$^{-1}$ - Disordered (amorphous) Graphite

1550 cm$^{-1}$ - Downshifted Microcrystalline Graphite

1140 cm$^{-1}$ - Amorphous Diamond (?)

Note ; $I_G \approx 50 I_D$



Raman spectra of diamond thin films grown under different biasing conditions. Appl. Phys. Lett. 56 (7), 12 February 1990.

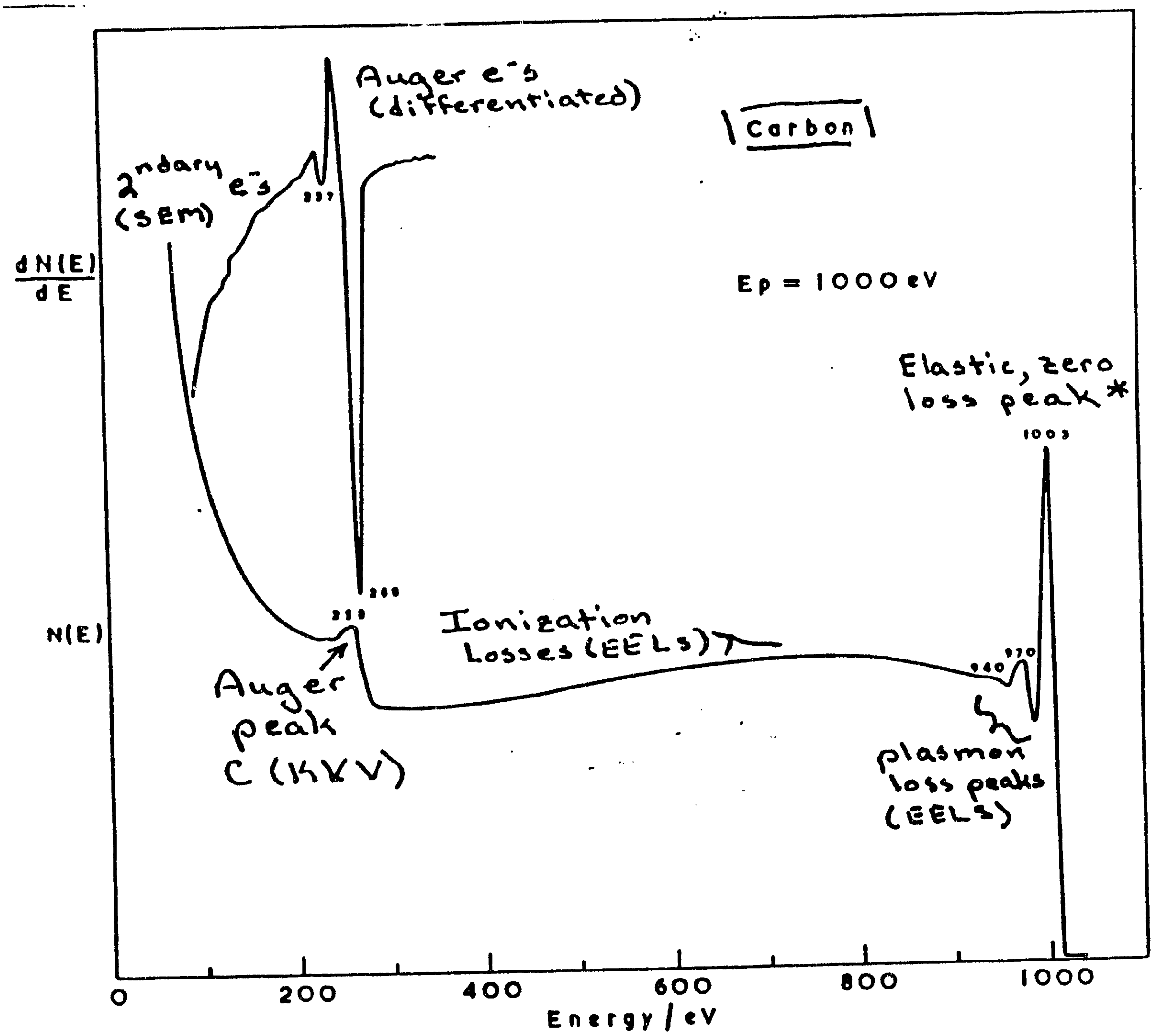
# Electron Spectroscopies

A. Auger Electron Spectroscopy

B. X-ray Photoelectron Spectroscopy

C. Electron Energy Loss Spectroscopy

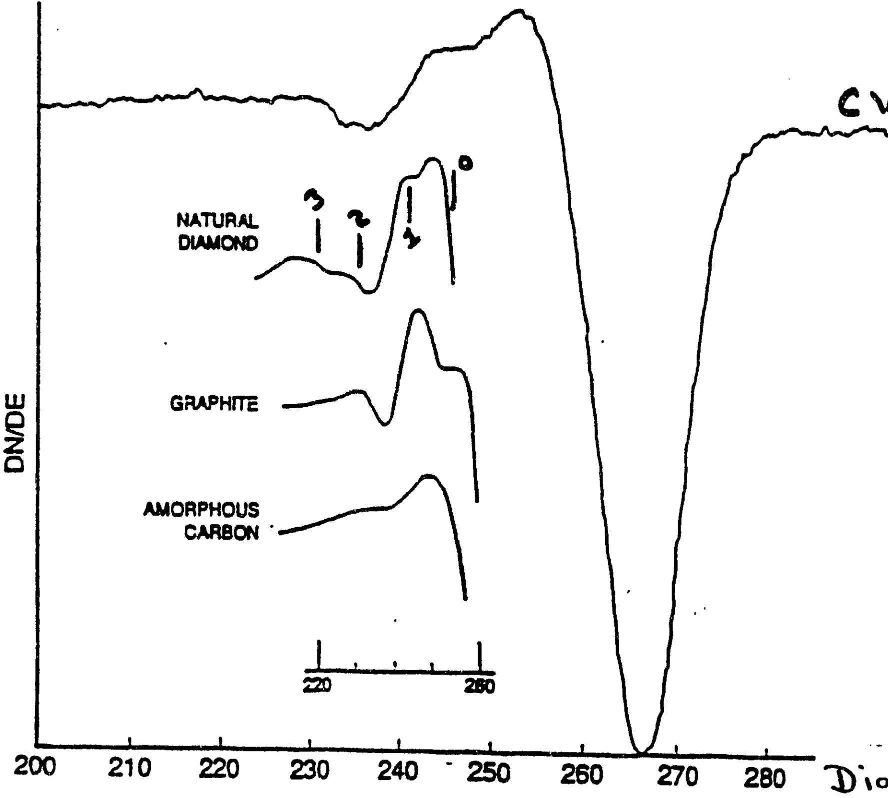
33



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

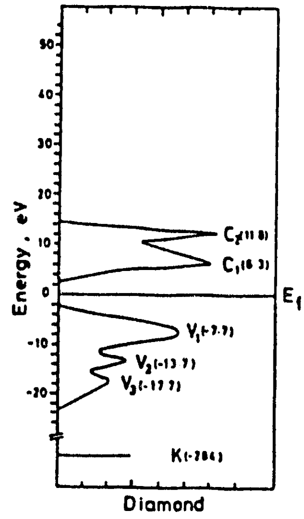
* contains diffraction information

Narrow window AES scan about the C (K.V.V) peak showing fine structure



KINETIC ENERGY, eV

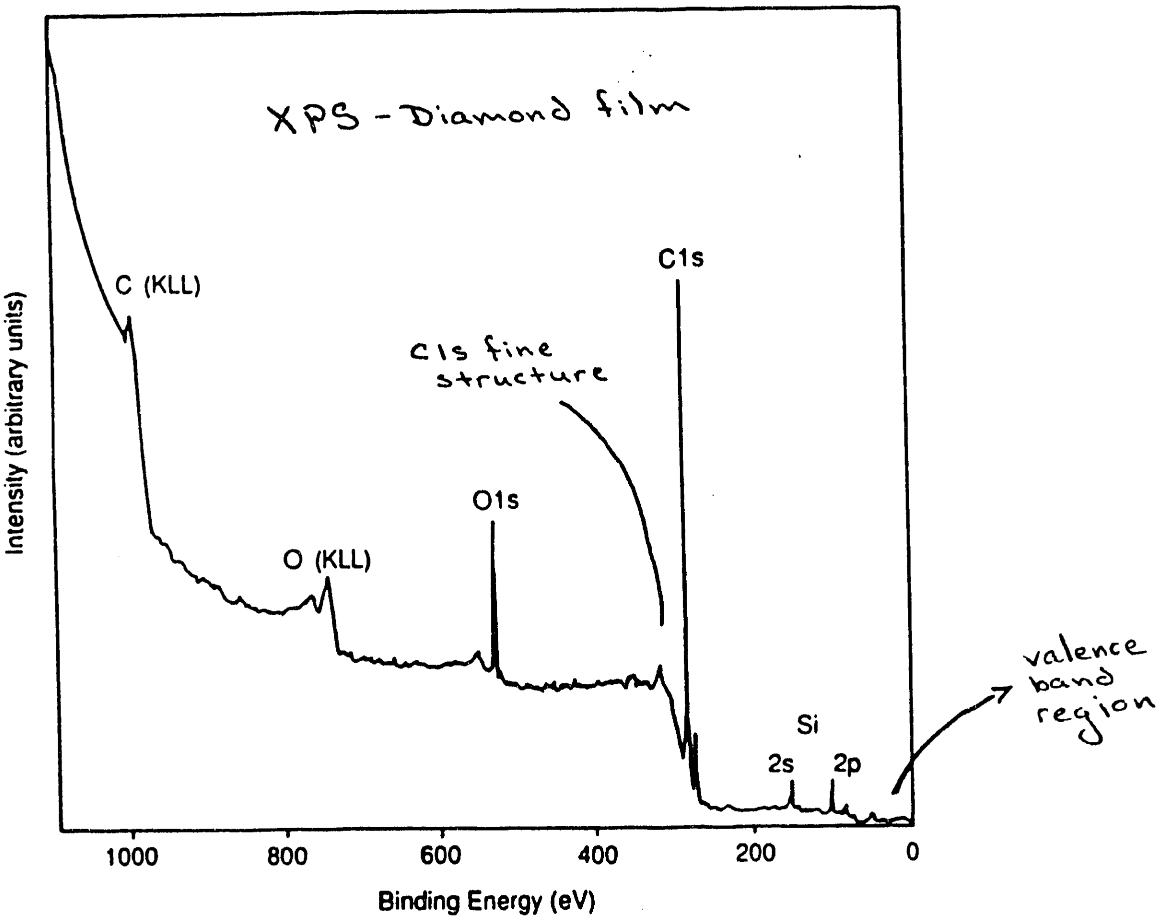
(Williams and Glass (1988))



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

| Diamond (Bulk) | $A_0 \pm 0.5$ | $A_1 \pm 1$ | $A_2 \pm 1$ | $A_3 \pm 1$ |
|---|---|---|---|---|
| Peak energy [a] | 268 | 256 | 240 | 230 |
| Peak position relative to $A_0$ | | 12 | 28 | 38 |
| Calculated energies (B.S.) | 269 | 256 | 245 | 235 |
| Identification | $(KV_1V_1)$ | $(KV_2V_2)$ | $(A_0 - \hbar\omega_s)$ | $(A_0 - \hbar\omega_p)$ |
| Calculated energies [19] (I.C.) | 266 | 252 | 243 | |
| Identification | $(^1D_2)$ | $(^1P_1)$ | $(^1S_0)$ | |
| Graphite | | | | |
| Peak energy [a] | 268 | 255 | 241 | |
| Peak position relative to $A_0$ | | 14 | 27 | |
| Other [11] | 270 | 253 | 239 | |
| Amorphous-carbon | | | | |
| Peak energy [a] | 268 | | 243 | |
| Peak position relative to $A_0$ | | | 25 | |

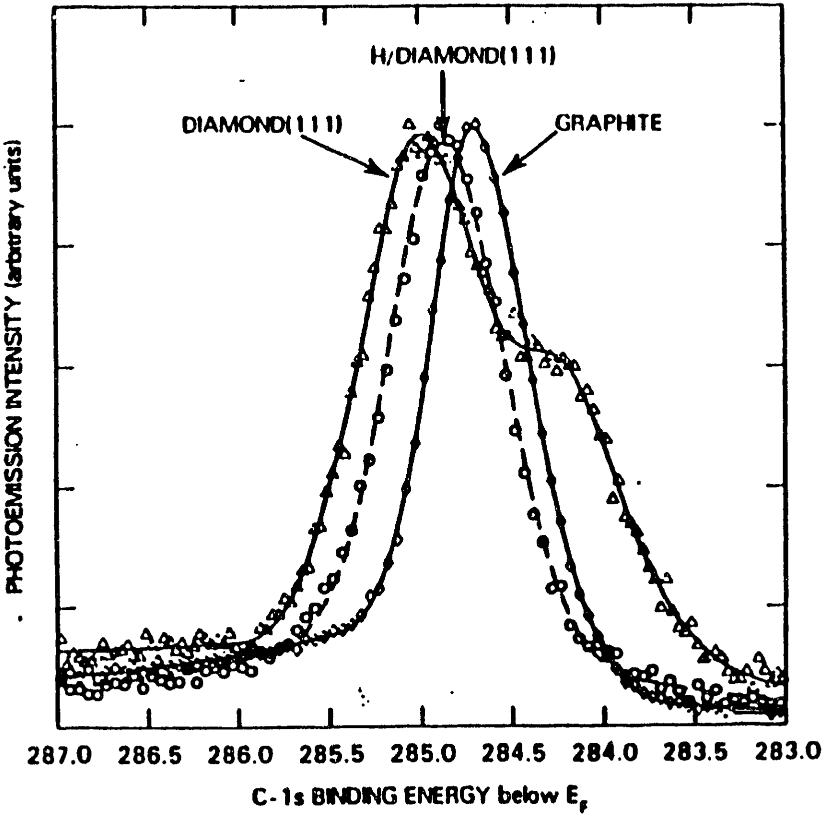
(Lurie and Wilson (1977))



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

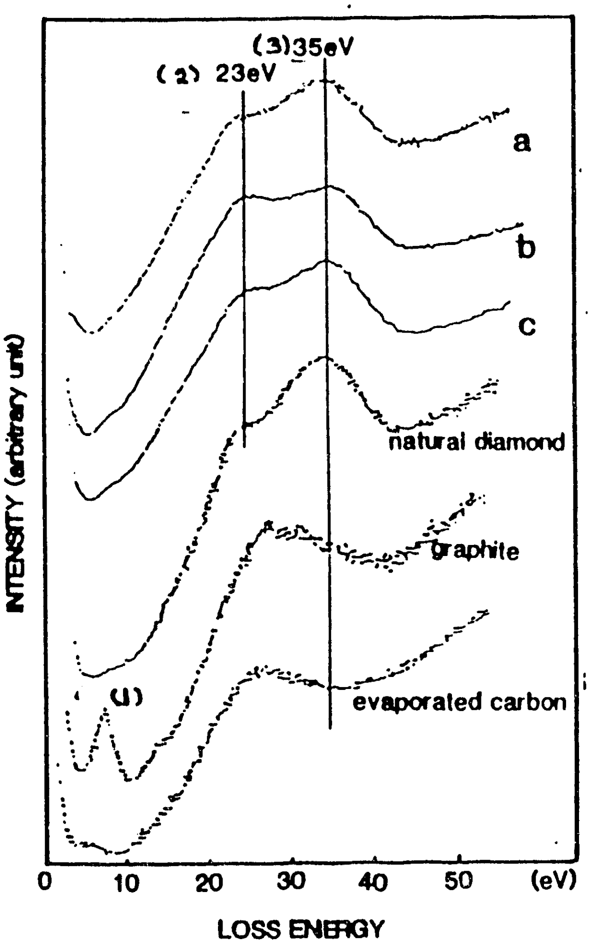


**Unprocessed photoemission spectra showing the peak positions for a clean diamond surface, a hydrogen-covered surface, and a graphite single crystal. The difference in binding energy between the hydrogen-covered and clean diamond bulk peak results from a shift in the Fermi-level pinning position when 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 $E_B$ shift.

Electron Energy Loss Spectra from Carbon - plasmo
loss region near zero loss peak

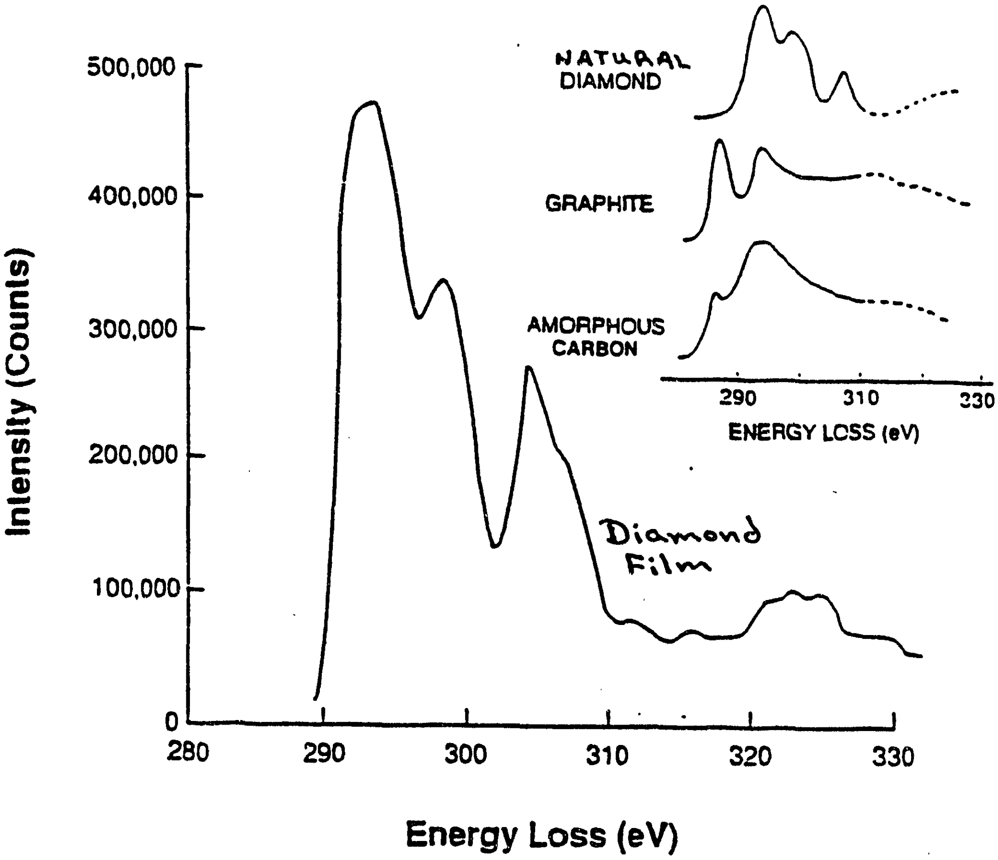
(1) $\pi$ $e^-$ excitation
(2) Surface plasmon or interband trans.
(3) Bulk plasmon



$E_{e^-} = 2{,}000$ eV

EELS of Diamond films grown by EACVD;
a) $CH_4 = 2.0\%$, $T_s = 1073$ K
b) $CH_4 = 2.0\%$, $T_s = 823$ K
c) Specimen (b) after acid wash
d) $CH_4 = 0.5\%$, $T_s = 823$ K
(Sawabe and Inuzuka (1986))

Definition - A Plasmon is a collective excitation o conduction electrons. Frequency is determined by oscilla of the valence 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 $sp^2$ component. However, only $sp^3$ bonding was observed throughout the film.

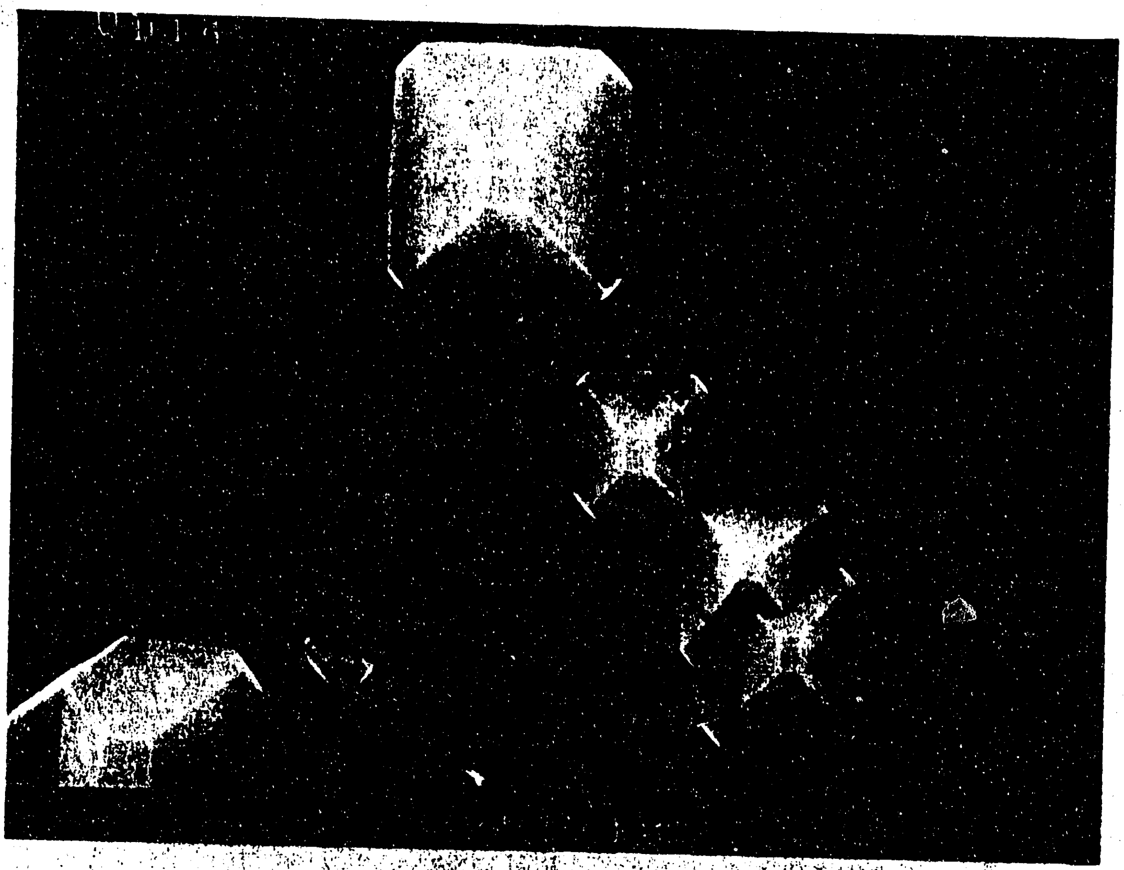
(Williams and Glass (1988)).

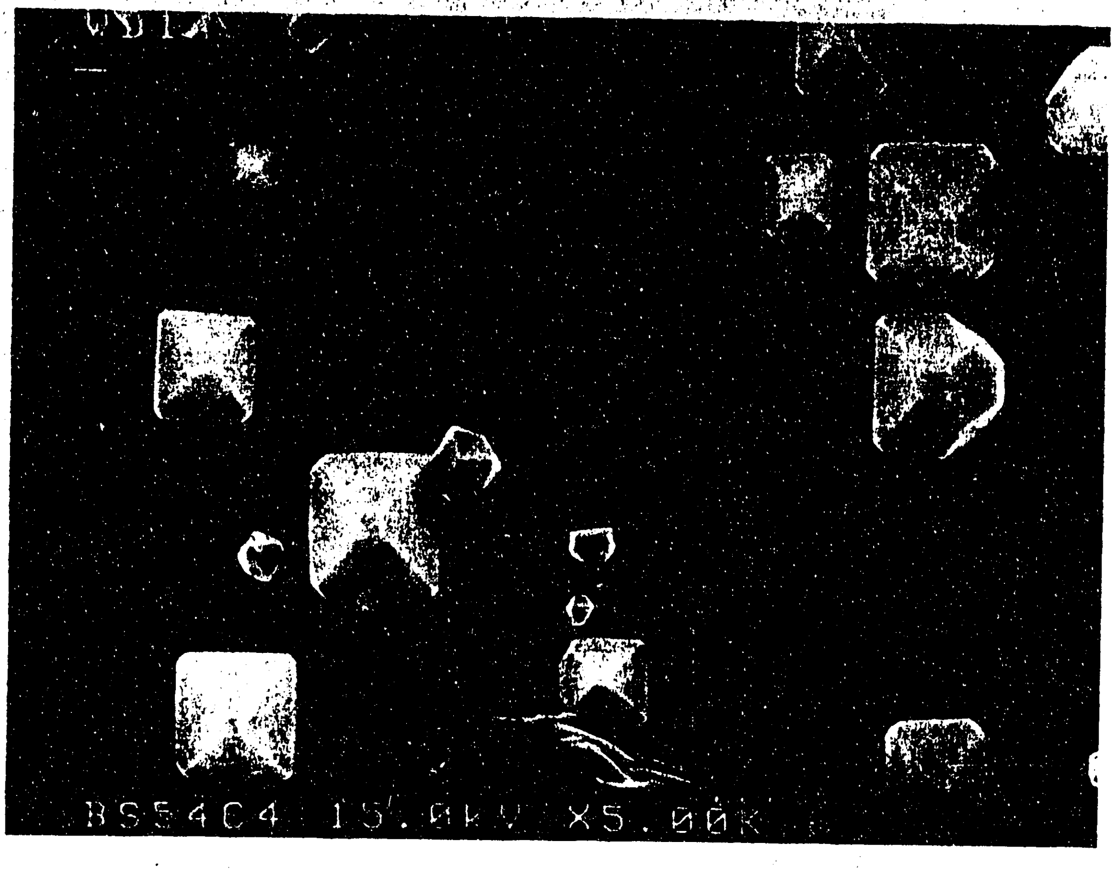
# Electron Microscopies

A. Scanning Electron Microscopy

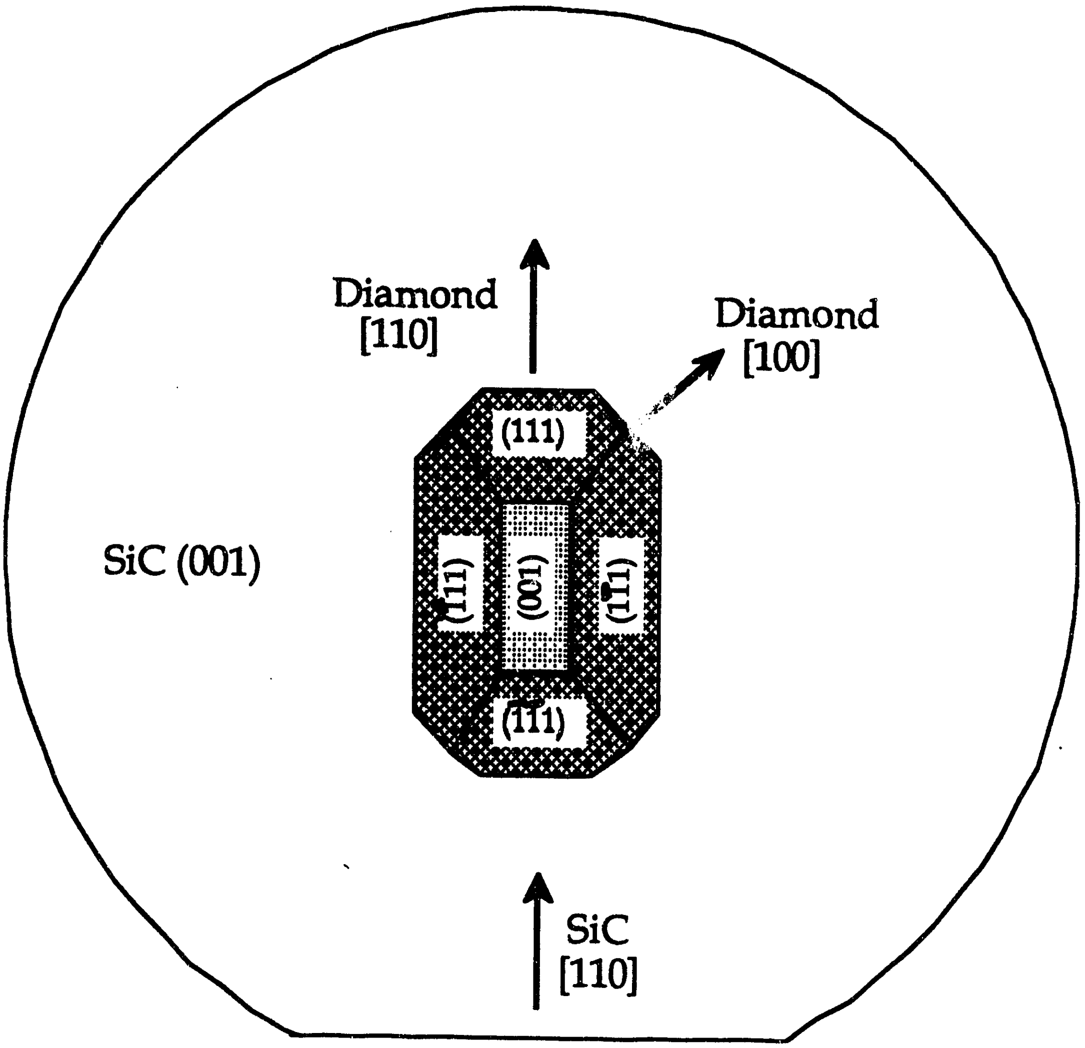
B. Transmission Electron Microscopy

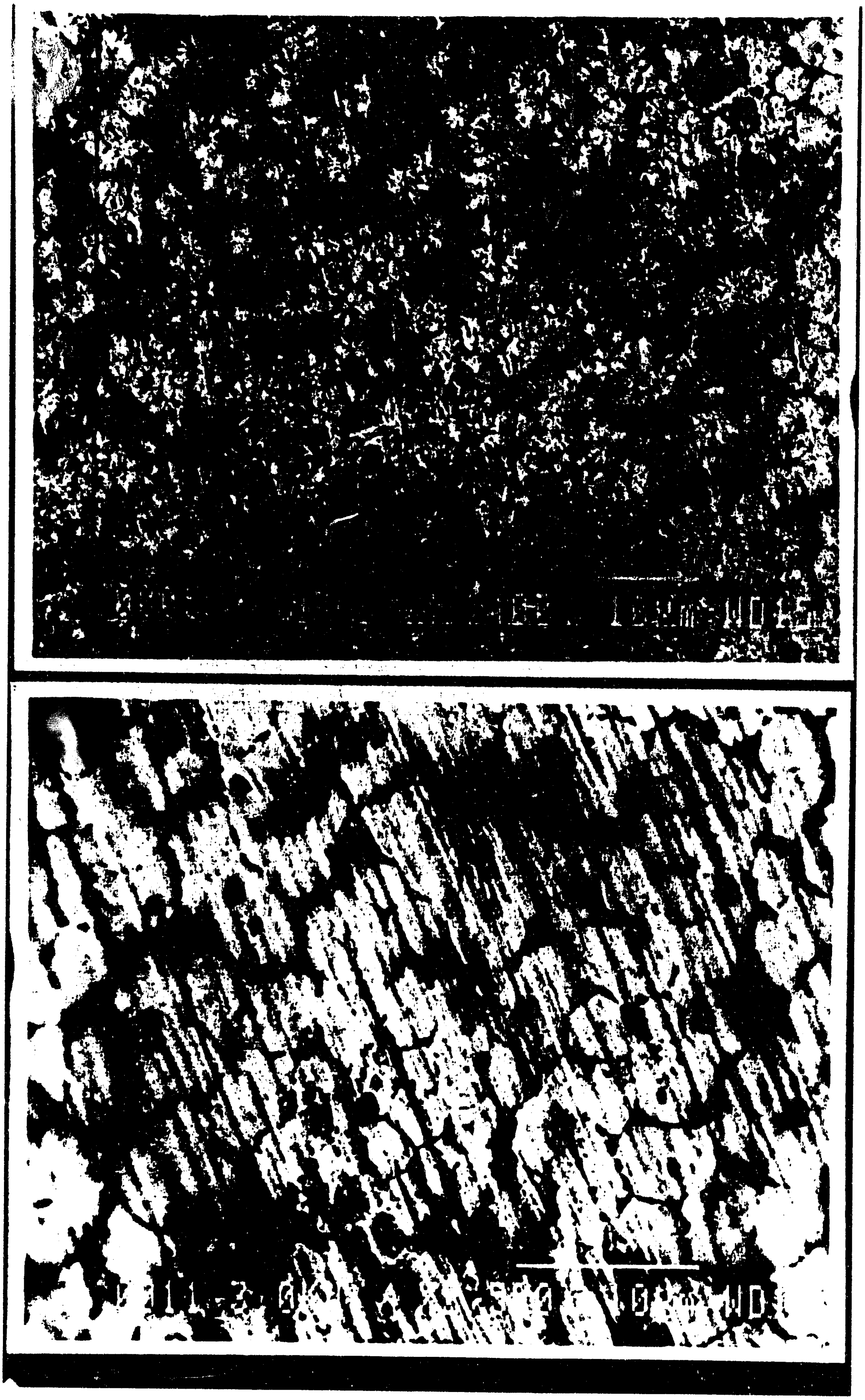
(C. Scanning Tunnelling Microscopy)



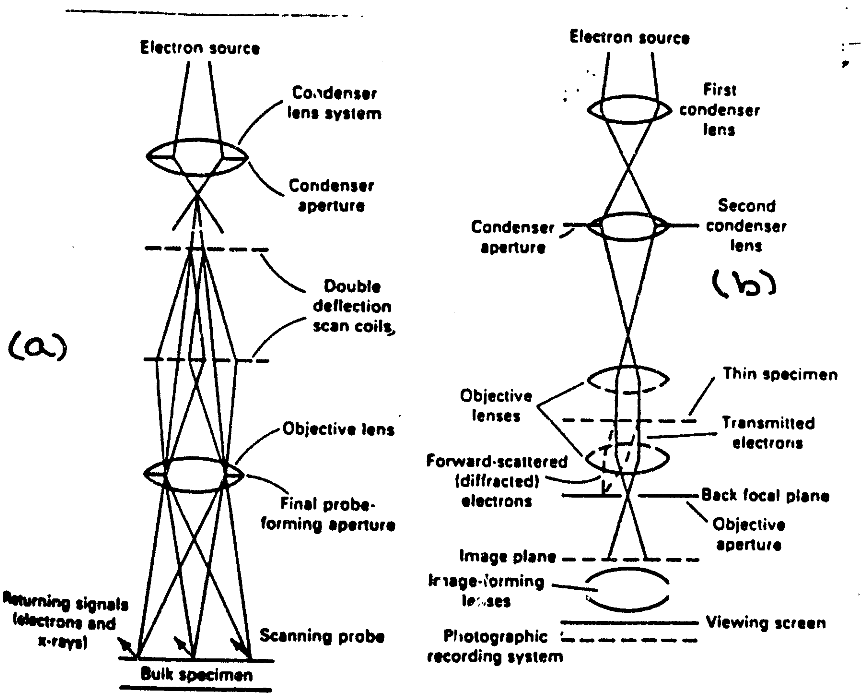

BS5404 15.0kV X5.00K

# Schematic of Diamond Nuclei on β-SiC

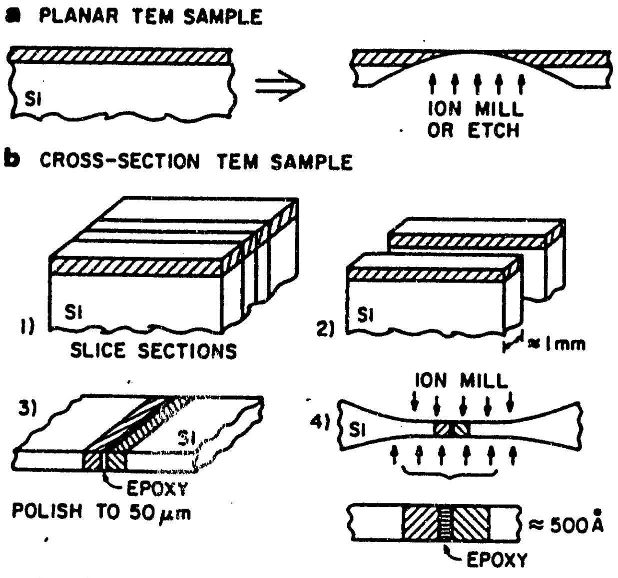




# Transmission Electron Microscopy (TEM)



Schematics of electron optics for (a) SEM & (b) TEM



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.

Advantages of TEM;
* Resolution
Diffraction info
EELS, EDS attachments

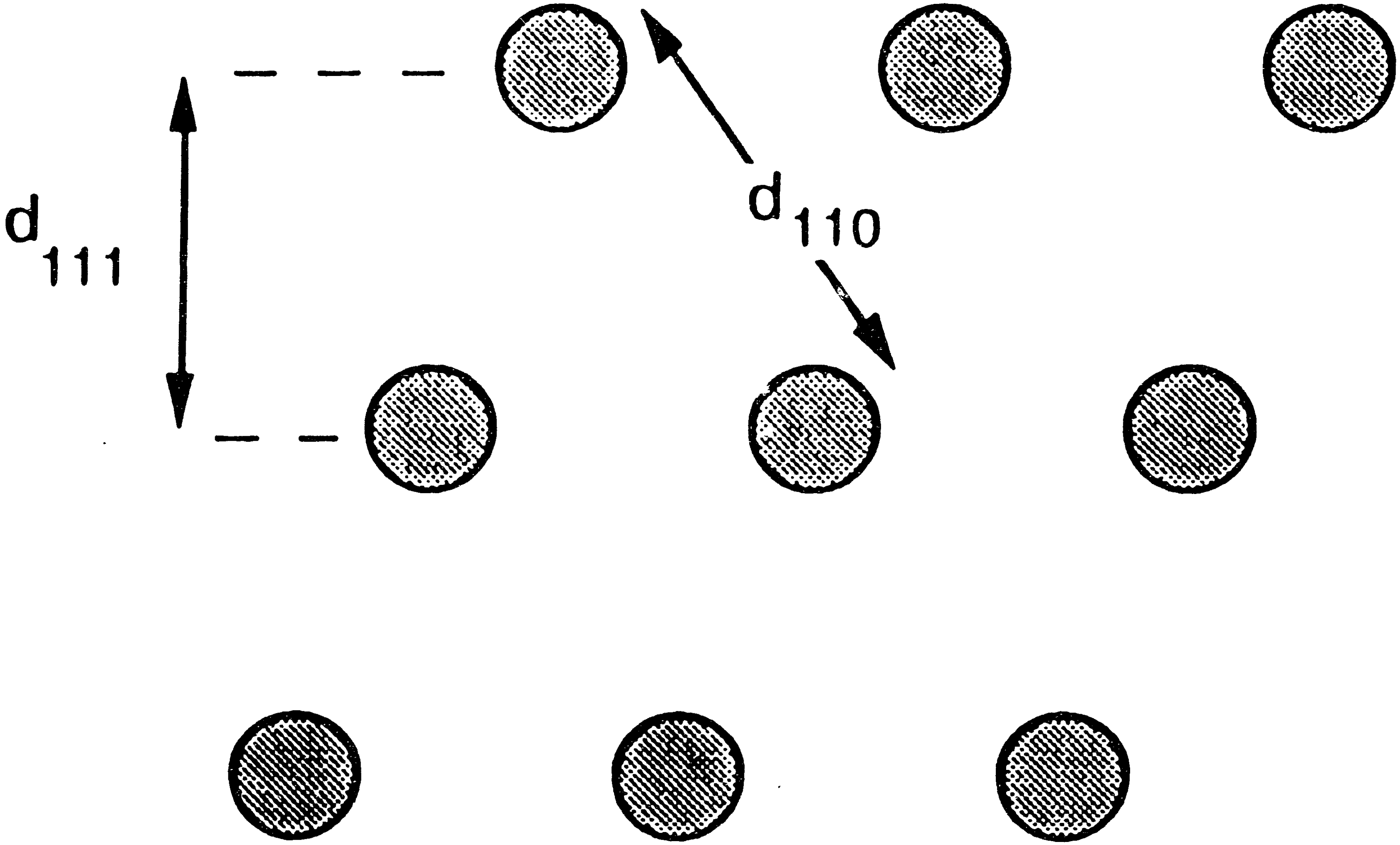
Limitations;
Sample prep
High vacuum
e-beam damage
Sampling volume.

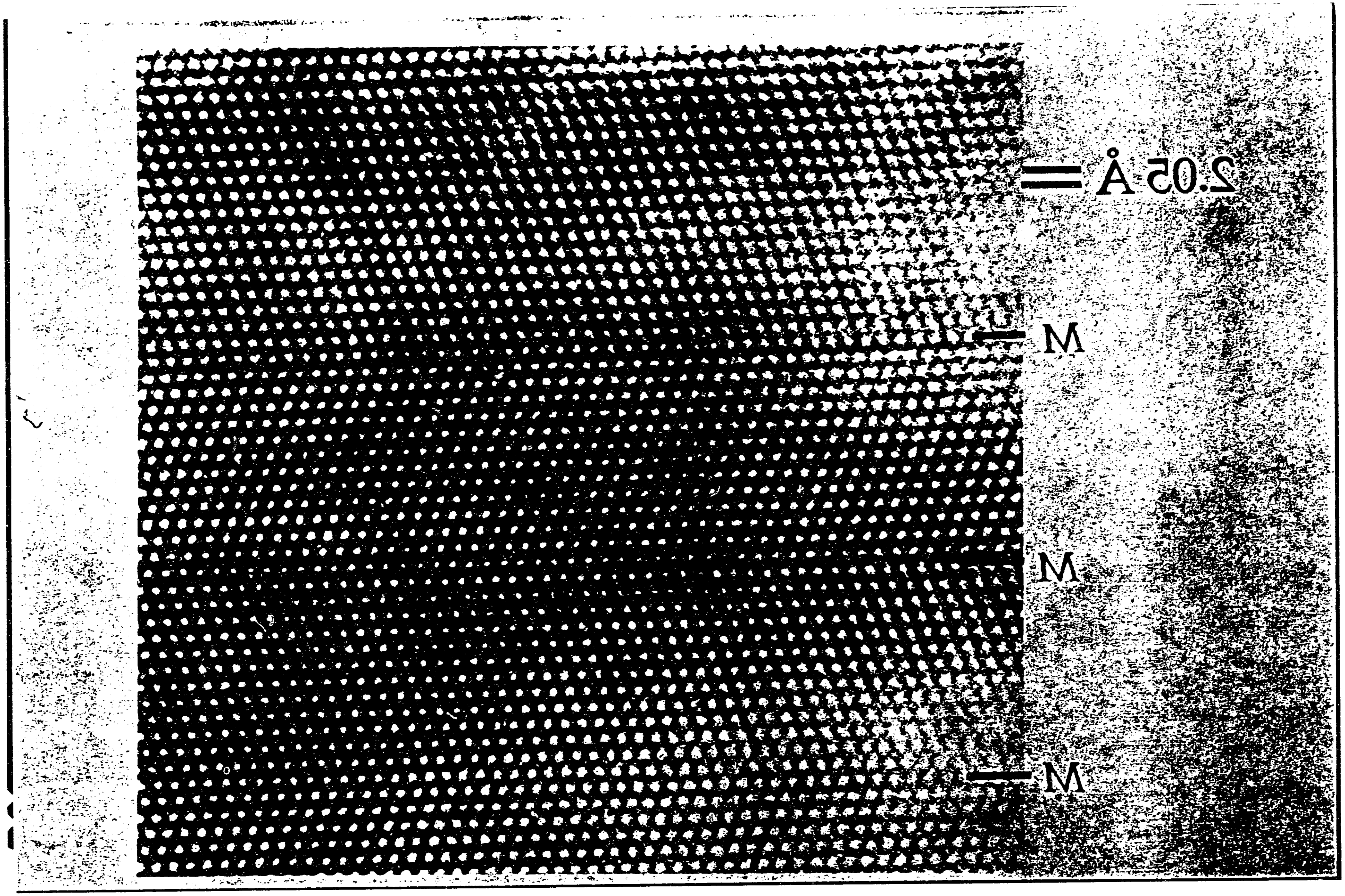

0.5 μm
Combustion Flame Grown Diamond, Substrate Mo, T = 500 °C


Combustion Flame Grown Diamond [illegible]


[illegible] 700 °C

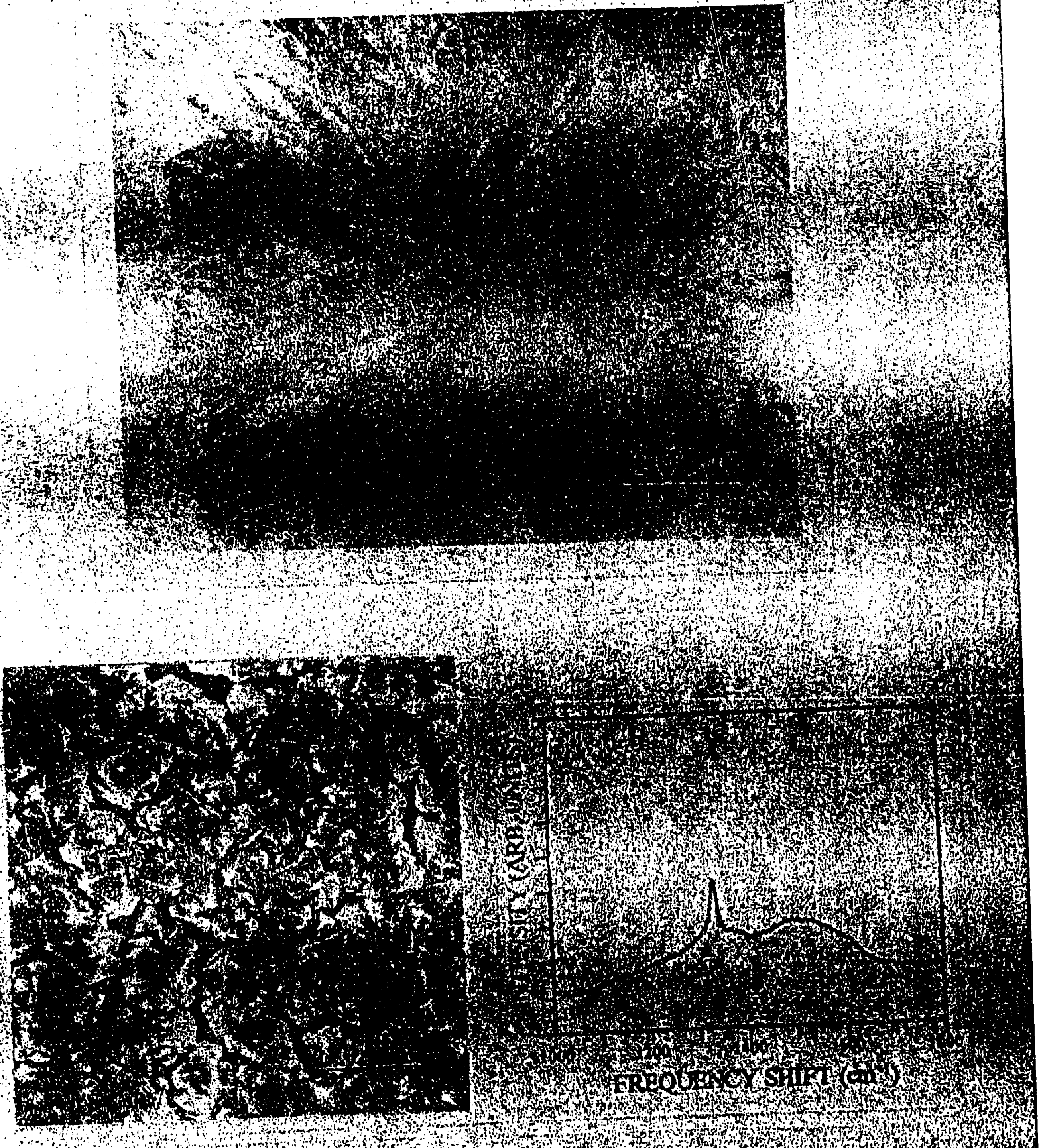

[illegible] Flame Grown [illegible]


$d_{111}$
$d_{110}$


2.05 Å
M
M
M

# Comparison of Different Methods

- SEM · TEM · Raman
- XPS · AES · Raman



Plan-view TEM micrographs of a single diamond grain grown under forward bias of 160 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

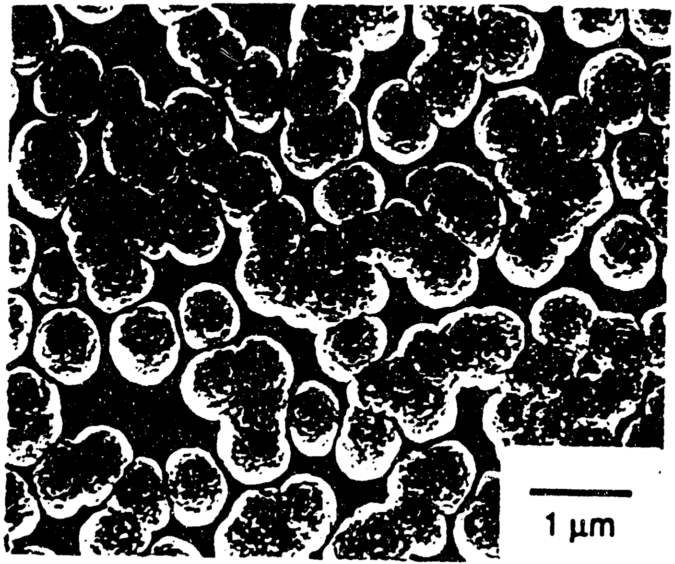
Goal: Provide a comparison between techniques used by different researchers to evaluate the quality of diamond films.

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.

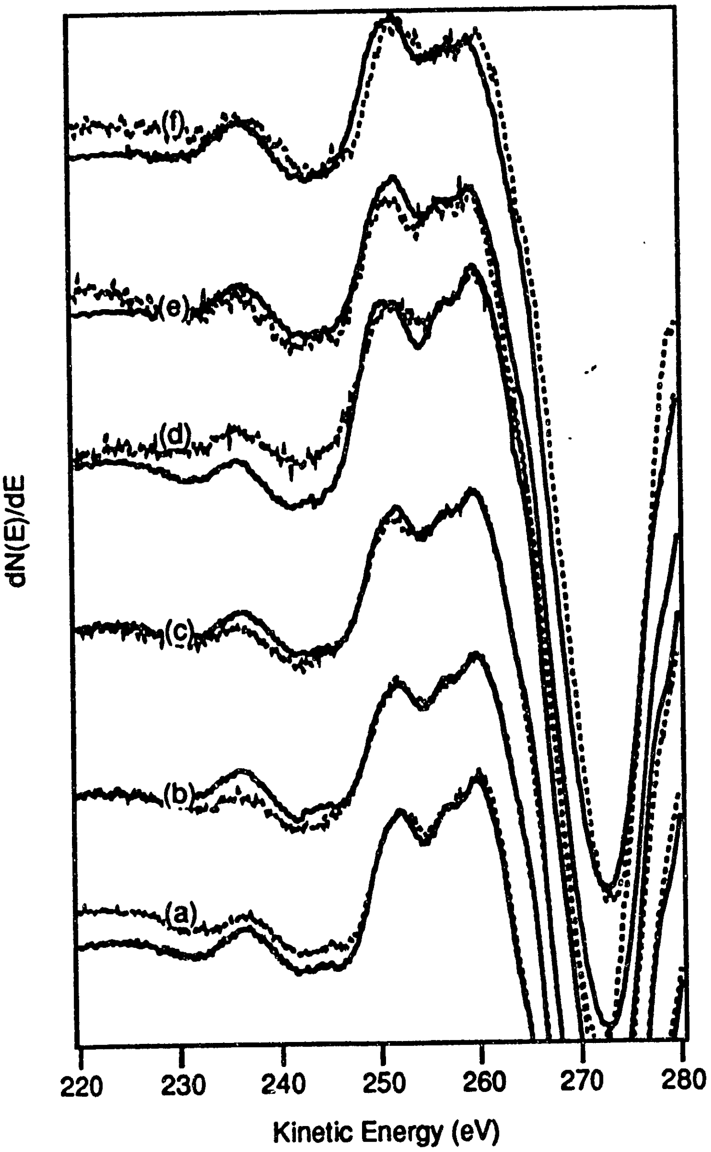
# Surface Morphology: SEM

SEM micrograph of diamond film grown with 1% methane in hydrogen.



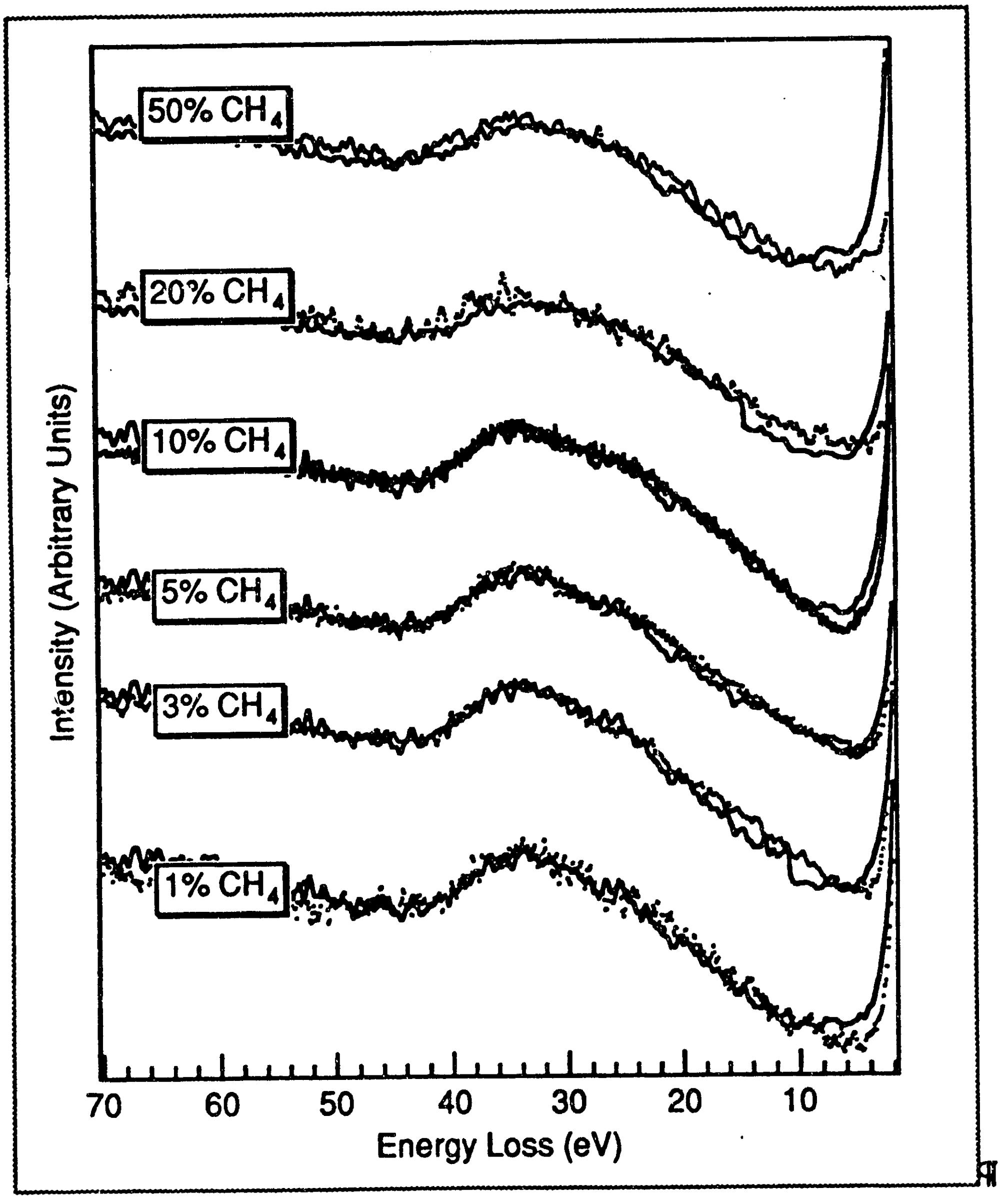
SEM micrograph of diamond film grown with 50% methane in hydrogen.

# AES Spectra from Diamond Films

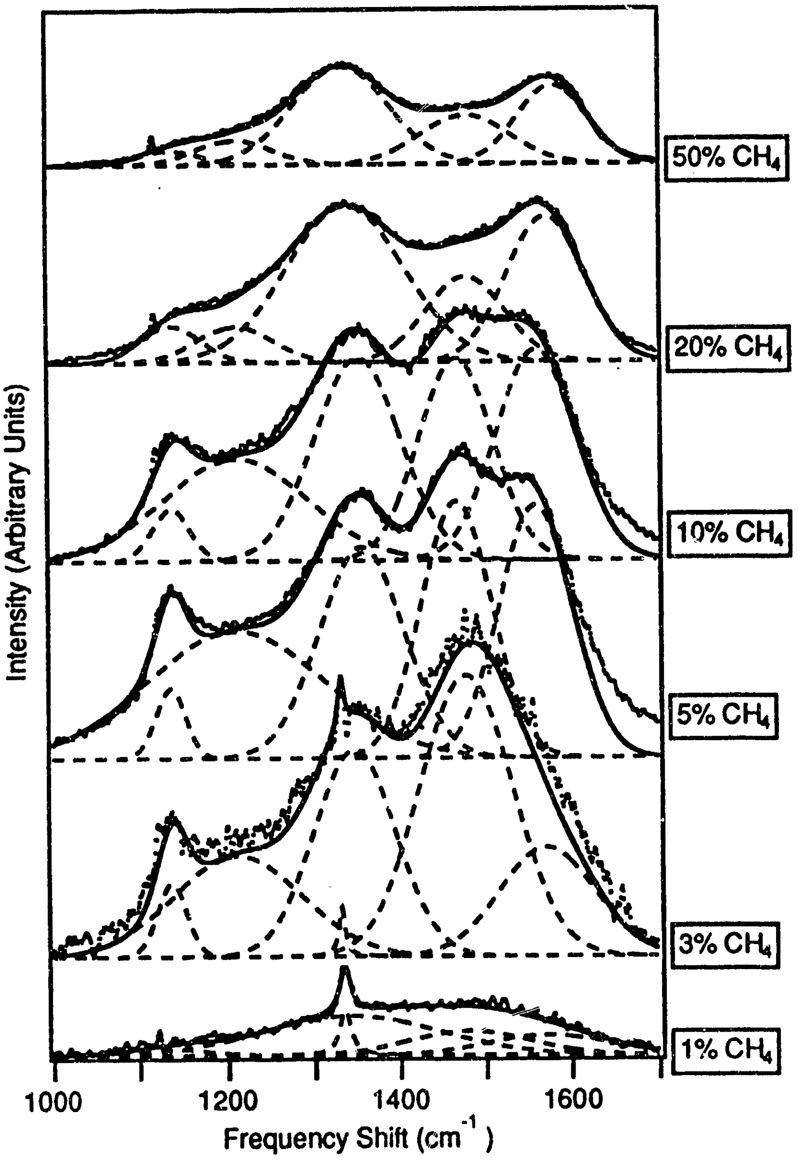


Auger spectra of diamond films grown with CH4 concentrations of a) 1%, b)3%, c)5%,d)10%, e) 20%, f) 50%.

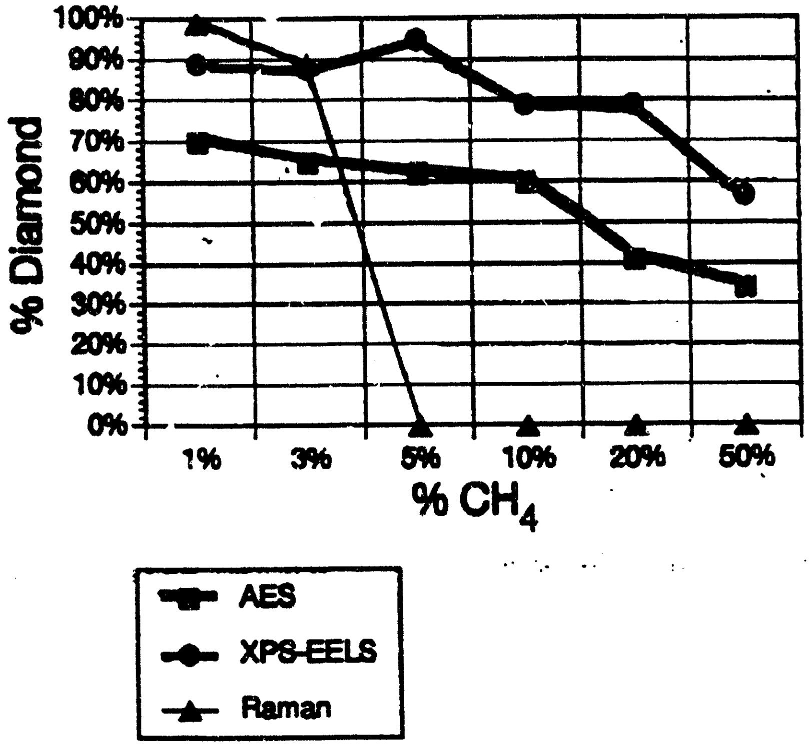
# XPS-EELS from Series of Diamond Films



# Raman Spectra of Diamond Films Grown with Different Methane Concentrations in the Feedgas



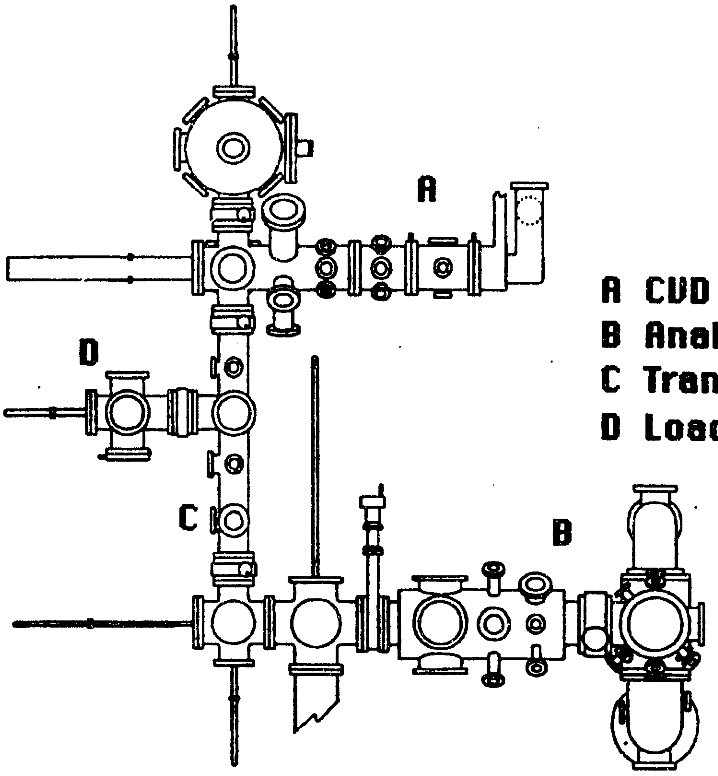
# Fraction of Diamond (sp3) Determined by Deconvolution of AES, XPS-EELS, and Raman



# In Vacuo Analysis

**Department of Materials Science & Engineering**
**Diamond Deposition and Analysis Laboratory**

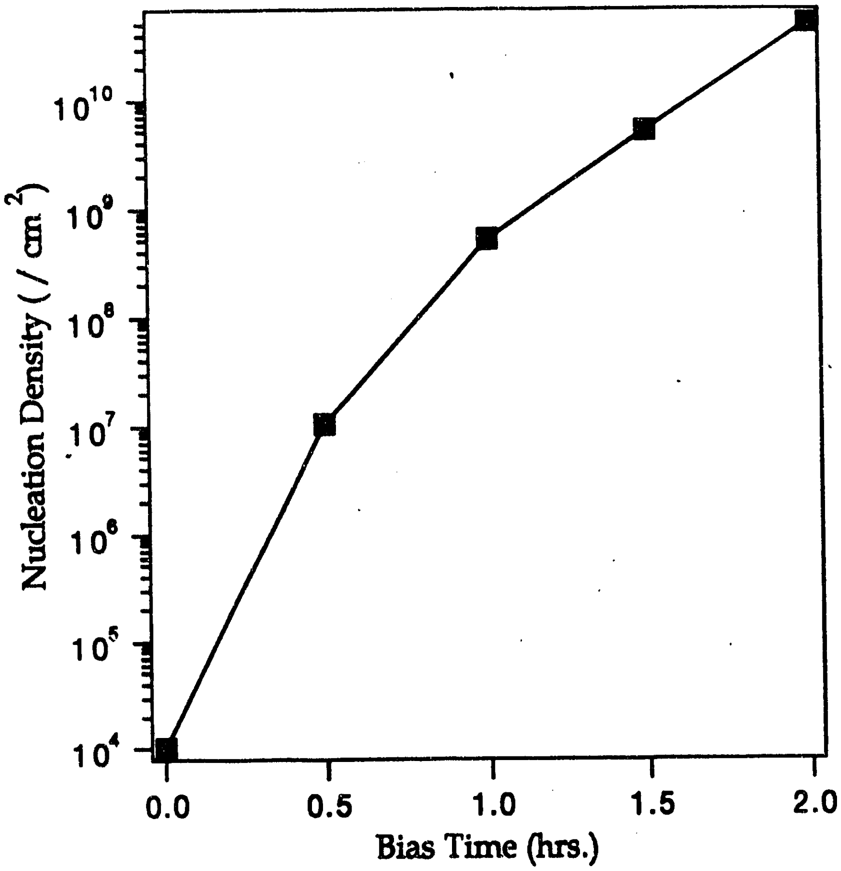
# IN-VACUO CVD/ANALYTICAL CHAMBER



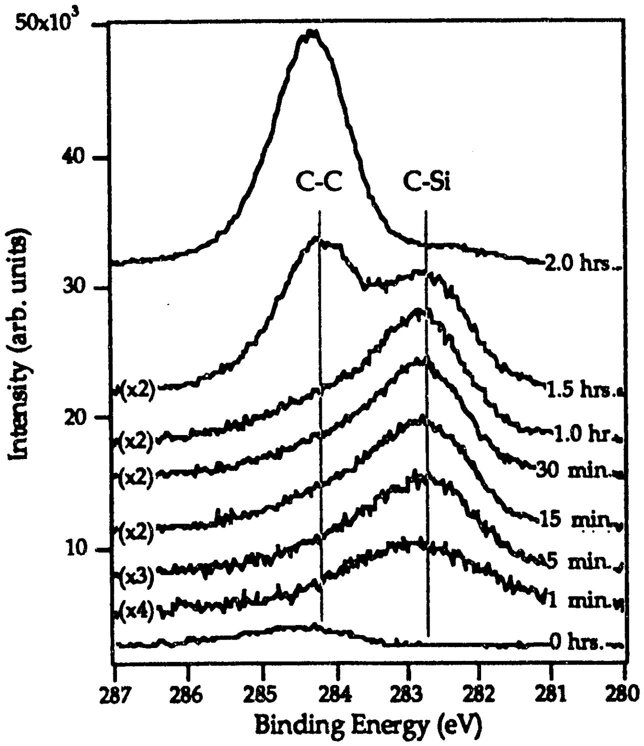
A CVD Chamber
B Analytical
C Transfer Tube
D Load Lock

NORTH CAROLINA STATE UNIVERSITY

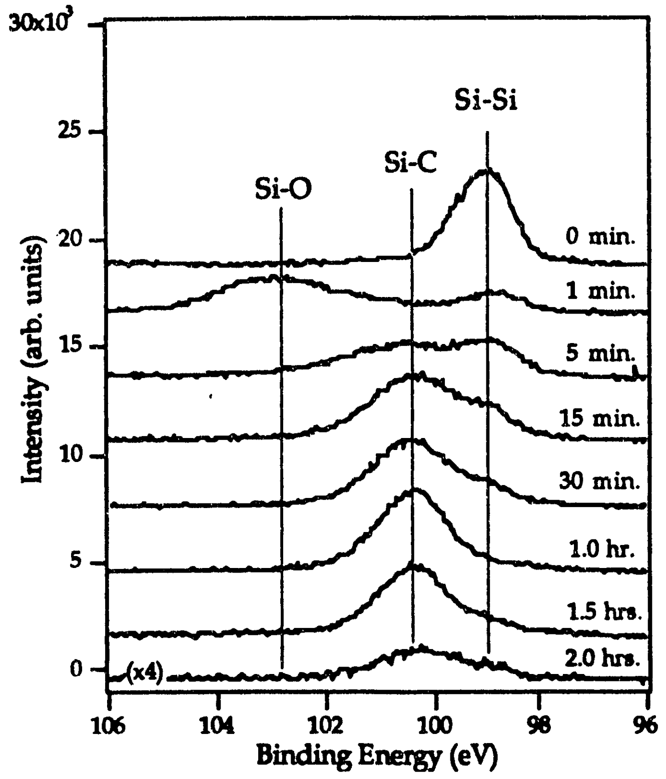
# Nucl. Density vs. Bias Time



# Surface Analysis During Biasing



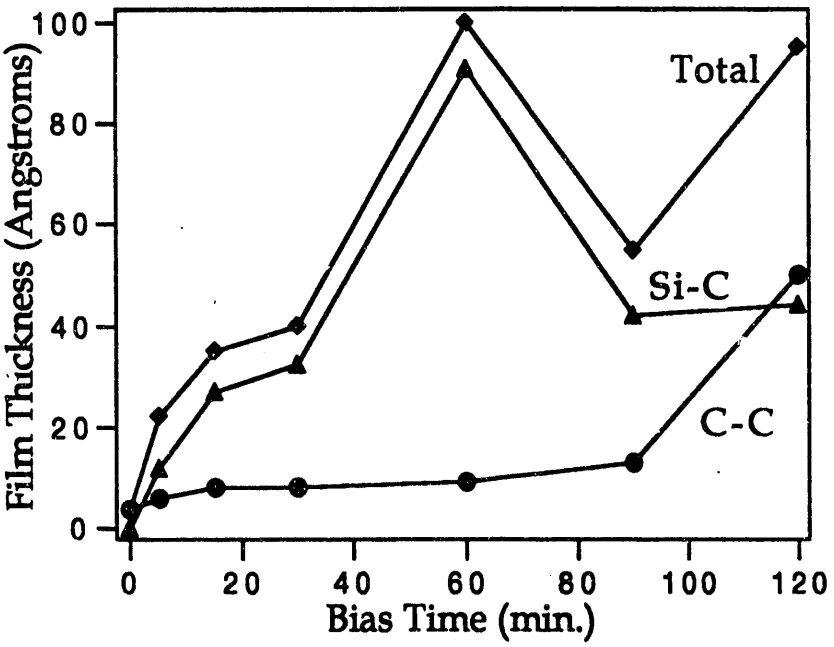
C1s



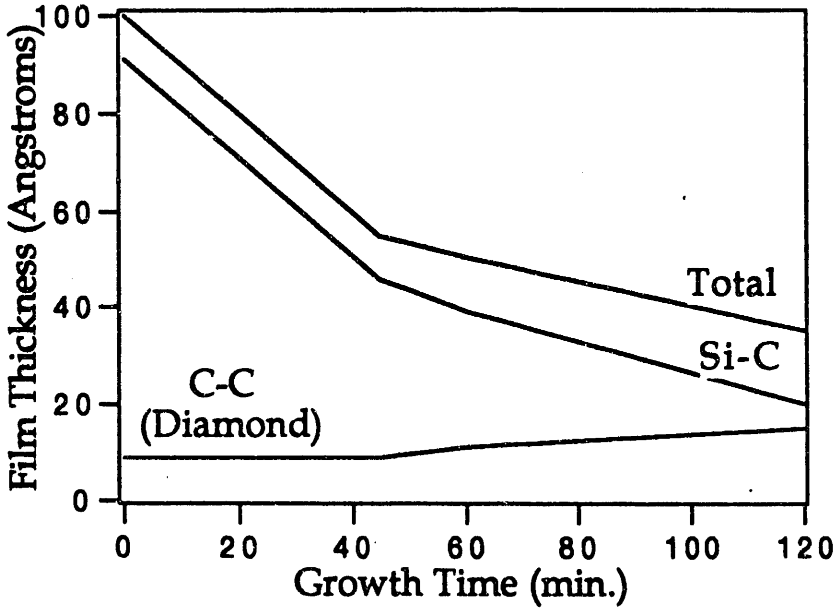
Si 2p

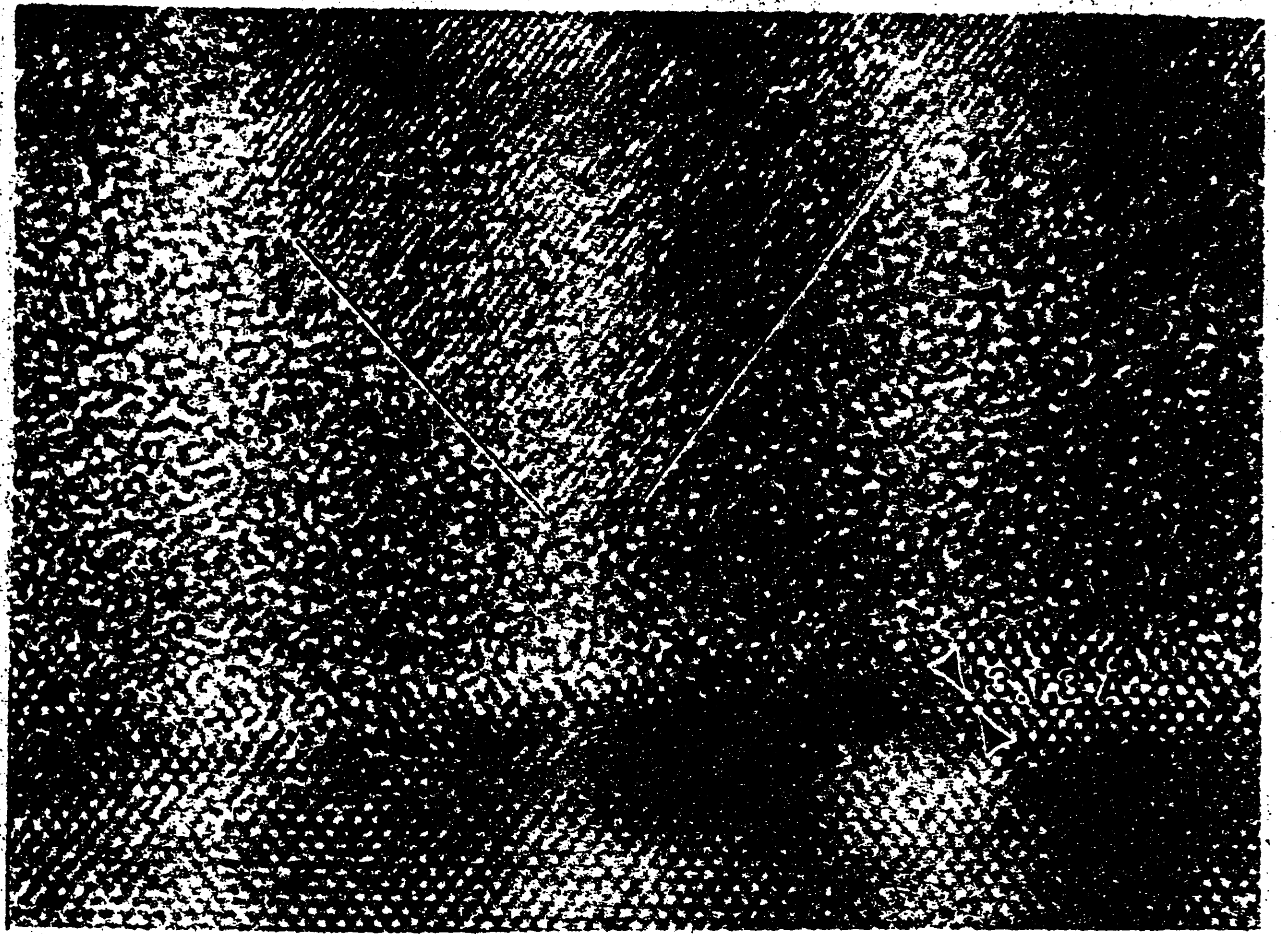
# Calculated Film Thicknesses From XPS Peak Area Ratios

**A: During Biasing Pretreatment**

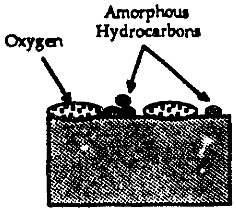


**B: During Growth, After 1 hr. Bias**



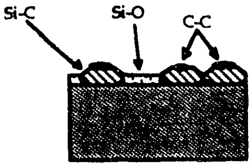


High magnification HRTEM showing an amorphous interfacial layer between the diamond and the silicon substrate.



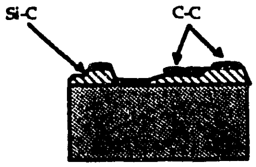
Before Bias

Adsorbed oxygen and amorphous hydrocarbons on the substrate prior to biasing



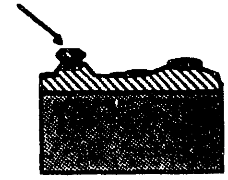
5 min

- 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.



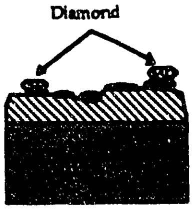
15 min

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



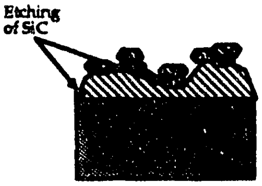
30 min

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



1 hr

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



2 hrs

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

NORTH CAROLINA STATE UNIVERSITY

# In Situ Analysis

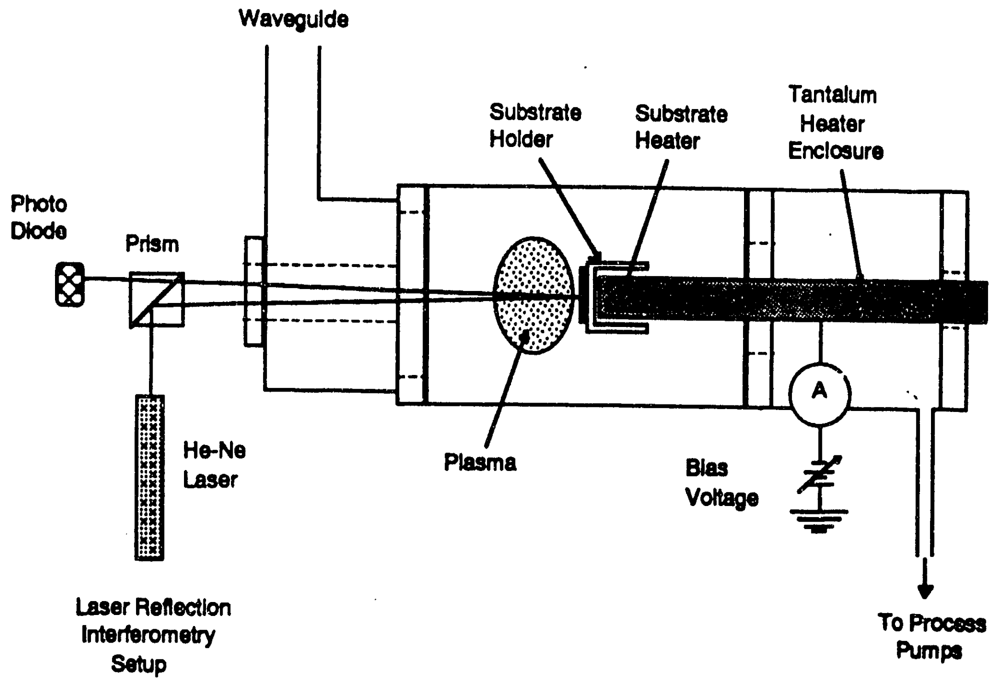
- LRI

(- Microbalance)

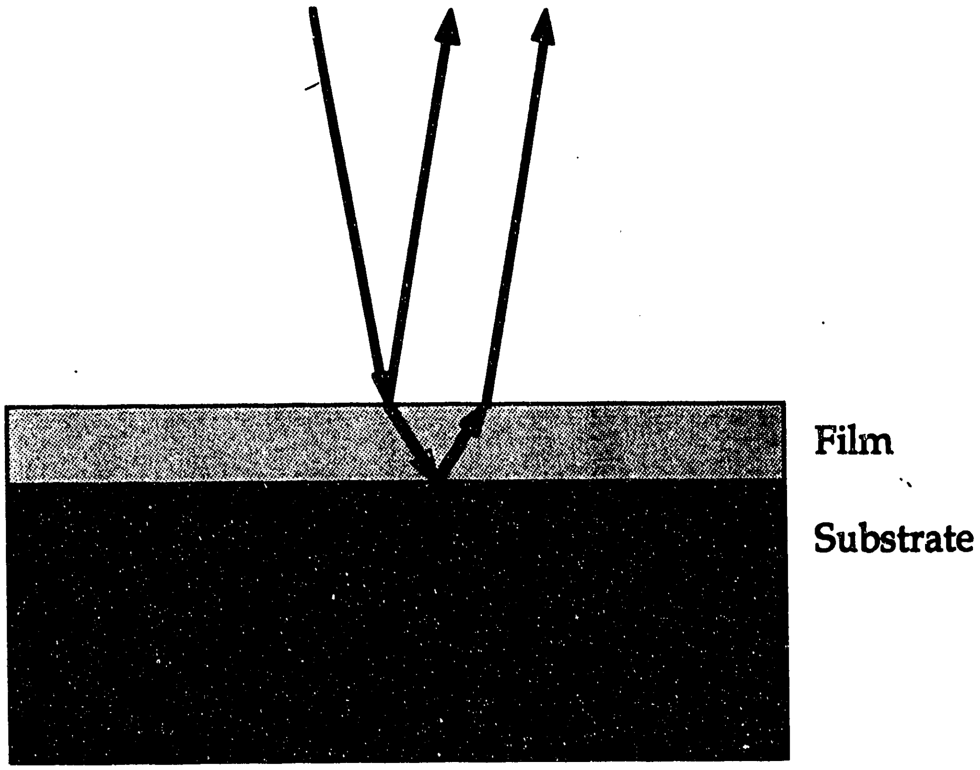
(- Ellipsometry)

(- IR absorption)

# MICROWAVE PLASMA CVD SYSTEM



## LRI Theory



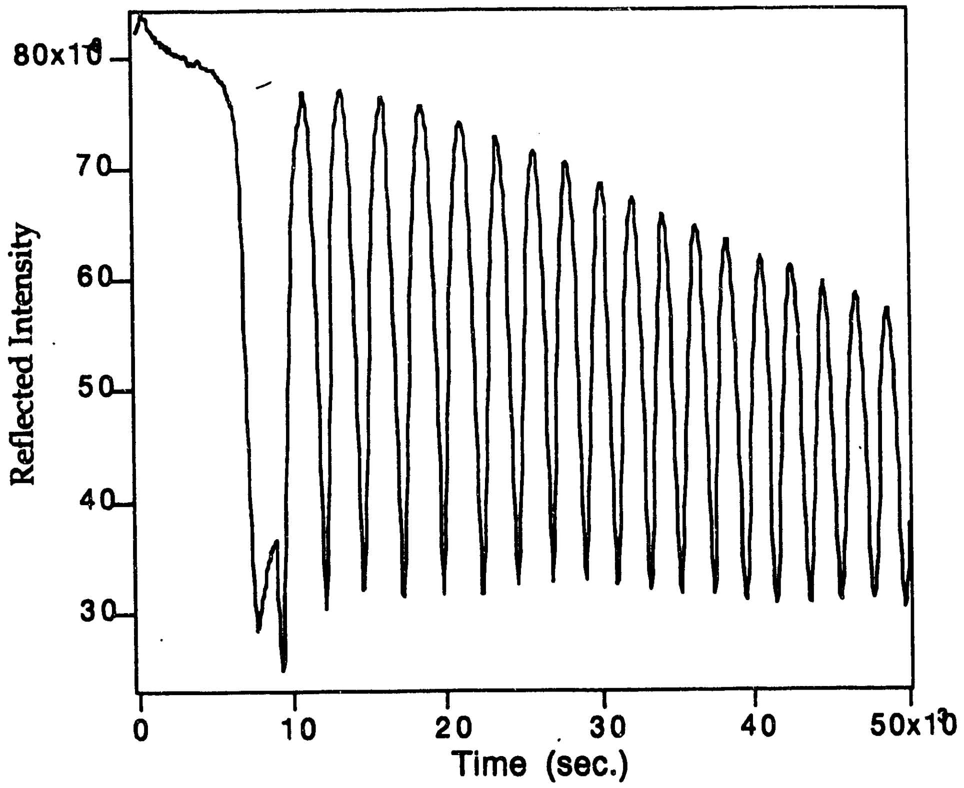
$$\text{Growth Rate} = (\lambda/2\eta)/T$$

Where $\lambda$ = laser wavelength

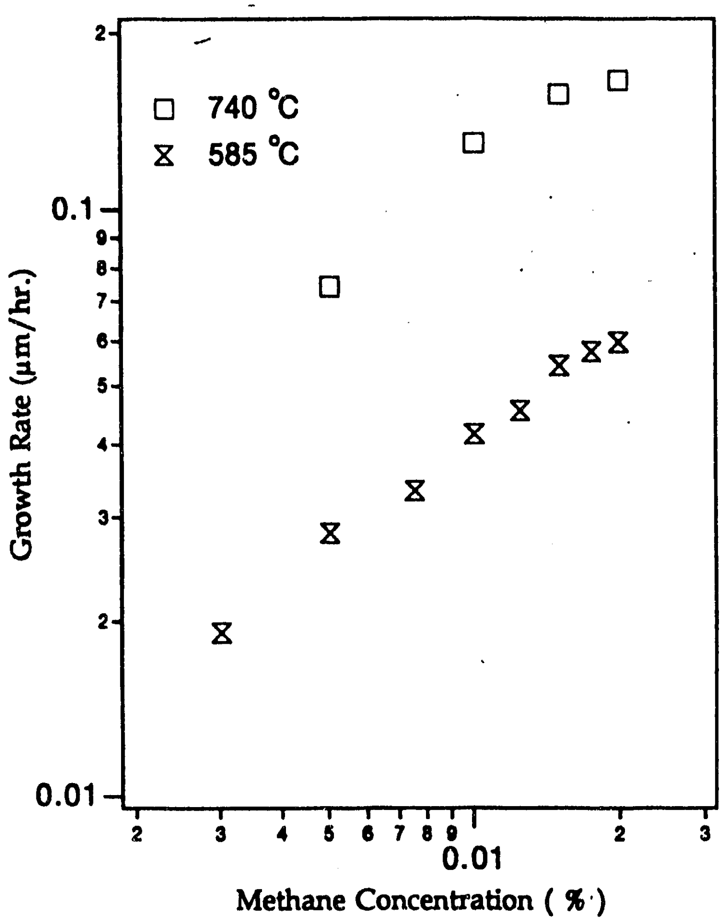
$\eta$ = film refractive index

T = Period between interference cycles

# LRI Scan


$80x10^{3}$
70
60
50
40
30
Reflected Intensity
0
10
20
30
40
$50x10^{3}$
Time (sec.)

# Growth Rate vs $CH_4$ Concentration



# 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**

# Structure and Properties of Diamond and Diamond-Like Films

- Introduction
- Natural IIa 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

**ornl**

# 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 ~425,000 psi

- Low Coefficient of Friction of ~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

| Property | Value | Units | Note | Table Ref. |
|---|---|---|---|---|
| Elastic (Young's) modulus | 1050. | GPa | | 1 |
| | 965. | GPa | Type Ia (nat.) | 2 |
| Bulk modulus | 440. | GPa | | 1 (p. 8) |
| | 440.-590. | GPa | Type IIa | 3 |
| Poisson's ratio | 0.2 | - - - | Type Ia (nat.) | 2 |
| | 0.2 | - - - | synth. polyxl. | 2 |
| | 0.1-0.29 | - - - | dep. on orient. | 1 |
| Tensile strength (theoretical) | 190. | GPa | (<111> dir.) | 1 (p. 285) |
| | 2.94 | GPa | (best value) | 1 |
| Shear strength (theor., <110> {111} system) | 121. | GPa | | 1 (p. 285) |
| Compressibility | $1.7 \times 10^{-7}$ | $cm^2/kg$ | Type IIa | 3 |
| Cleavage velocity | 7.2 | km/s | | 1 (p. 289) |

**References:**

1. J. E. Field, ed., <u>The Properties of Diamond</u>, Academic Press, New York (1979).

2. R. M. Chrenko and H. M. Strong, "Physical Properties of Diamond," Gen. Electric Report #75 CRD 089, (1975).

3. W. G. Ebersol, U. S. Patents 3,030,187 and 3,030,188 (1962).

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

| Material | E (GPa)* | ($E_{diamond}/E$) |
|---|---|---|
| Pyrex$^{TM}$ glass | 70. | 15.4 |
| mild steel | 206. | 5.1 |
| partially-stabilized zirconia | 205. | 5.1 |
| titanium nitride | 251. | 4.2 |
| α - silicon nitride | 304. | 3.5 |
| α - silicon carbide | 400. | 2.6 |
| titanium carbide | 430. | 2.4 |
| α - alumina | 380. | 2.4 |

* 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**

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

# $cm^2$/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

| DIAMOND | HARD CARBON |
|---|---|
| Crystalline | Amorphous |
| Hardness Material Known | 0.1 Hardness of Diamond |
| Limited size (few $cm^2$) | Large Areas Possible |
| Thickness typically limited to <1mm | Thickness Limited to few $\mu$m |
| Growth Rate typically 1$\mu$m/hr | Growth Rates of 10's $\mu$m/hr |
| Grown by Activated CVD | Grown by Plasma and Ion Techniques |
| Uniform Properties Possible | Variable Properties/Composition |
| Rapidly Moving Technology | Commercial Process |

# 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

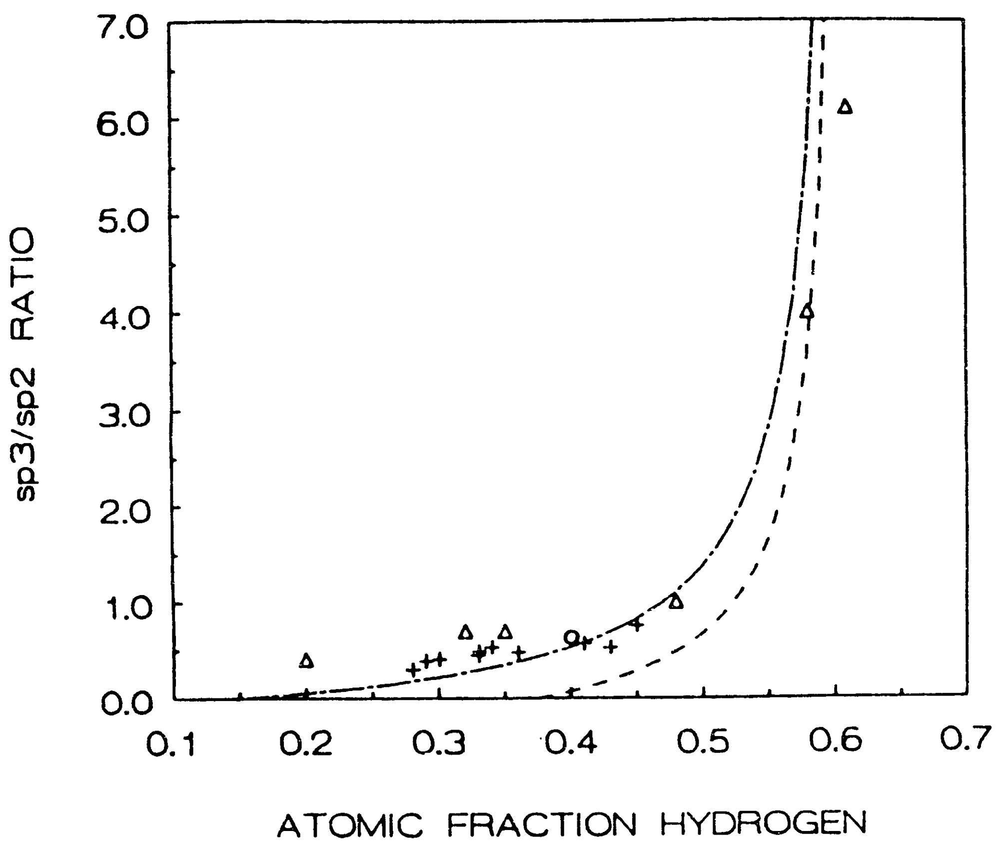


Figure 5

The ratio of $sp^3$ to $sp^2$ sites in a–C:H; The points labeled Δ are from reference (23), the point labeled o 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

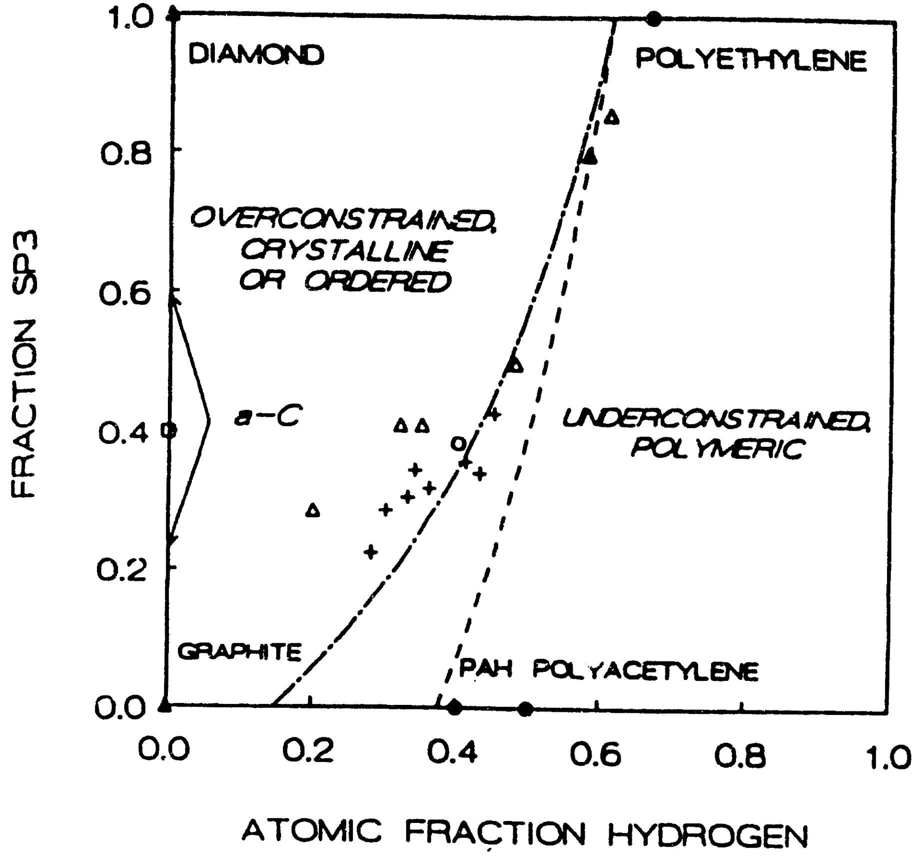


Figure 6

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 Δ and o 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 □ is for an a–C sample reported by Cuomo.[8]

# CHARACTERISTICS OF DLC FILMS

- Tetrahedral bonding ,$sp^3$, increases with hydrogen content
- Band gap and optical transmission increase with $sp^3$ 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 = 3.51g $cm^{-3}$, Graphite = 2.26 g $cm^{-3}$)
    - Hardness reported to equal or exceed diamond

# 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
- Excelent 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 IIa 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[20])**

| Diamond | Colour | Nitrogen/ ppm atomic | Cleavage/ pressure[a]/GPa | Hardness[b]/ GPa | Abrasion resistance[c] |
|---|---|---|---|---|---|
| 70 | Yellow | 70 | 20.3 | 95 | 0.84 |
| 12 | Yellow | 20 | --- | 106 | 1.31 |
| 82 | Pale green | ~2 | 24.5 | --- | 1.72 |
| 15 | Colourless | ~0.3 | --- | 110 | 3.05 |
| 87 | Pale green | ~0.1 | ~30.0 | 131 | 3.11 |

(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 $Al_2O_3$ grit and with grinding ratio expressed as volume of wheel wear in $m^3$ 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])**

| Plane | Direction | Type I | Type II |
|---|---|---|---|
| (001) | [110] | 81.0 | 89.0 |
| (001) | [100] | 96.0 | 101.0 |
| (110) | [110] | 86.0 | 92.0 |
| (110) | [001] | 106.0 | 113.0 |
| (111) | [110] | 55.0 | 75.0 |
| (111) | [112] | 62.0 | 108.0 |

# 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[54])**

| | Plane and Direction | | |
|---|---|---|---|
| Plane | Dodecahedron (011) | Cube (001) | Octahedron (111) |
| Direction | [100] [011] | [100] [110] | $[11\bar{2}]$ $[\bar{1}\bar{1}2]$ |
| Depth of cut ($\lambda/2$) | 10.0 1.8 | 8.5 1.1 | 3.9 2.1 |

# ABRASION RESISTANCE IS A FUNCTION OF CRYSTAL PLANE AND DIRECTION

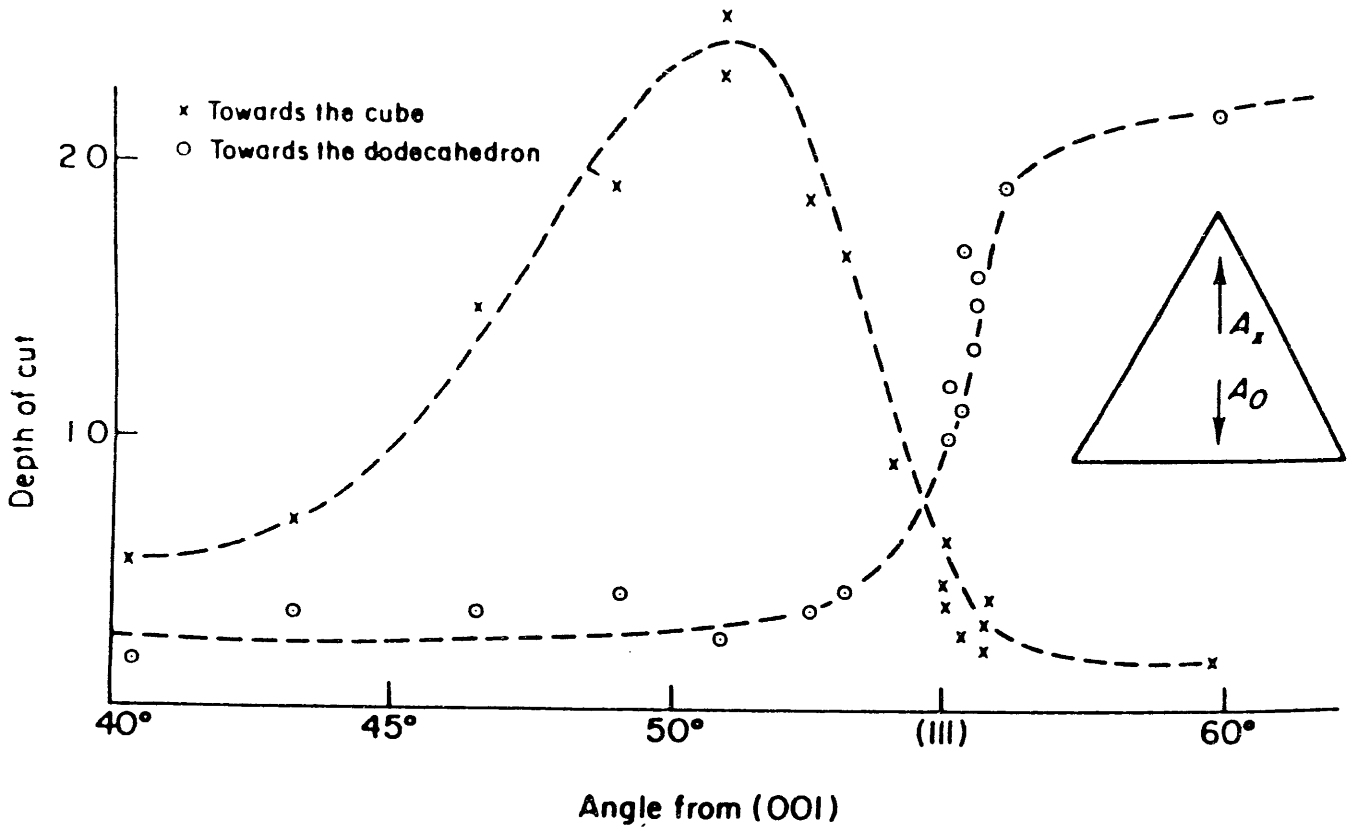


*Fig. 11.1.* The relative depths of cuts when abrading diamond facets near (1 1 1). The symbols 0 and *x* correspond to the directions shown in the inset.

# CLEAVAGE ON {111} DOMINATES FRACTURE

**Theoretical cleavage energy for diamond**

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

Note: to obtain a fracture surface energy, $\gamma$, divide by 2.

# Structure and Properties of Diamond and Diamond-Like Films

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

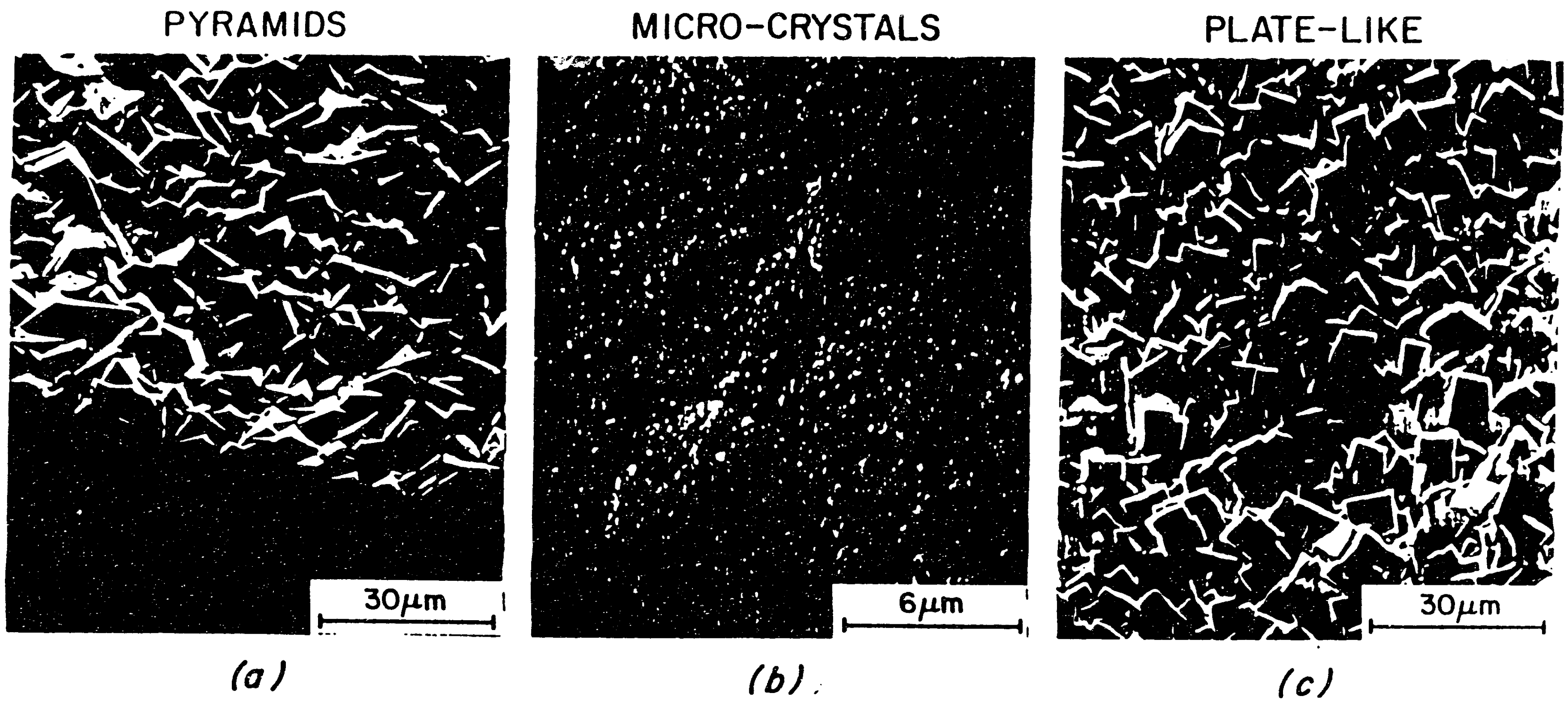
# PROPERTIES OF DIAMOND ARE SENSITIVE TO FILM STRUCTURE AND DEFECTS

- 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

ornl

ORNL-PHOTO 4908-85

# DIAMOND FILM MORPHOLOGIES



PYRAMIDS

MICRO-CRYSTALS

PLATE-LIKE

(a) (b) (c)

ornl

ORNL-DWG 89-

DATA FOR SAPPHIRE SLIDERS ON DIAMOND FILMS

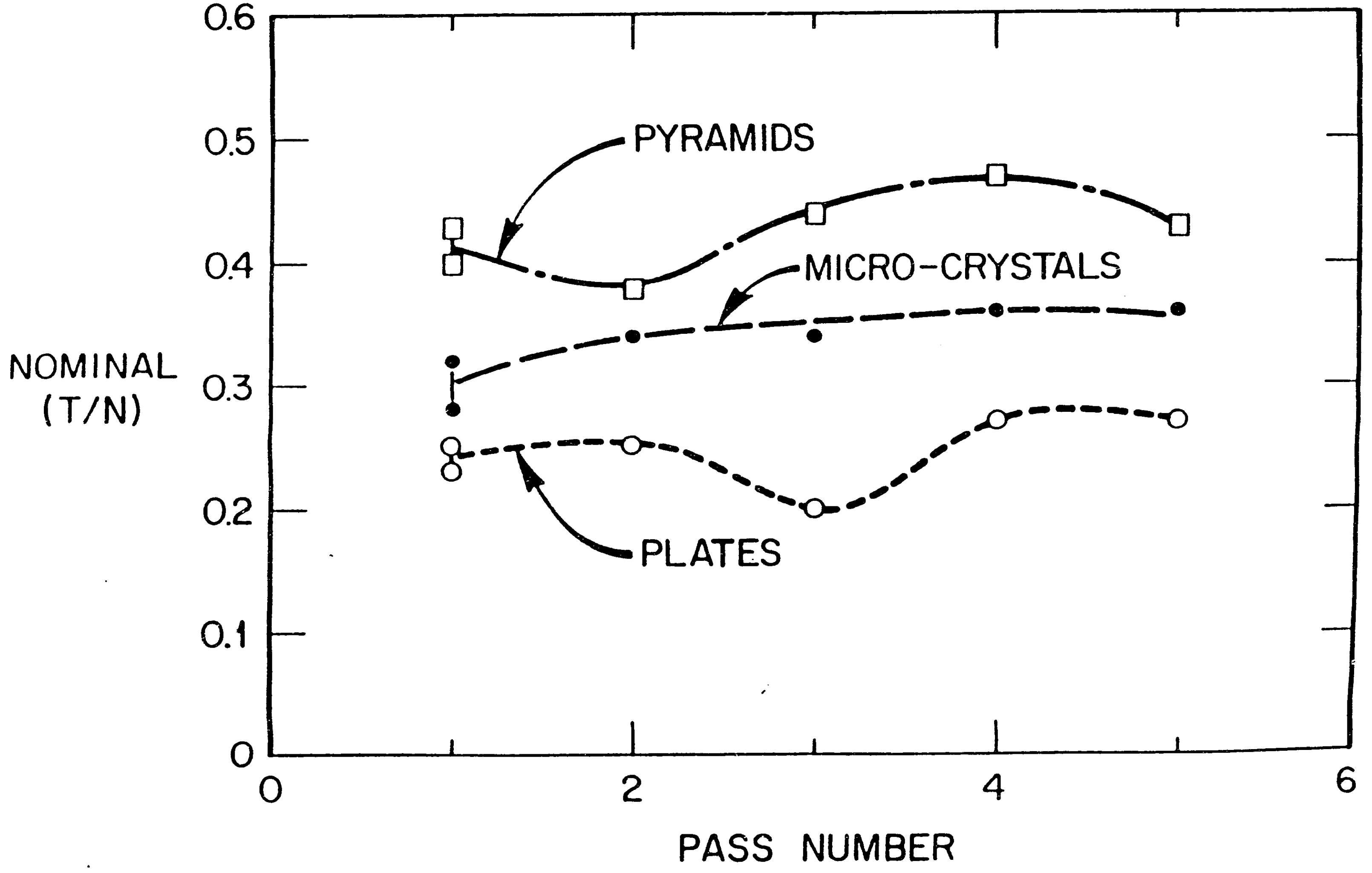


Figure 7. Scanning electron micrograph of a steel cutting chip removed as a steel ball slid against a diamond film with sharp facets.

# FRICTION COEFFICIENTS OF DIAMOND AND DLC FILMS

## Single Crystal IIa

- Typically 0.5 to o.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

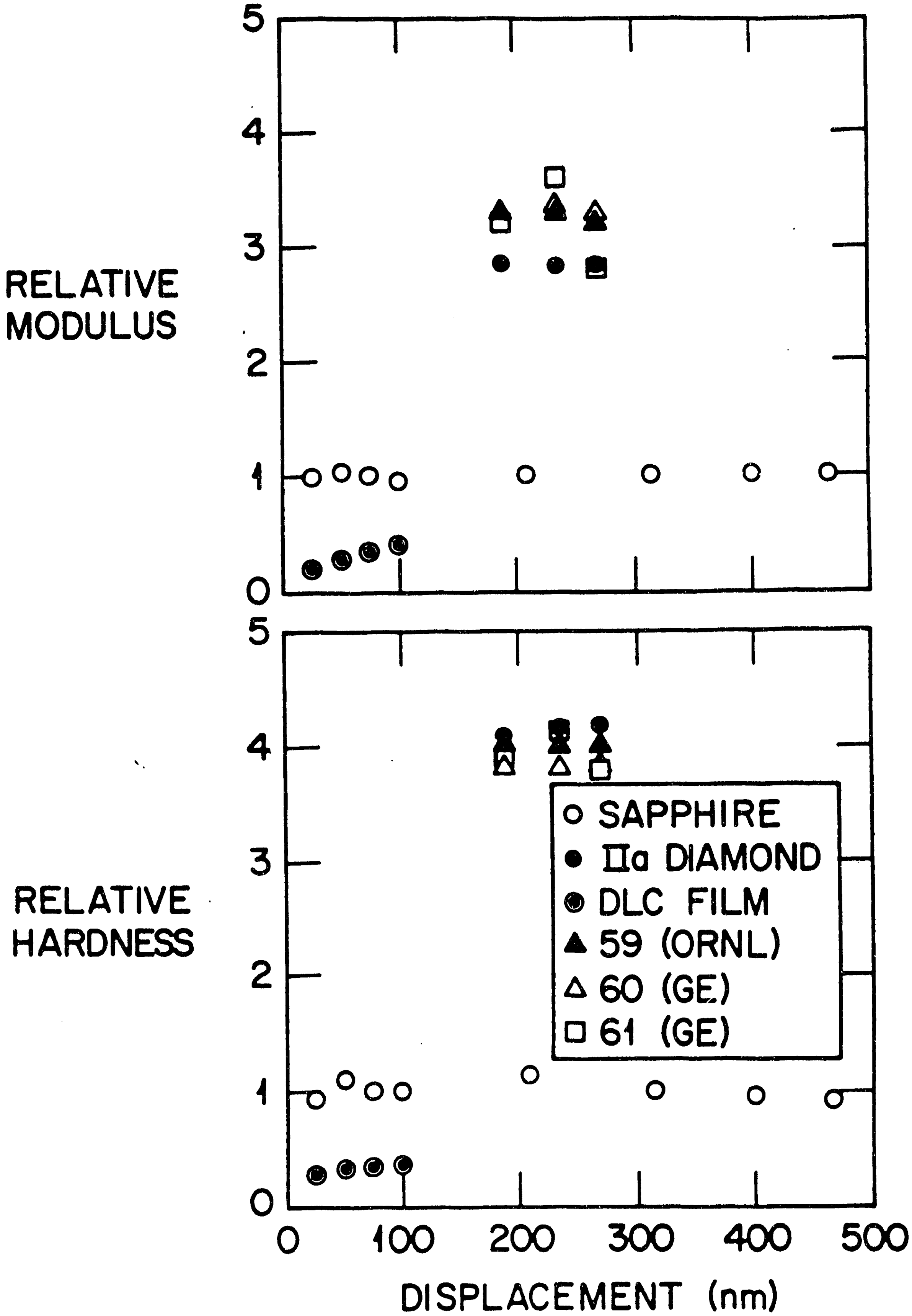
- Reported Values Range From 0.01 to 0.3, (Typically 0.1 to 0.2)
- Friction Coeficients Increase with High Humidity to 0.3 or 0.4
- Films Alloyed with Si Gave Values Near 0.05

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

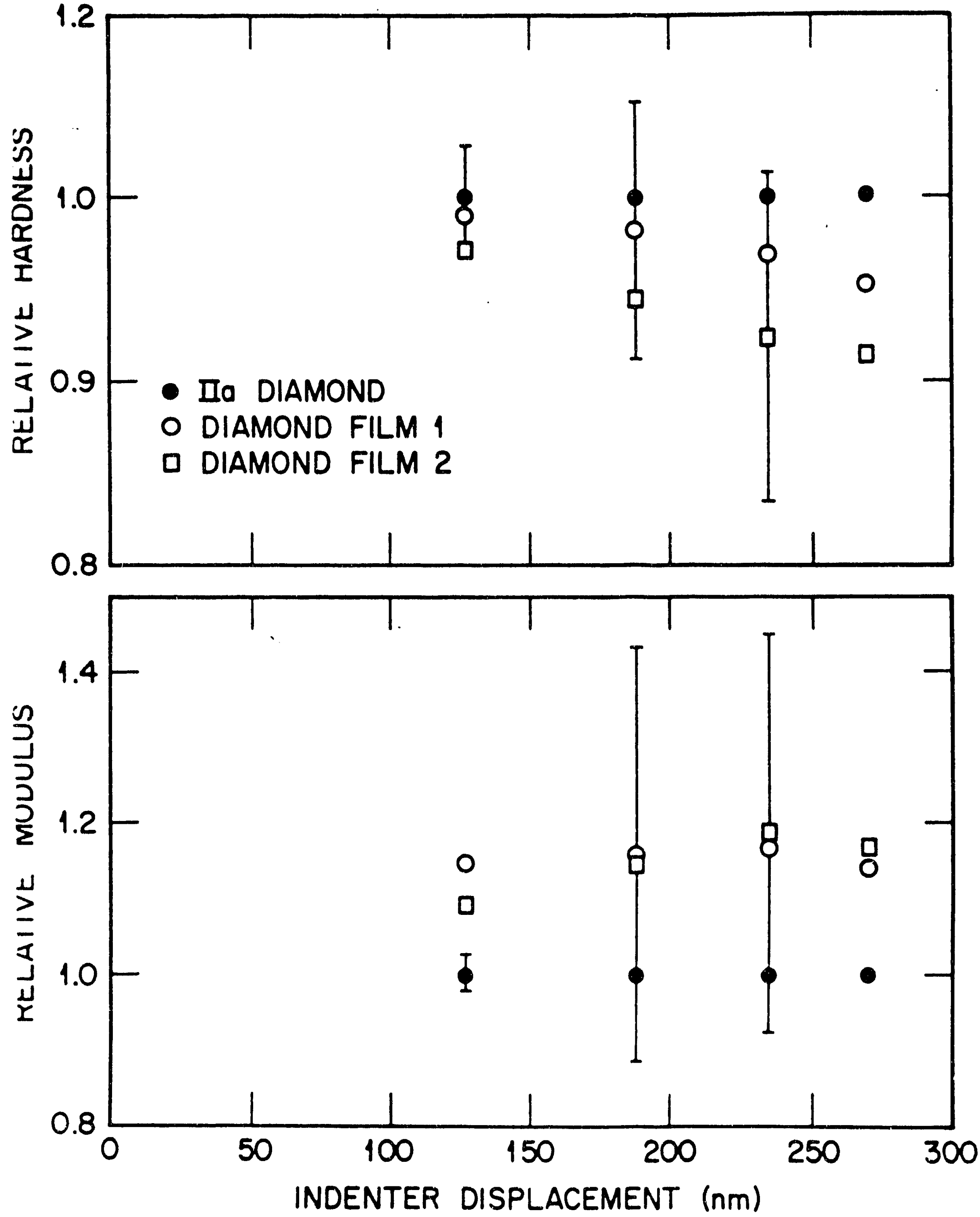
Note: All above results depend on details of the test and materials

# 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 Slighly Softer and Deform Slighly in Indentation Tests Suggesting That They May Be Tougher Than Coarser Grained Polycrystalline CVD Films


RELATIVE MODULUS
RELATIVE HARDNESS
0
1
2
3
4
5
0
100
200
300
400
500
DISPLACEMENT (nm)
○ SAPPHIRE
● IIa DIAMOND
◉ DLC FILM
▲ 59 (ORNL)
△ 60 (GE)
□ 61 (GE)

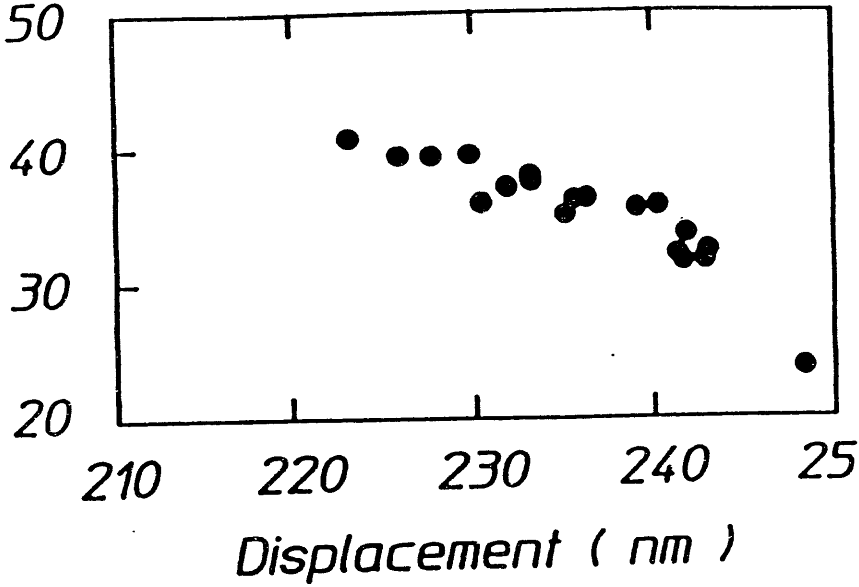
ORNL-DWG 90-8160



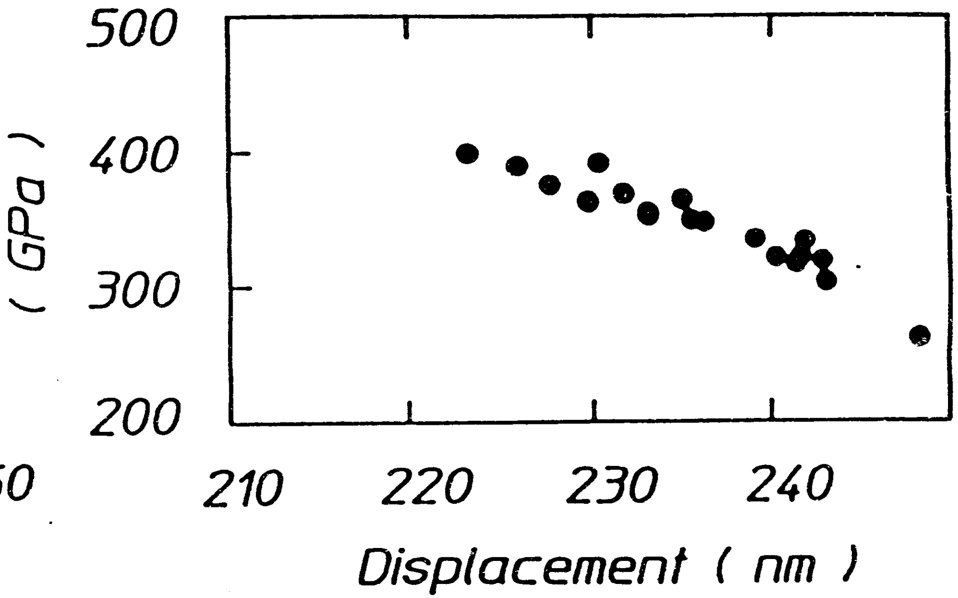
# "MICROCRYSTALLINE"

- **Mixture of diamond and otther bonding types**

  **(~75% $sp^3$ )**



**Hardness = 37 GPa**

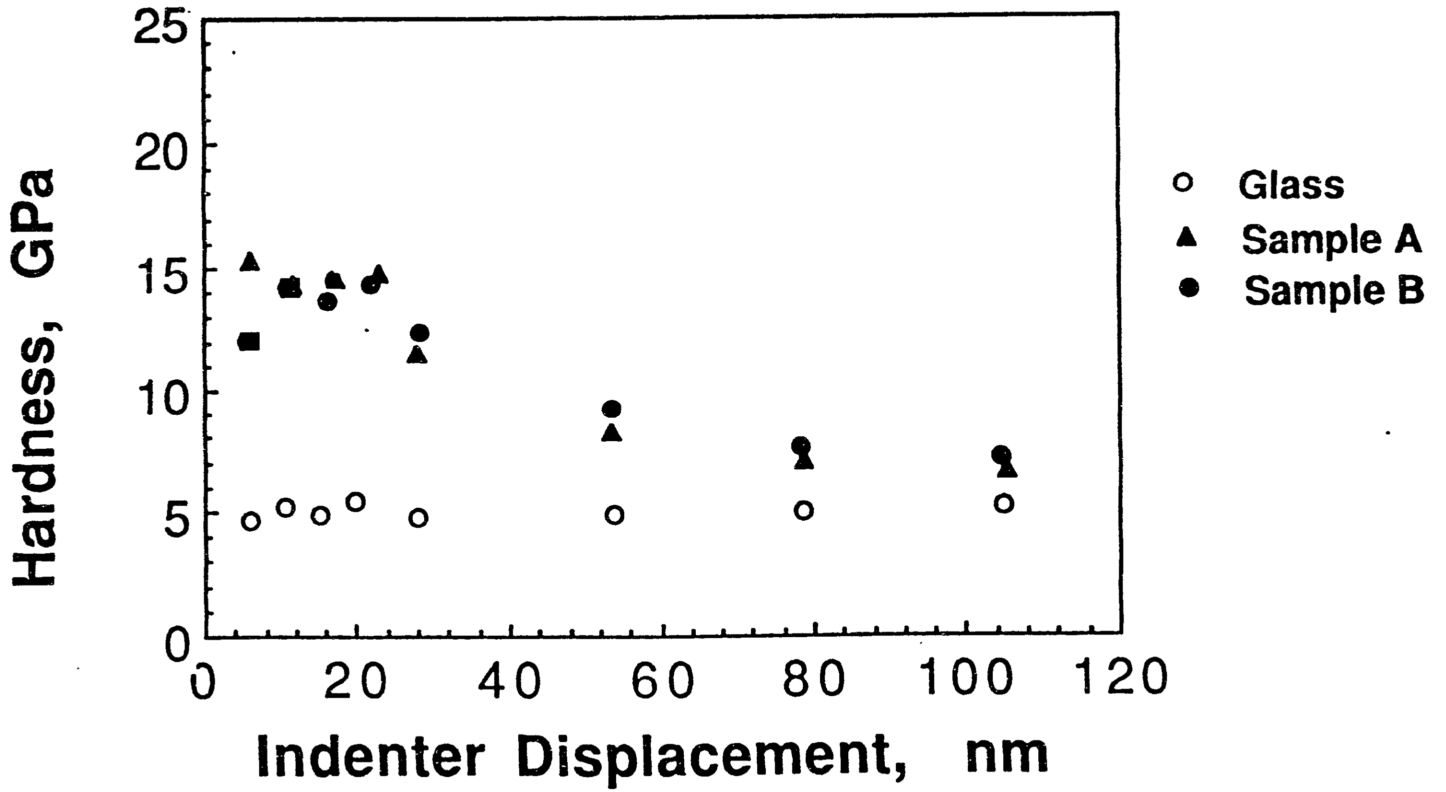


**Elastic Modulus = 370 GPa**

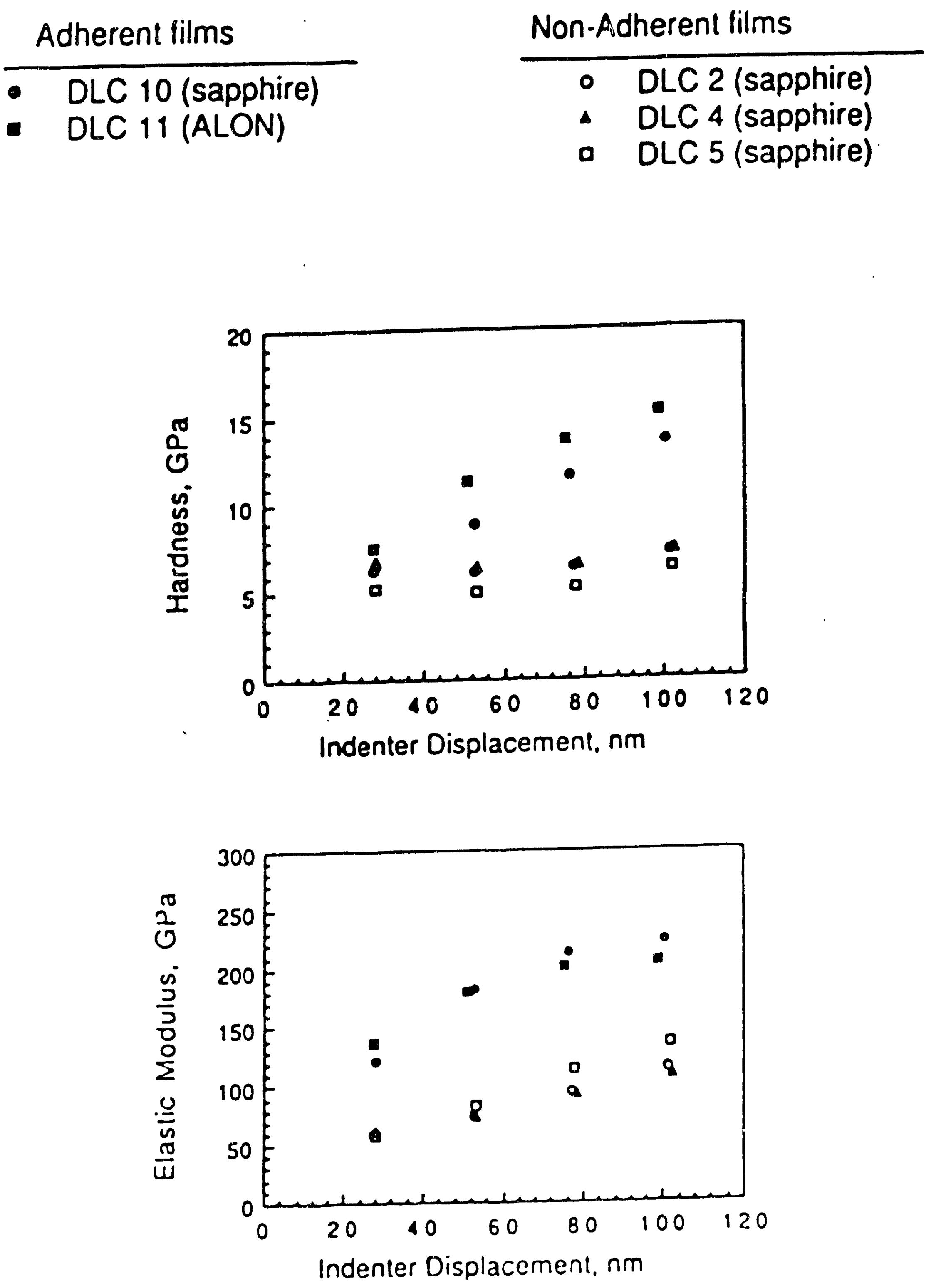
**(Collins et al)**

# THIN FILMS: DEPTH OF INDENT RELATIVE TO FILM THICKNESS

- **Softer substrate - HCC on glass**



**ornl**


Adherent films
● DLC 10 (sapphire)
■ DLC 11 (ALON)
Non-Adherent films
○ DLC 2 (sapphire)
▲ DLC 4 (sapphire)
□ DLC 5 (sapphire)
Hardness, GPa
0
5
10
15
20
0
20
40
60
80
100
120
Indenter Displacement, nm
Elastic Modulus, GPa
0
50
100
150
200
250
300
0
20
40
60
80
100
120
Indenter Displacement, nm

# RESULTS FOR DLC FILMS

"HCC" FILMS

| HARDNESS (GPA) | ELASTIC MODULUS (GPA) |
|---|---|
| 5 | 40 - 60 |
| 10 | 100 - 120 |
| 15 | 130 - 170 |

MICROCRYSTALLINE MIXTURE

| HARDNESS (GPA) | ELASTIC MODULUS (GPA) |
|---|---|
| 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

$\mathrm{II}_a$ $C^{12} = 3320$

$\mathrm{II}_a = 2000$

Akira ONO, Tetsuya BABA, Hiroyuki FUNAMOTO and Akira NISHIKAWA

Japanese JAP
Vol 25 p L808-810

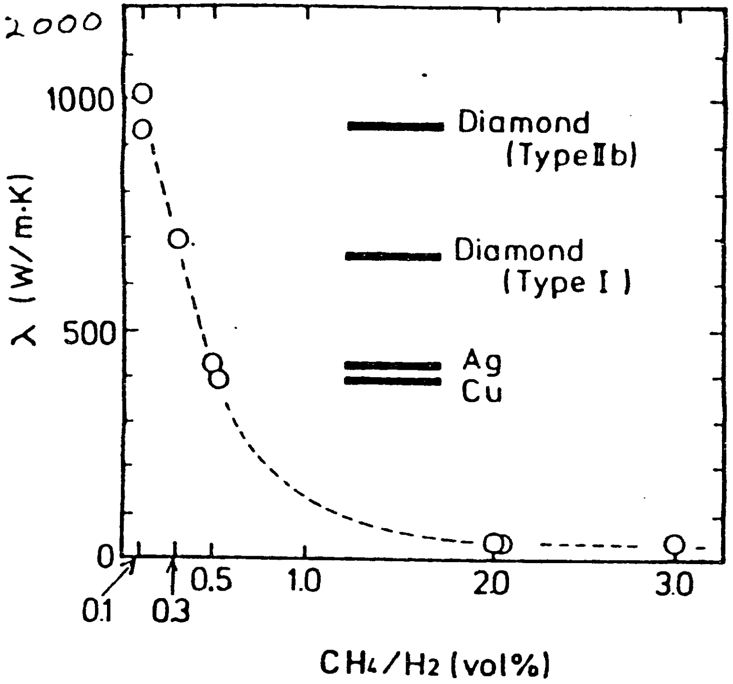


Fig. 3. Thermal conductivity of diamond films for different methane concentrations.

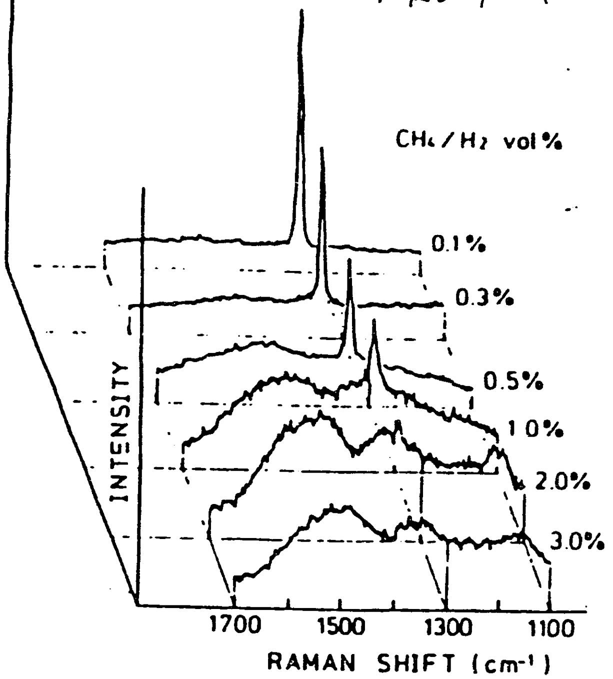
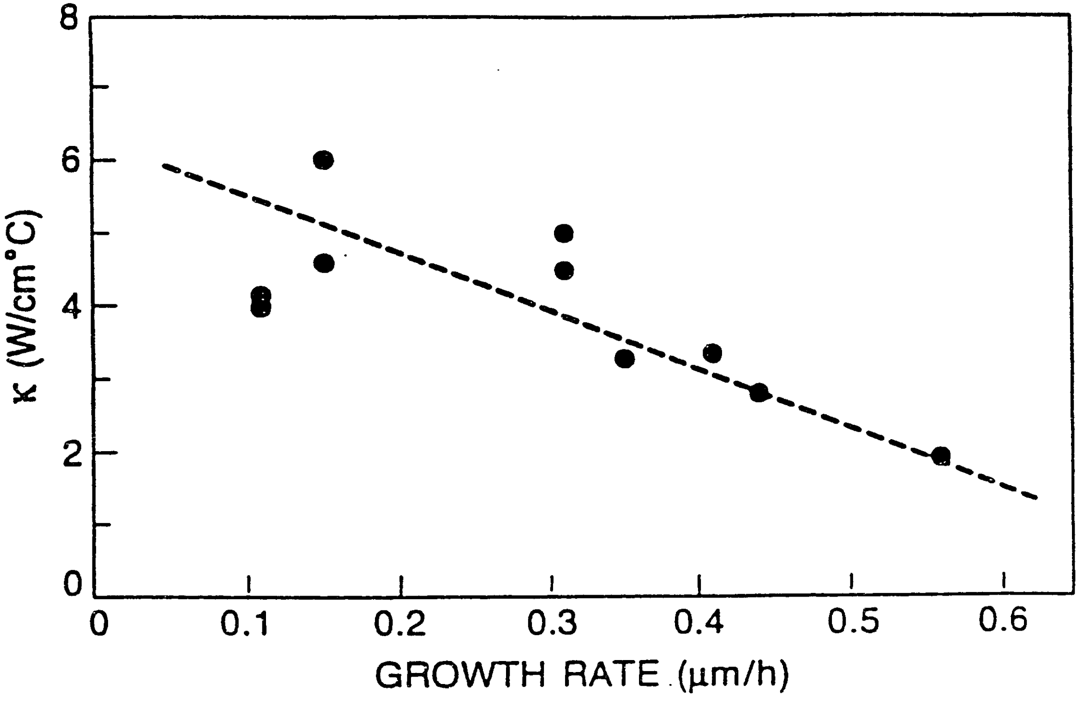


Fig. 4. Raman spectra of diamond films for different methane concentrations.

# GROWTH CONDITIONS CHANGE STRUCTURE AND THERMAL CONDUCTIVITY



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

GON 1M22459 03

# THERMAL CONDUCTIVITY IS BETTER FOR FILMS WITH A NARROW 1332 CM$^{-1}$ RAMAN LINE

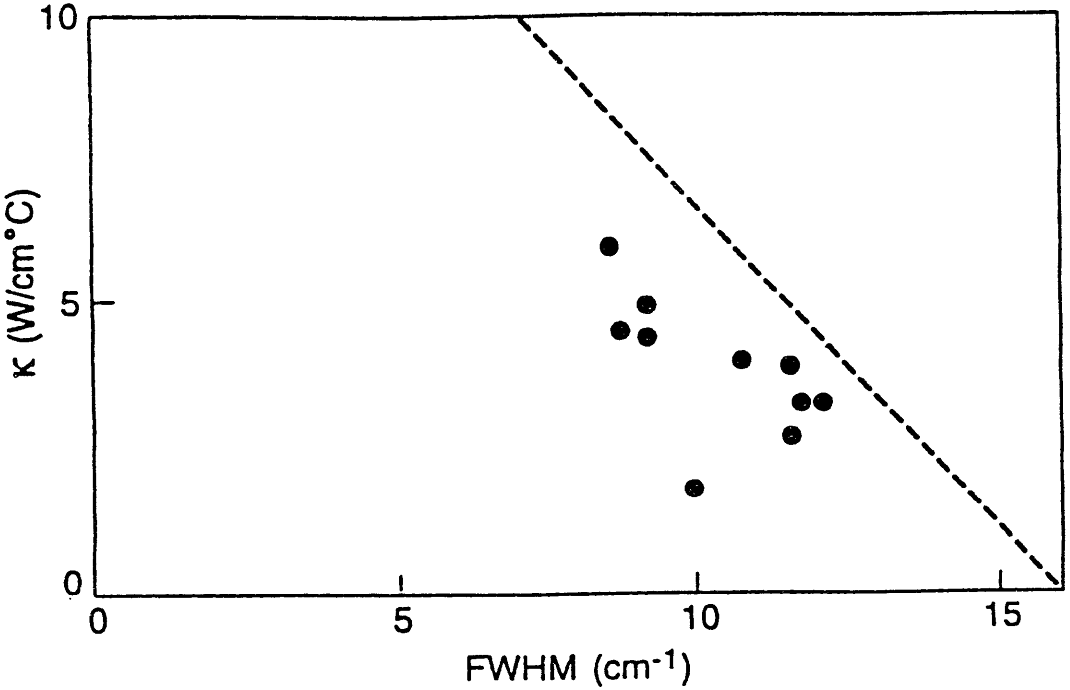


Figure 4. Thermal conductivity $\kappa(T = 25^\circ C)$ vs. linewidth $\Delta\nu$ of the diamond-like Raman line at 1332 cm$^{-1}$ for the CVD films listed in Table 1. The dashed

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

GCN 1M22453 00

# THERMAL CONDUCTIVITY OF DIAMOND FILMS CAN BE DIRECTIONAL BECAUSE OF STRUCTURE

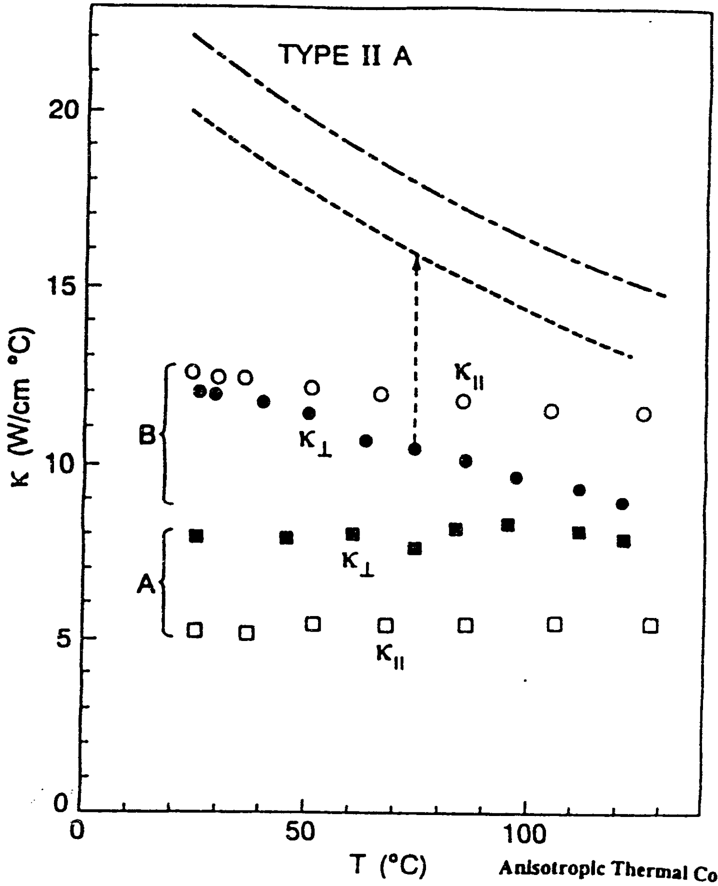


Fig. 5 Thermal conductivity vs. temperature for samples A (squares) and B (circles). The thermal conductivity for heat flowing parallel to the plane of the film is given by open symbols, perpendicular by closed symbols. κ for single-crystal Type IIa diamond (Ref. 13) is shown by the dot-dashed line. 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**

*J. E. Graebner*
*S. Jin*
*G. W. Kammlott*
*B. Bacon**
*L. Seibles*

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

*W. Banholzer*

General Electric Research Center
Schenectady, N.Y.

FIG. 5

# THERMAL CONDUCTIVITY OF DIAMOND FILMS CAN BE A FUNCTION OF THICKNESS WHEN THE STRUCTURE CHANGES WITH THICKNESS

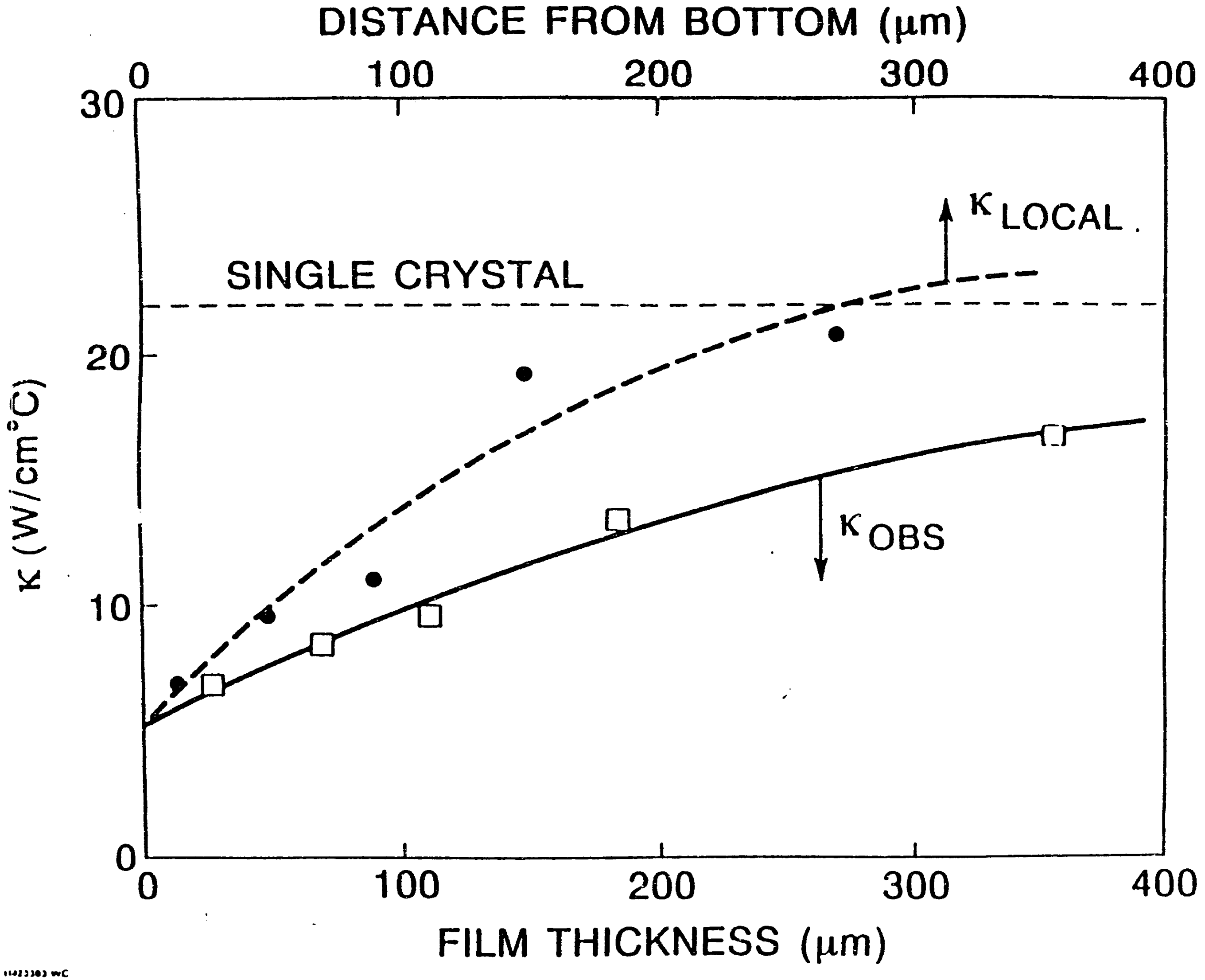
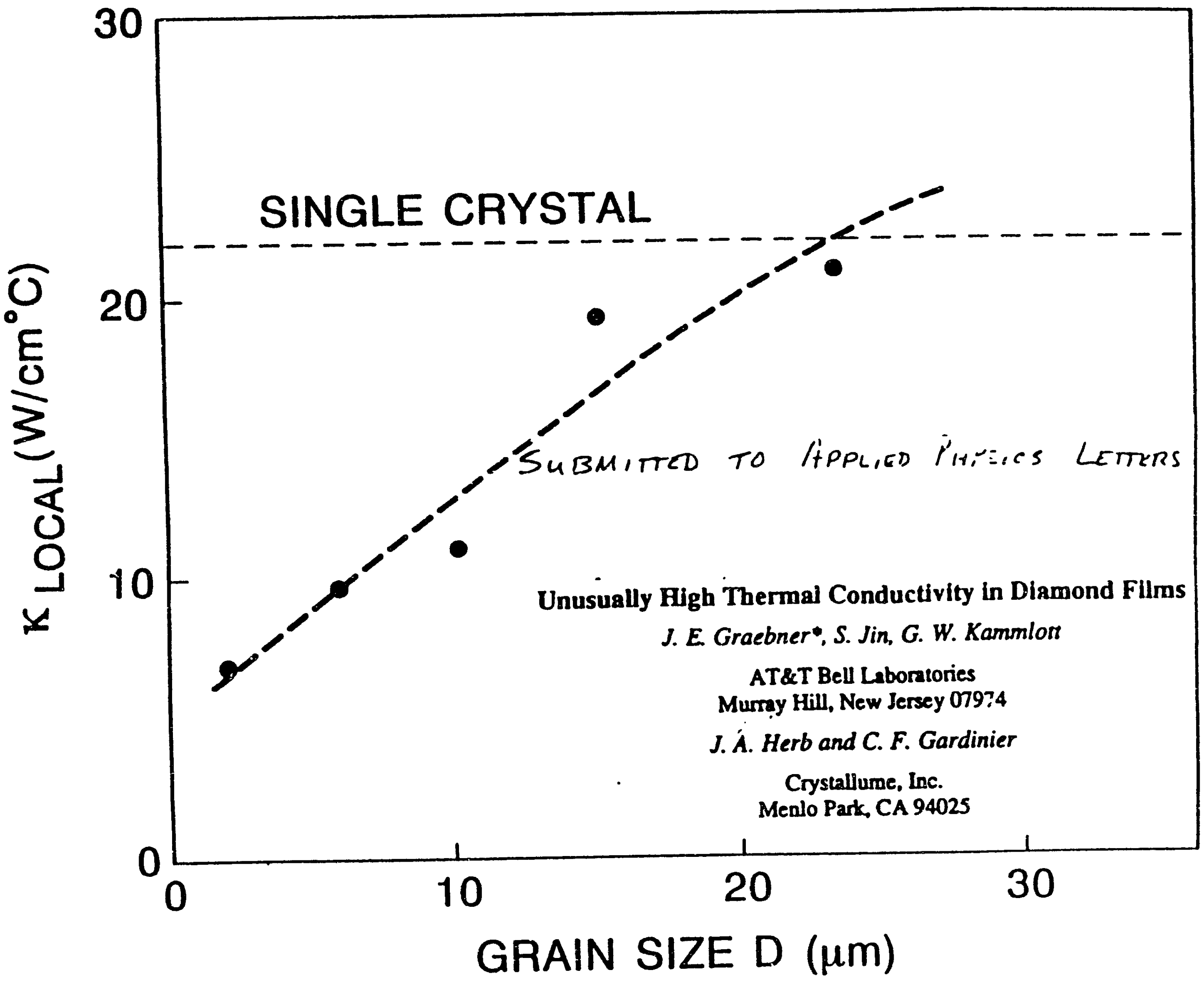


Fig. 4 Measured thermal conductivity $\kappa_{obs}$ at 25°C for five samples (squares). The local conductivity as derived according to Eq 2 is shown by solid circles. The line through the $\kappa_{obs}$ data is a 3-term polynomial (Eq. 2) least-squares fitted to the data. The dashed curve is the derived local conductivity $\kappa_{local}$ 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 IIa)

# EFFECT OF GRAIN SIZE ON THERMAL CONDUCTIVITY



SUBMITTED TO APPLIED PHYSICS LETTERS

**Unusually High Thermal Conductivity in Diamond Films**

*J. E. Graebner*, S. Jin, G. W. Kammlott*

AT&T Bell Laboratories
Murray Hill, New Jersey 07974

*J. A. Herb and C. F. Gardinier*

Crystallume, Inc.
Menlo Park, CA 94025

Fig. 5 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) $0.15 \times 10^{-4}$mm min$^{-1}$
  - (110) $0.8 \times 10^{-4}$mm min$^{-1}$
  - (111) $01.5 \times 10^{-4}$mm min$^{-1}$

Field p405

**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

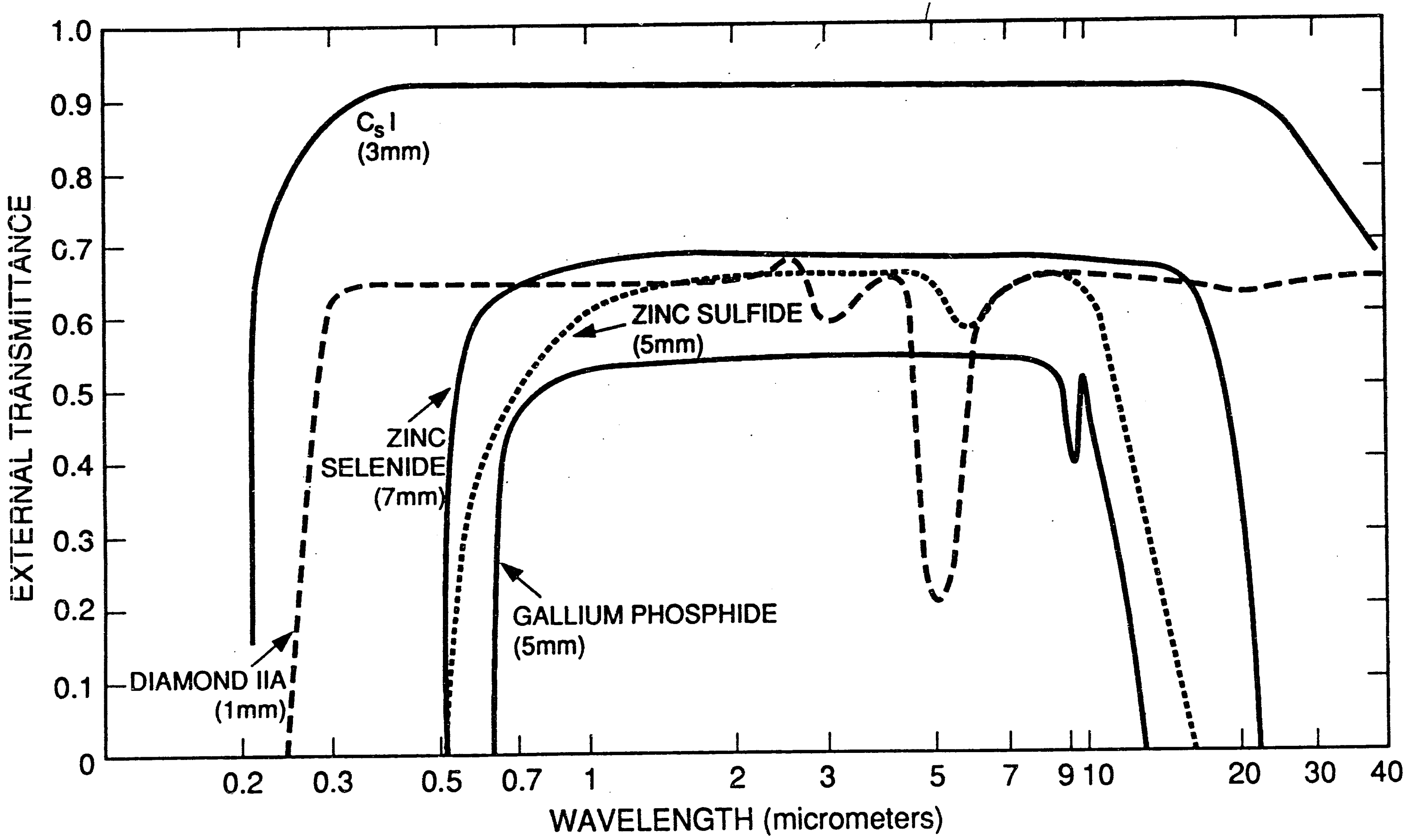
Oxygen Plasma Etching seems to follow qualitatively in the same order

# Structure and Properties of Diamond and Diamond-Like Films

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

ORNL-DWG 90M-16996

TRANSMISSION SPECTRA OF BROAD BAND INFARED OPTICAL MATERIALS



# Structure and Properties of Diamond and Diamond-Like Films

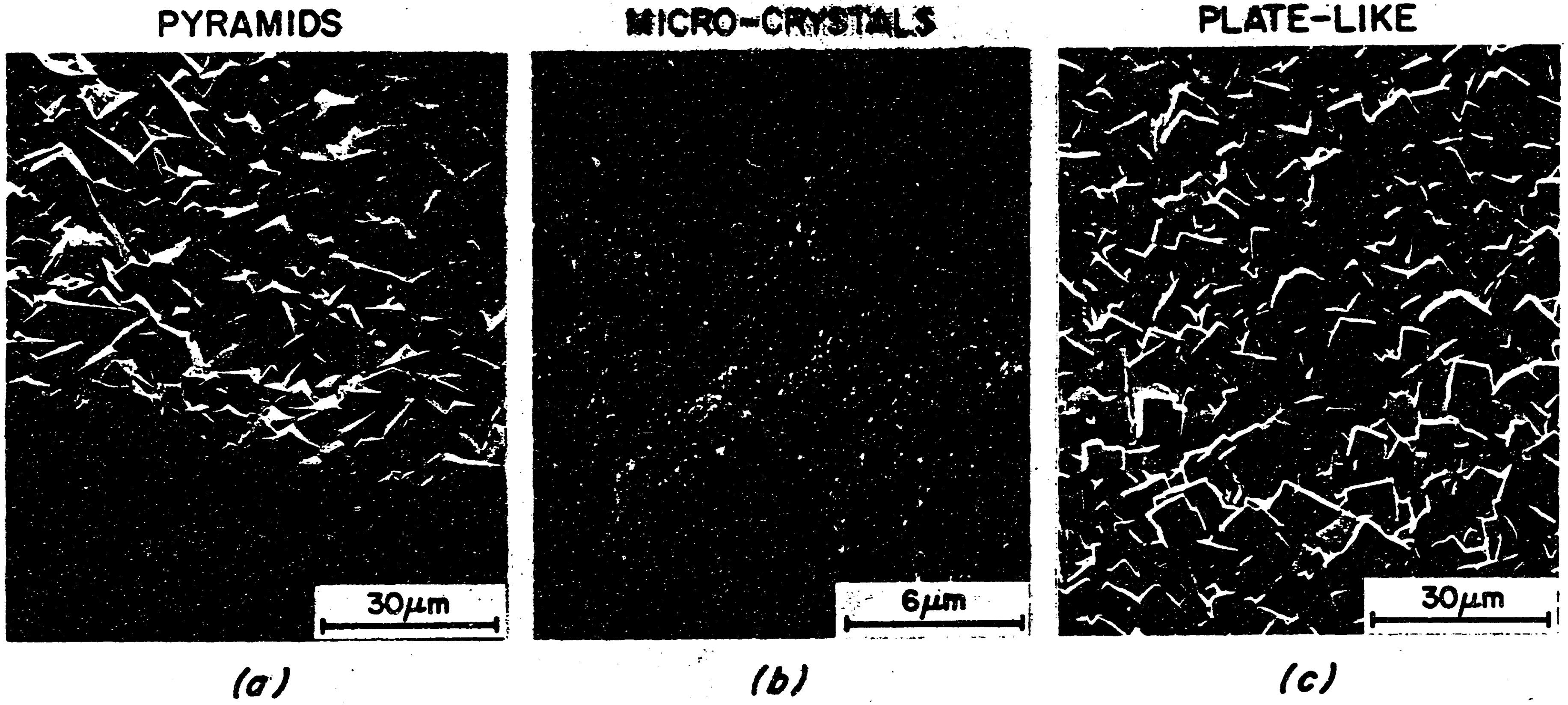
- Introduction
- Natural IIa Diamond (The Standard)
- Importance of Structure and Composition
- Control of Structure and Properties

# 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

ORNL-PHOTO 4908-89

# DIAMOND FILM MORPHOLOGIES



ornl

# Thesis

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.

ornl

## Hypothesis #1

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

ornl

## 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.

ornl

# 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.

ornl

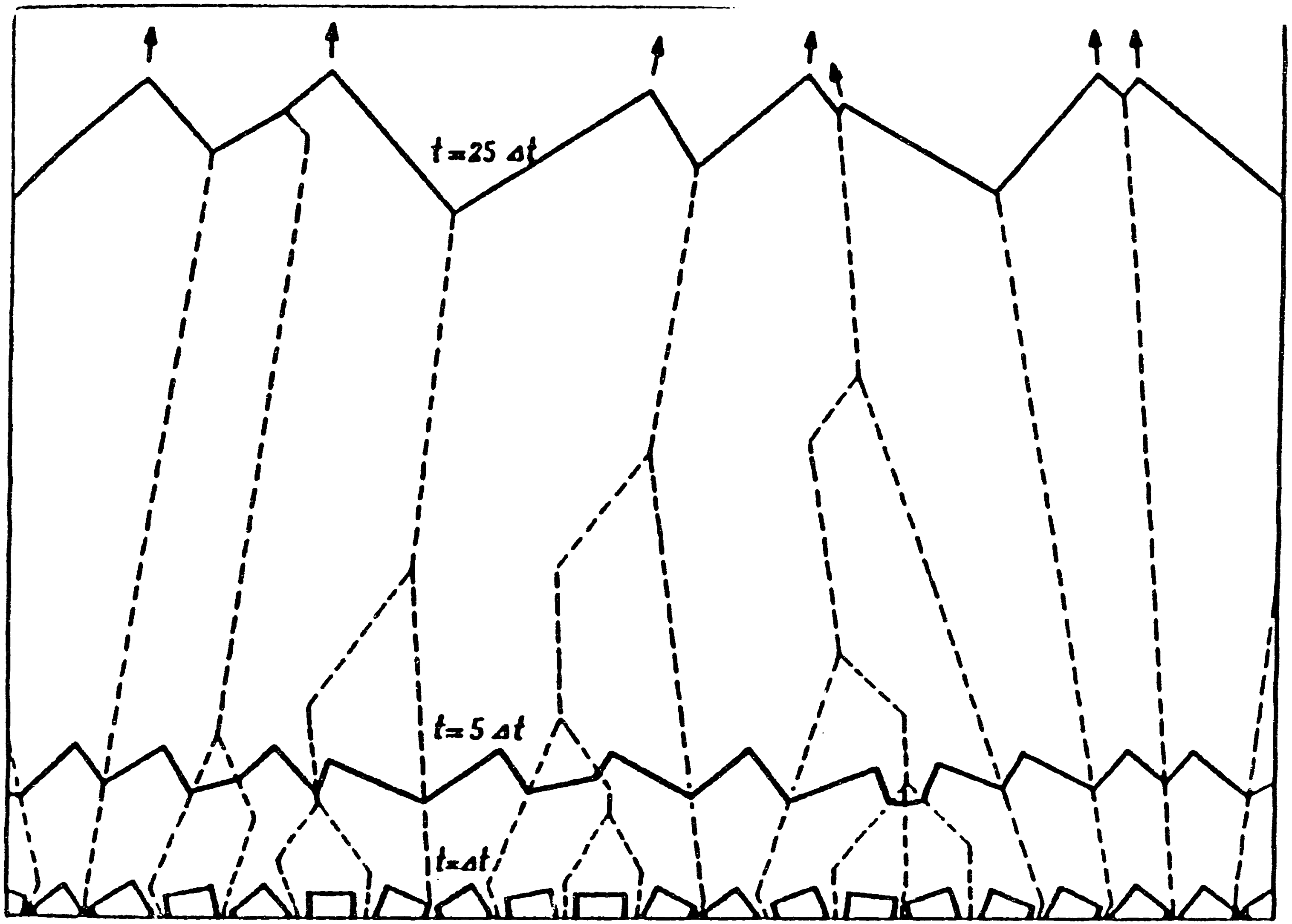
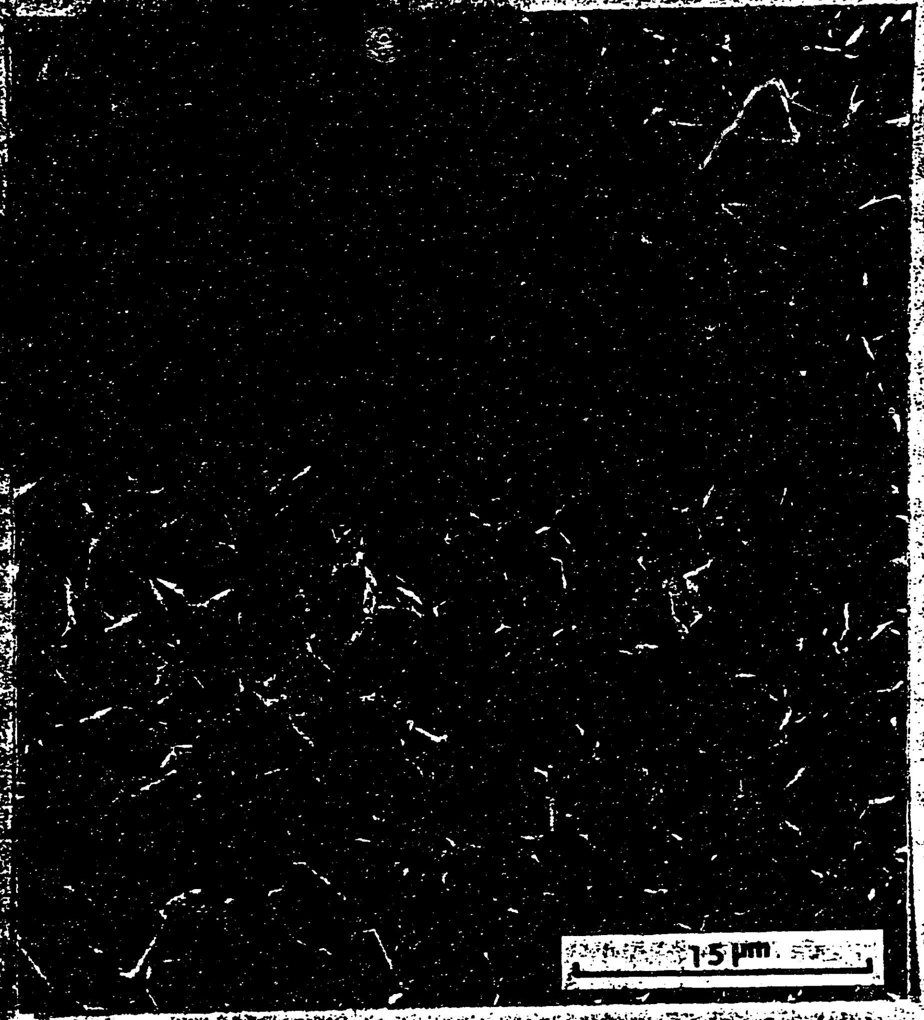


Fig. 4*a*. Starting from random-orientated equidistant (10)-bounded "cubic" crystals in a two-dimensional space and assuming infinite surface diffusion even along the substrate, the inter-crystal boundaries (dashed lines) as well as the crystal front at different times (at $t = \Delta t$, $t = 5\,\Delta t$ 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.

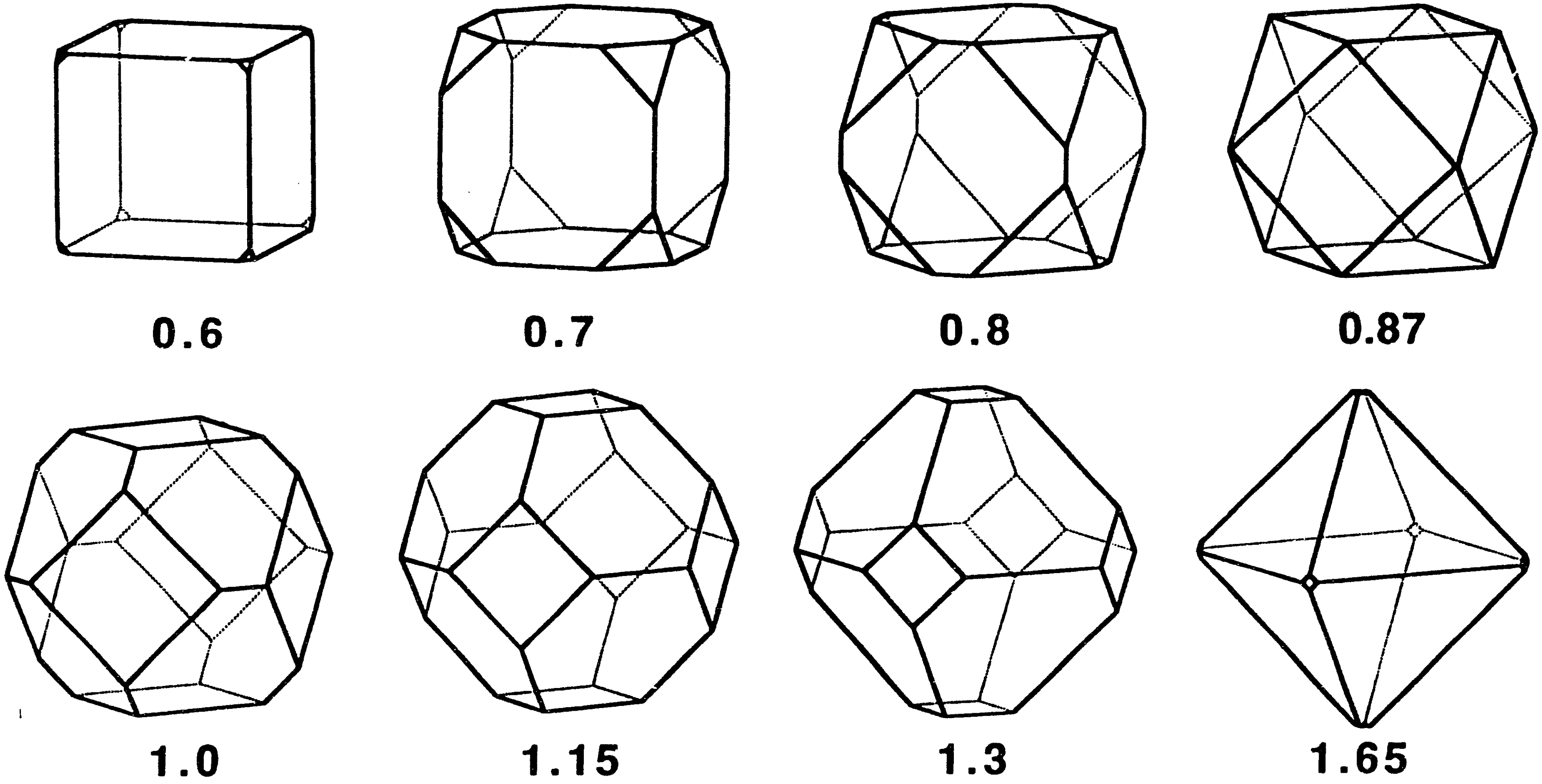
# FILMS EXHIBIT TYPICAL PYRIMIDAL, "{111}" MORPHOLOGIES

- Cubo-octahedral Crystallites
- Twinned Microstructure



1% methane
1050C

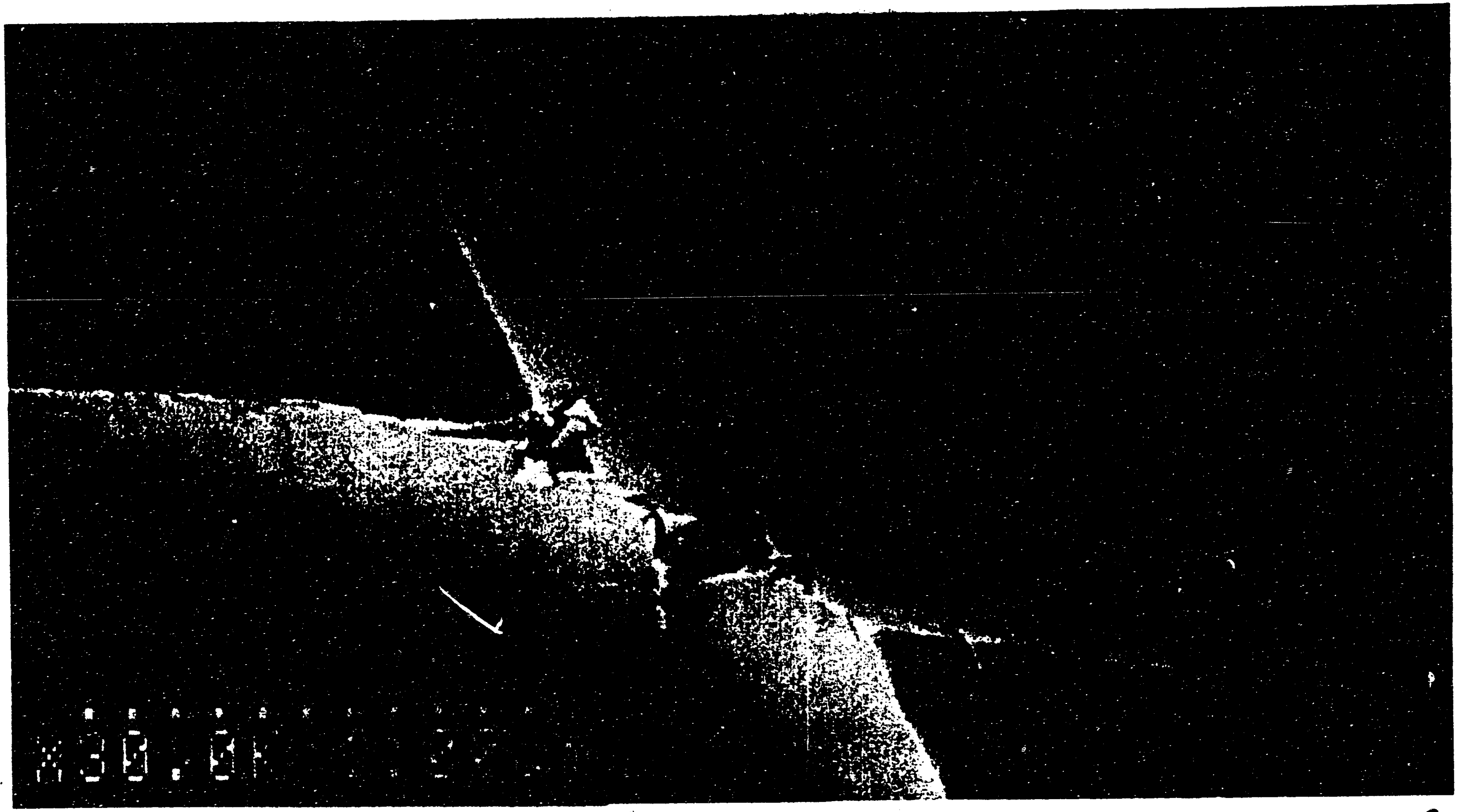
Cubo-octahedral shapes reveal the ratio of growth rates in the <100> and <111>directions. The <100>/<111> value is given.



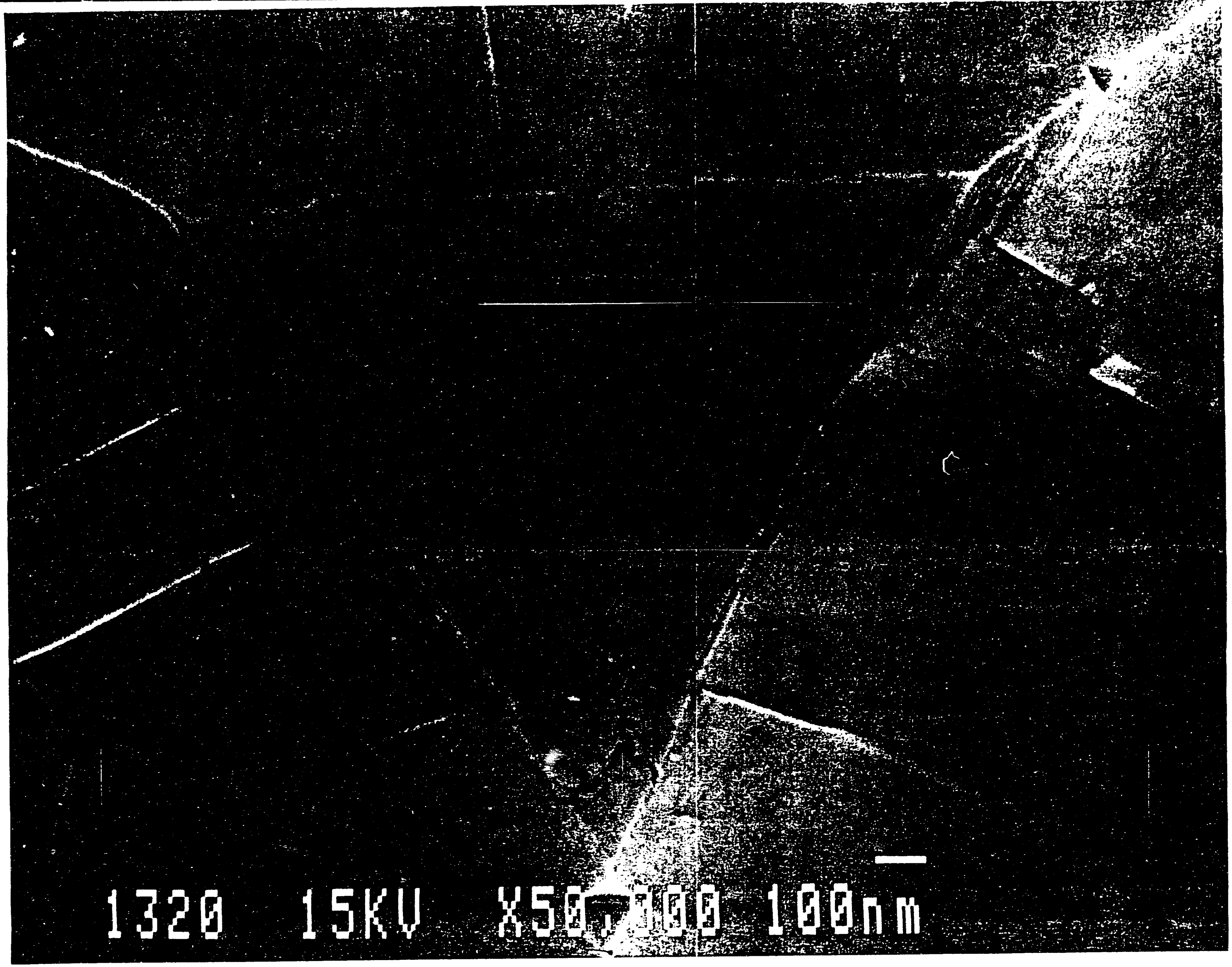
0.6 0.7 0.8 0.87

1.0 1.15 1.3 1.65

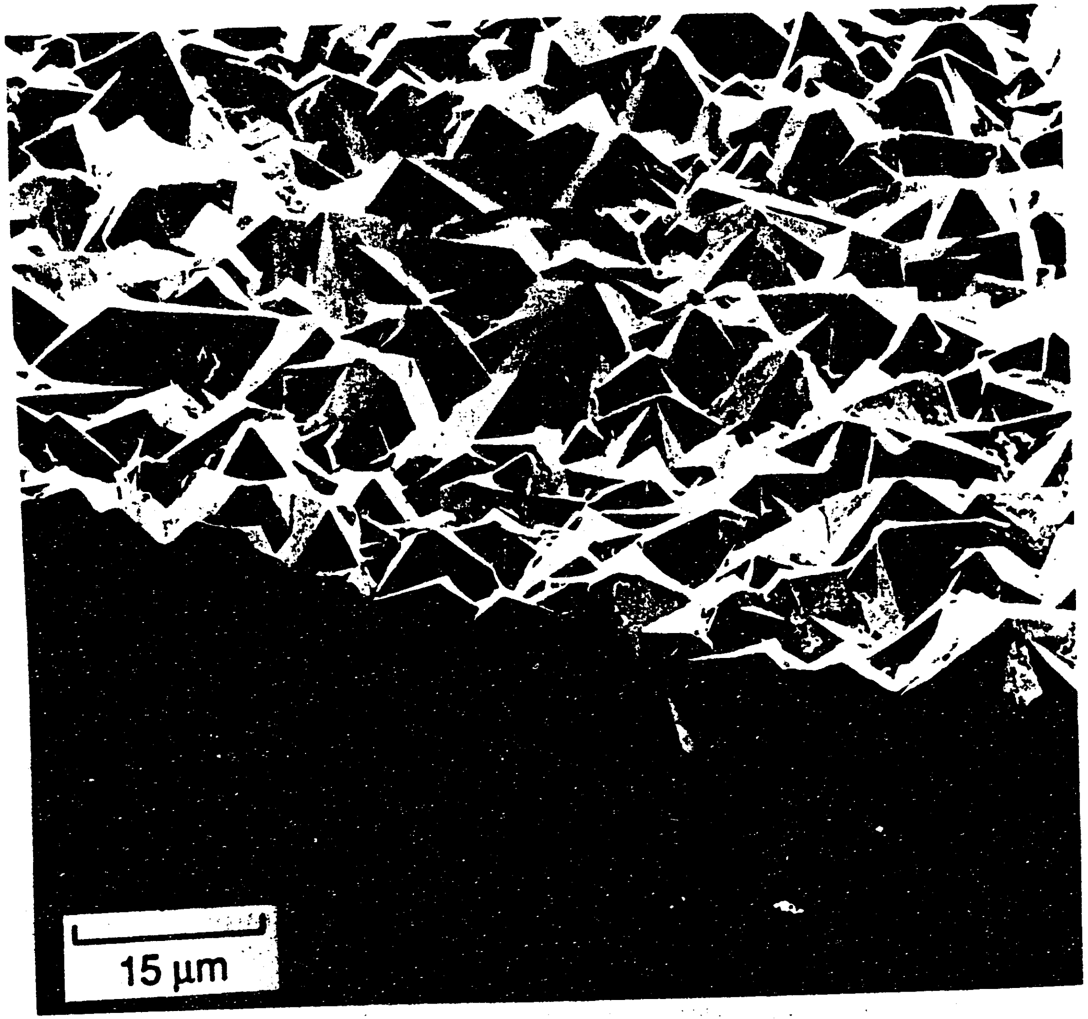
# [111] faces have rough micro-faceted surfaces
# [100] faces are smooth



ornl


1320 15KV X50,000 100nm

# The fractured edge of a free standing film shows the rough faceted surface and the columnar grain structure



YP10180

ornl

# TEM shows ubiquitous twinned structures

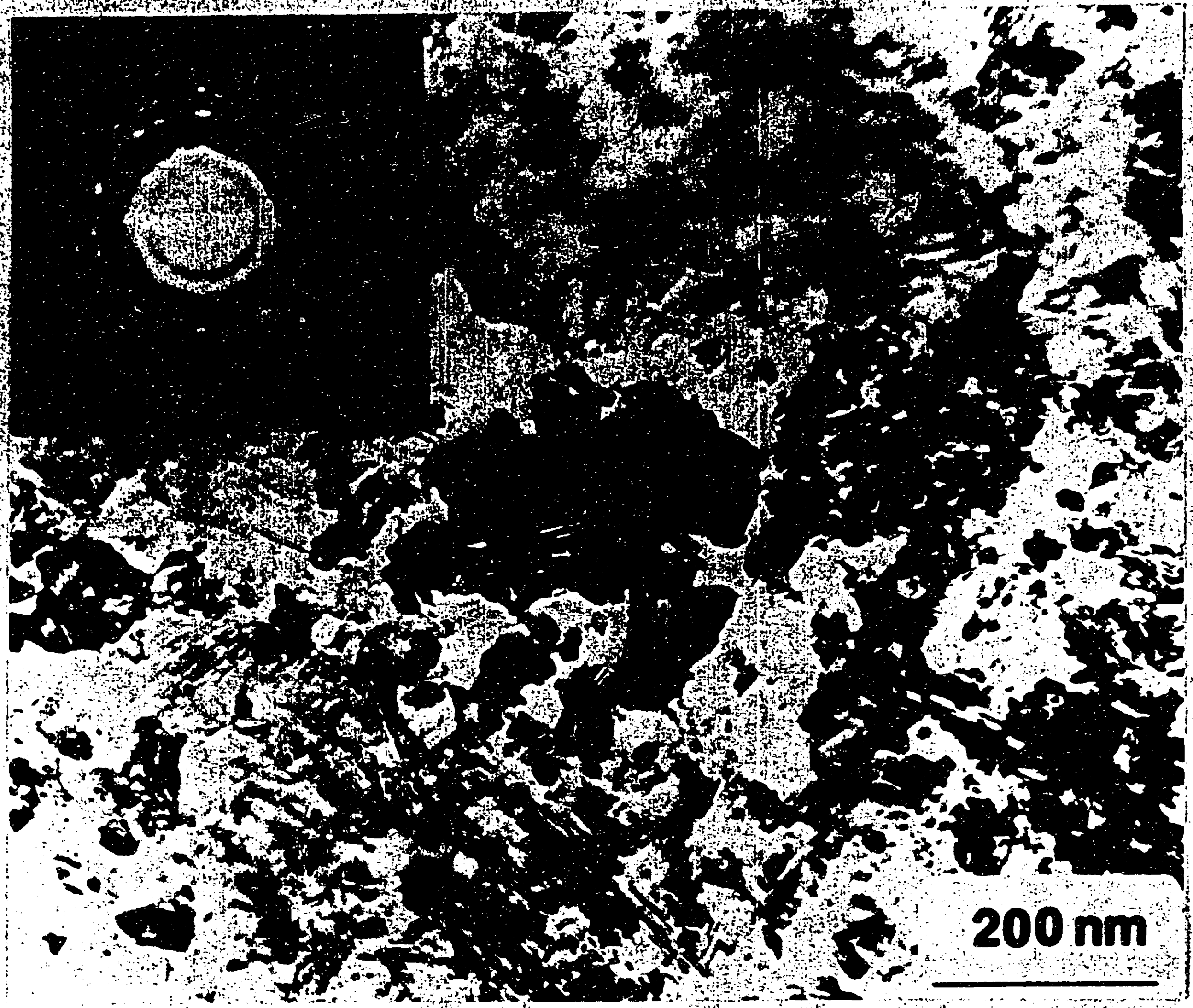
orml

4010186

# At 920C and below films are microcrystalline.

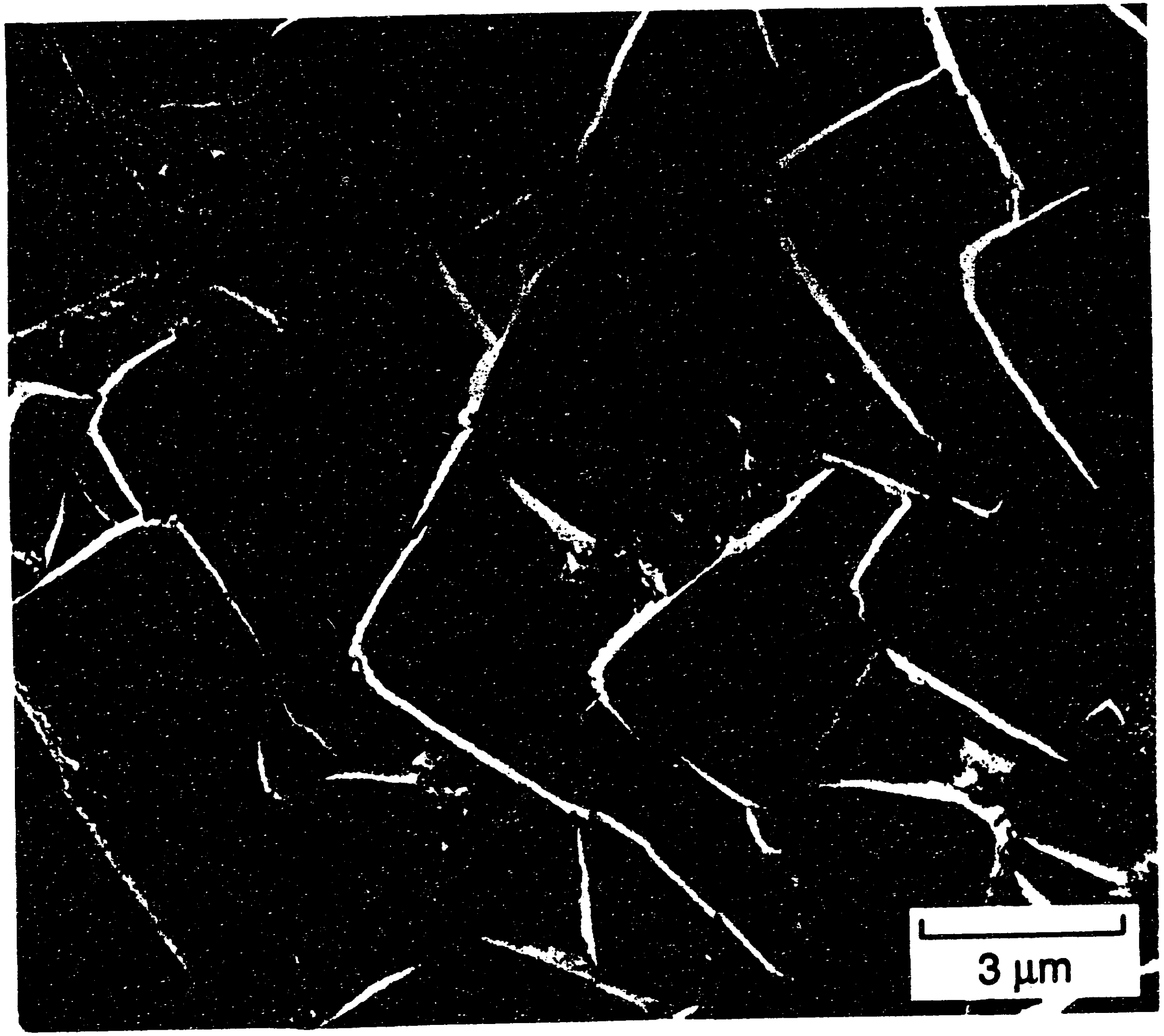
ornl

# Microcrystalline material is full of micro-twins and defects.



ornl

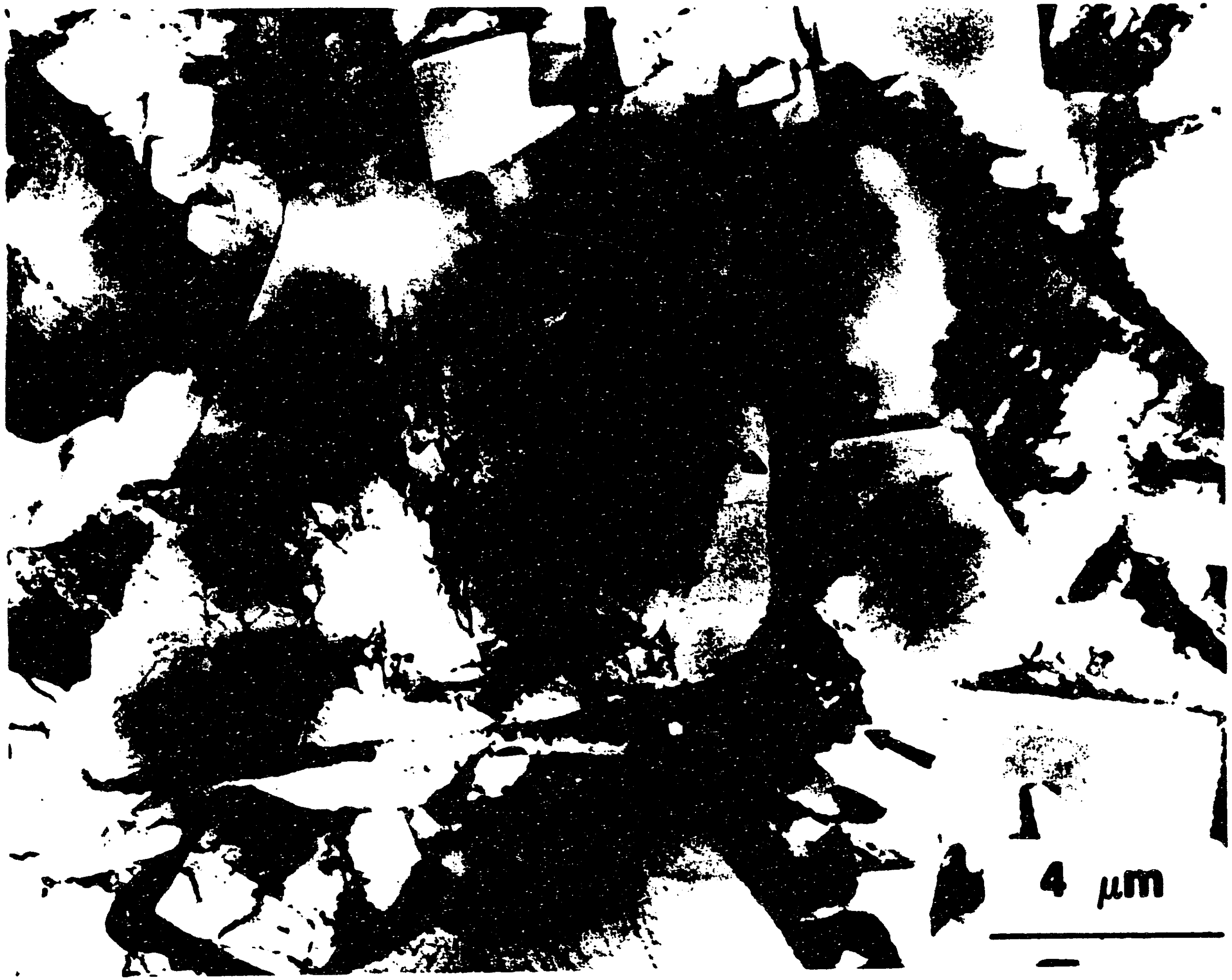
# In a narrow range near 950C square [100] Facets develop



ornl

4P10182

# The grains contain no twins or stacking faults



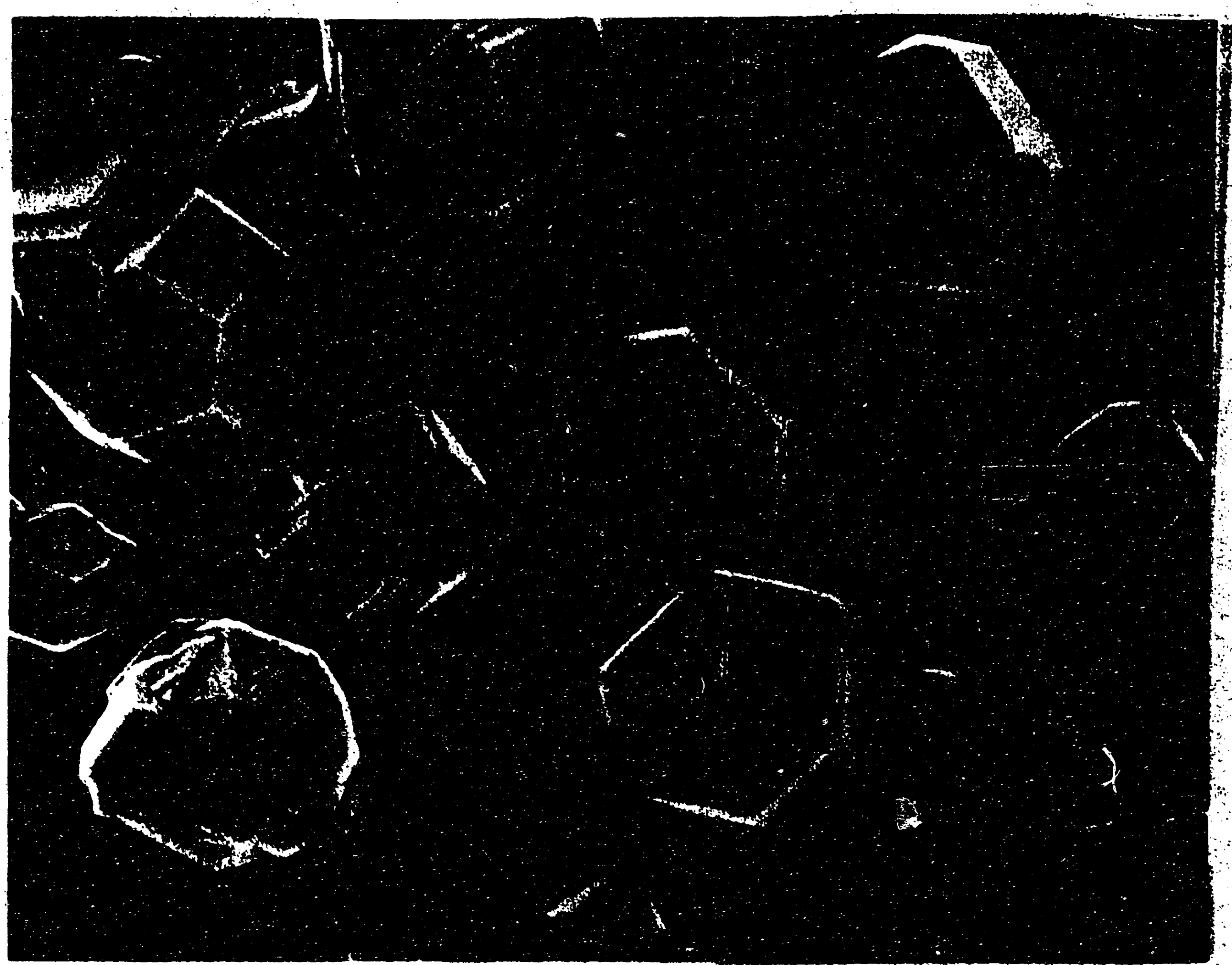
ornl

9P10138

# Grainboundary regions included very defective material.

ornl

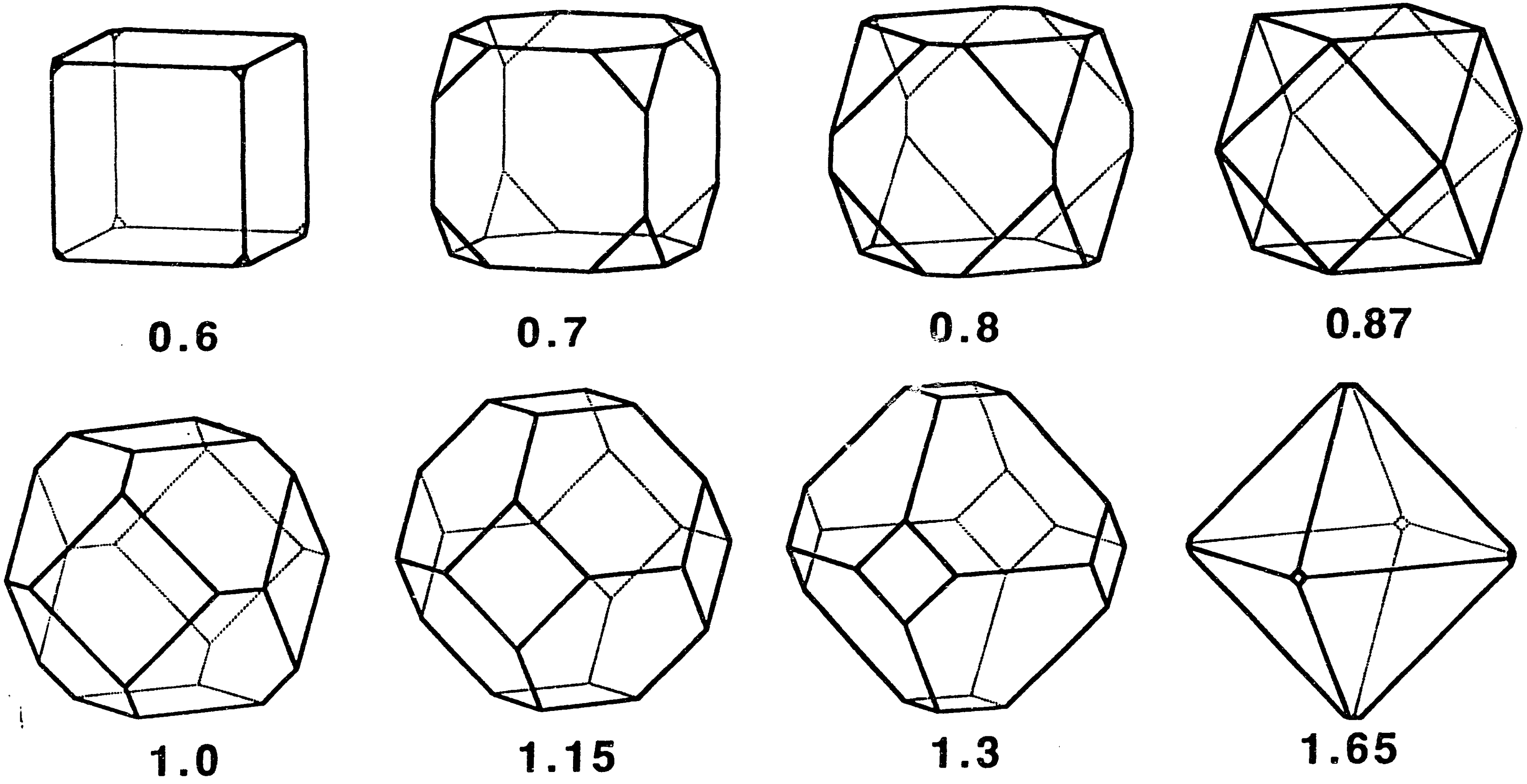
# The initial nuclei are randomly oriented cubo-octahedra.



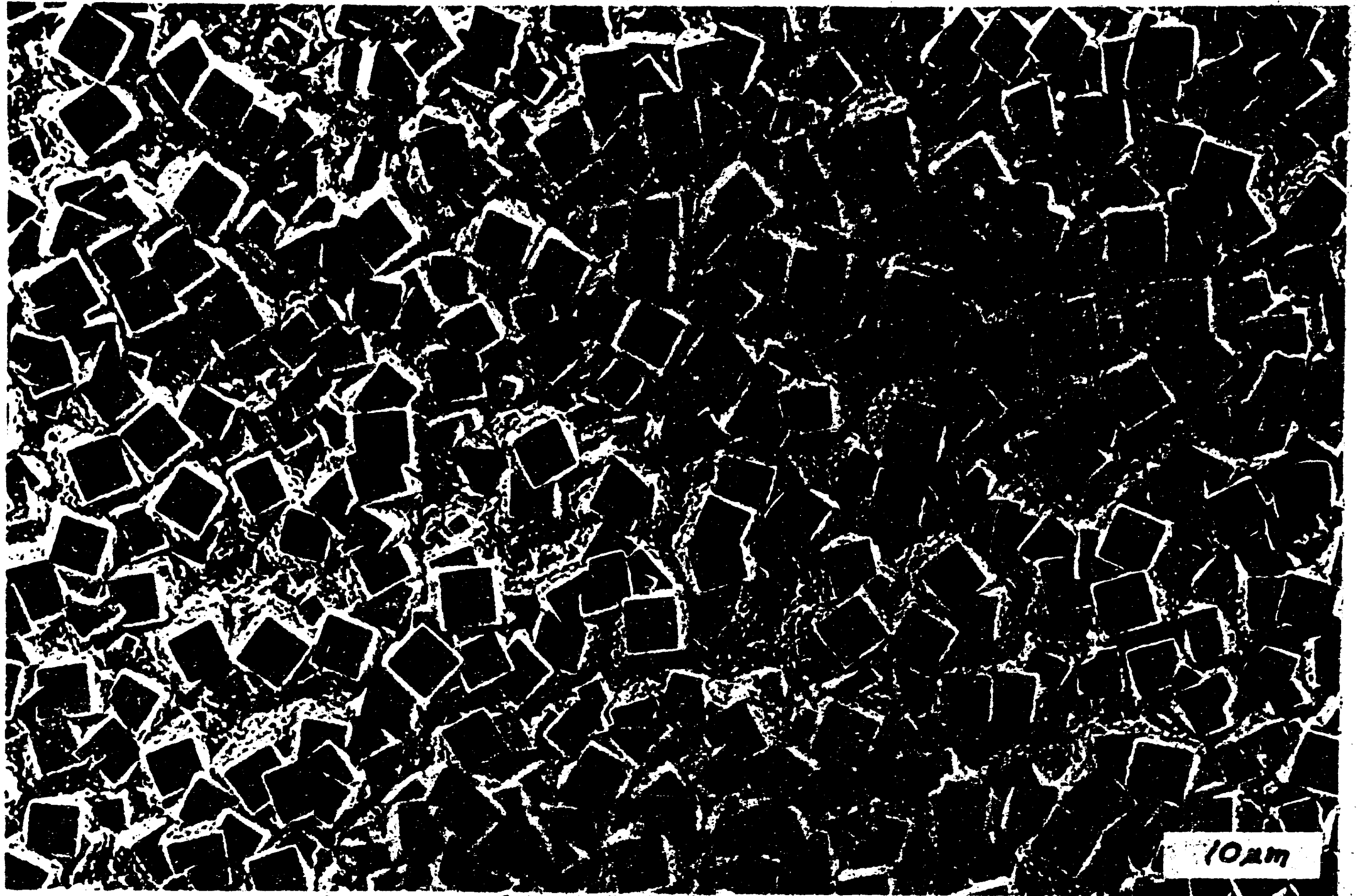
R ~ 1.05

ornl

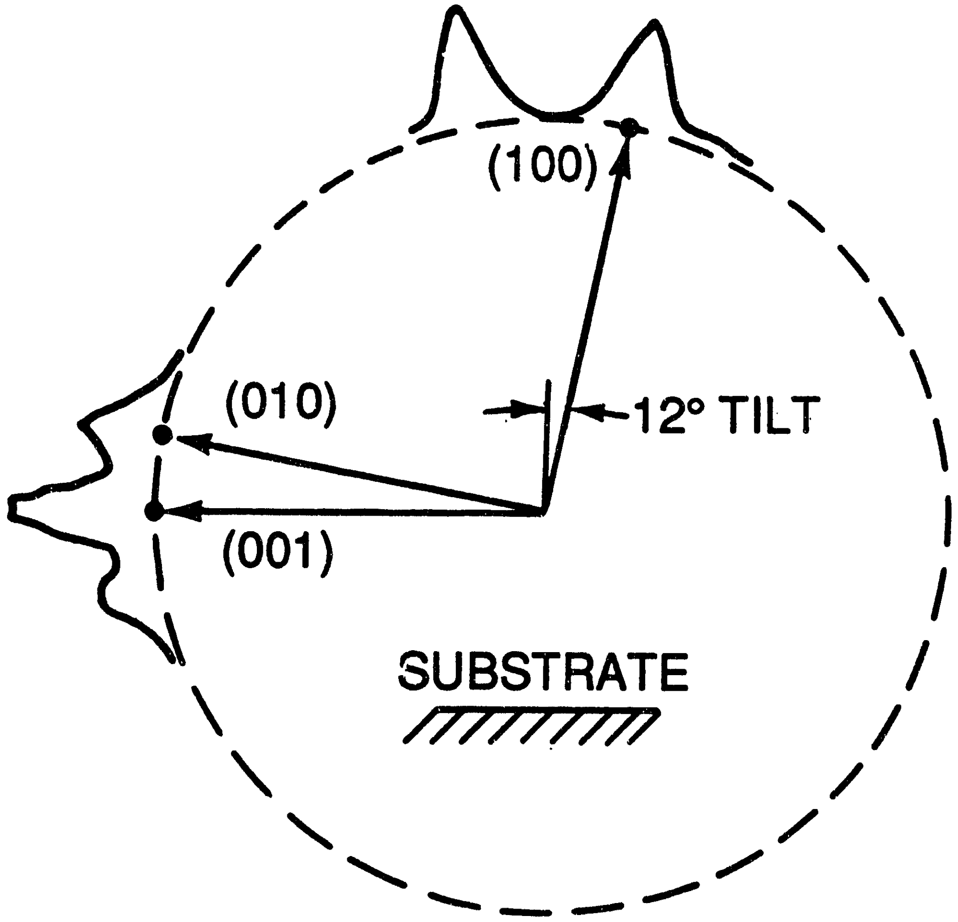
Cubo-octahedral shapes reveal the ratio of growth rates in the <100> and <111>directions. The <100>/<111> value is given.



# After 20 hours the <100> texture is clearly developed.



89-13439



Si (1,0,0) PARALLEL TO
C (1,0.2,0)

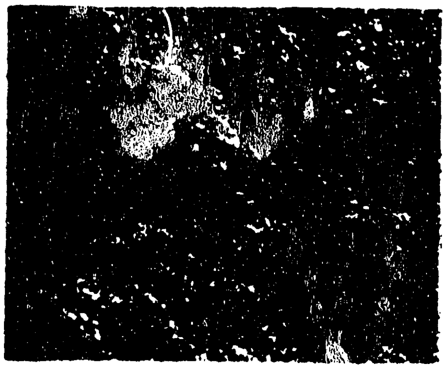
X-RAY TEXTURE DIAGRAM FOR DIAMOND FILM GROWN AT 930–950°C USING 1% $CH_4$ IN HYDROGEN

# Growth Conditions Determine the Internal and External Morphology of Diamond Films

SEM

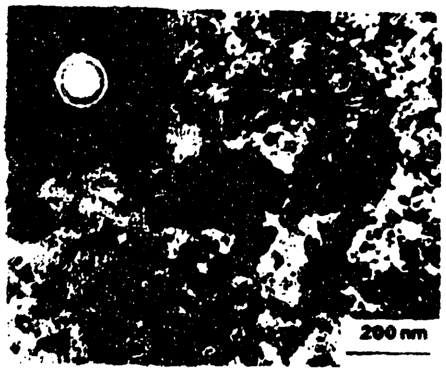
TEM

900°C



**Microcrystalline**

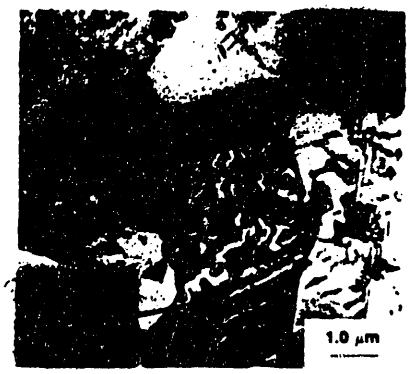
- smooth surface
- very fine grain size (<0.2 μm)
- poor crystal perfection



1050°C

**(100) & (111) Facets**

- sharp angular faceted surfaces
- grain size of 2-30 μm
- good crystal perfection but twins and stacking faults

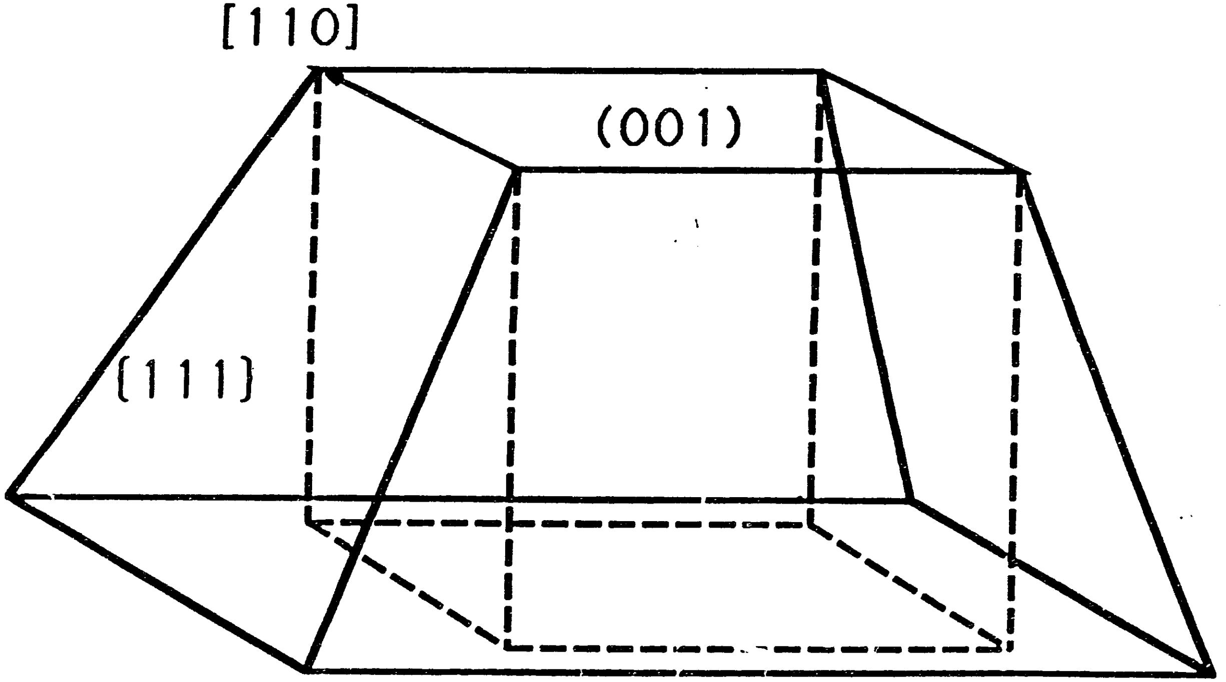


930°C

**(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

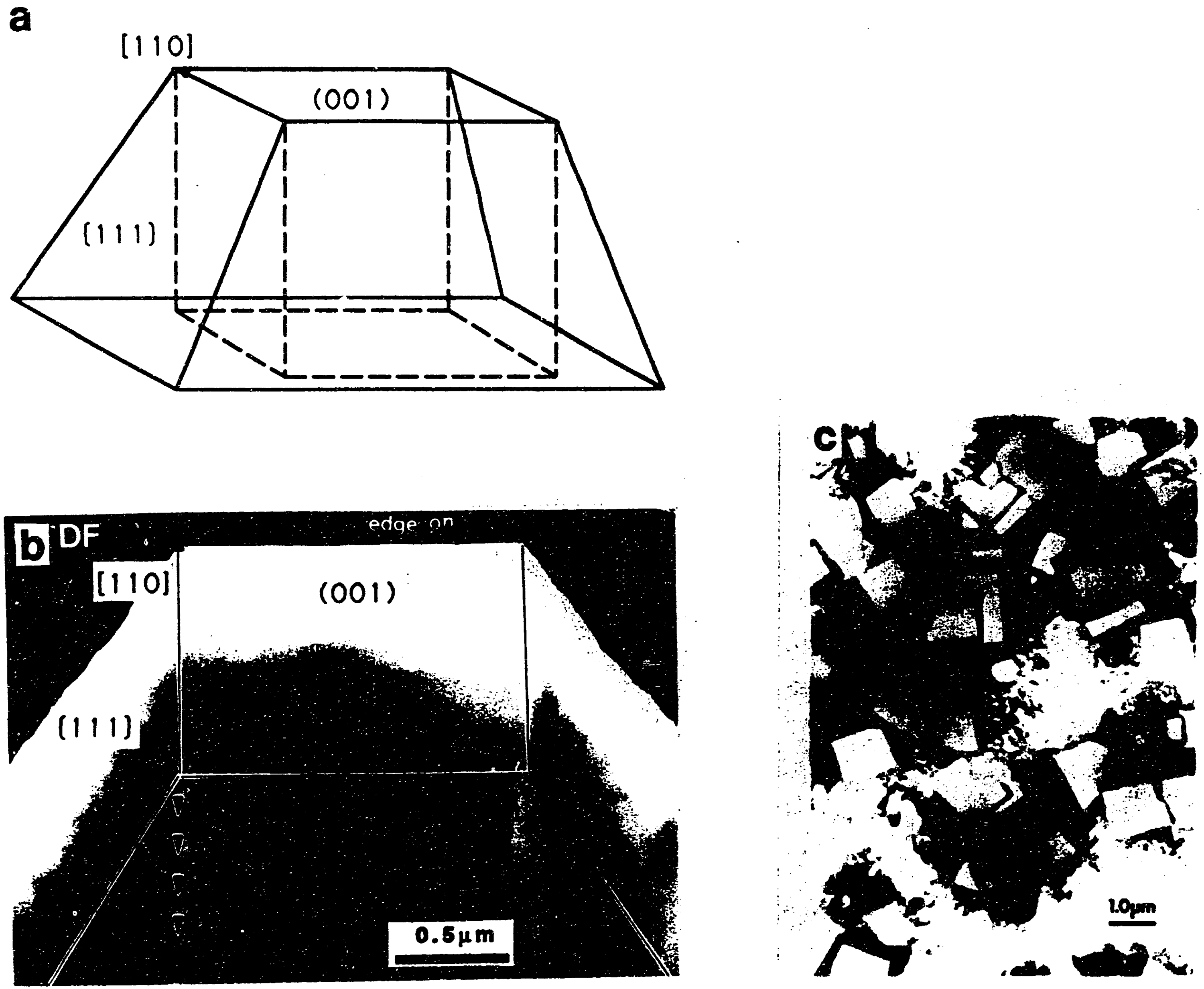
# <100> TEXTURED MATERIAL GROWN WITH BOTH (001) AND {111} FACES HAS A CENTRAL VOLUME GROWN FROM A (001) FACE SURROUNDED BY MATERIAL GROWN FROM {111} FACES.



ornl

YP10170

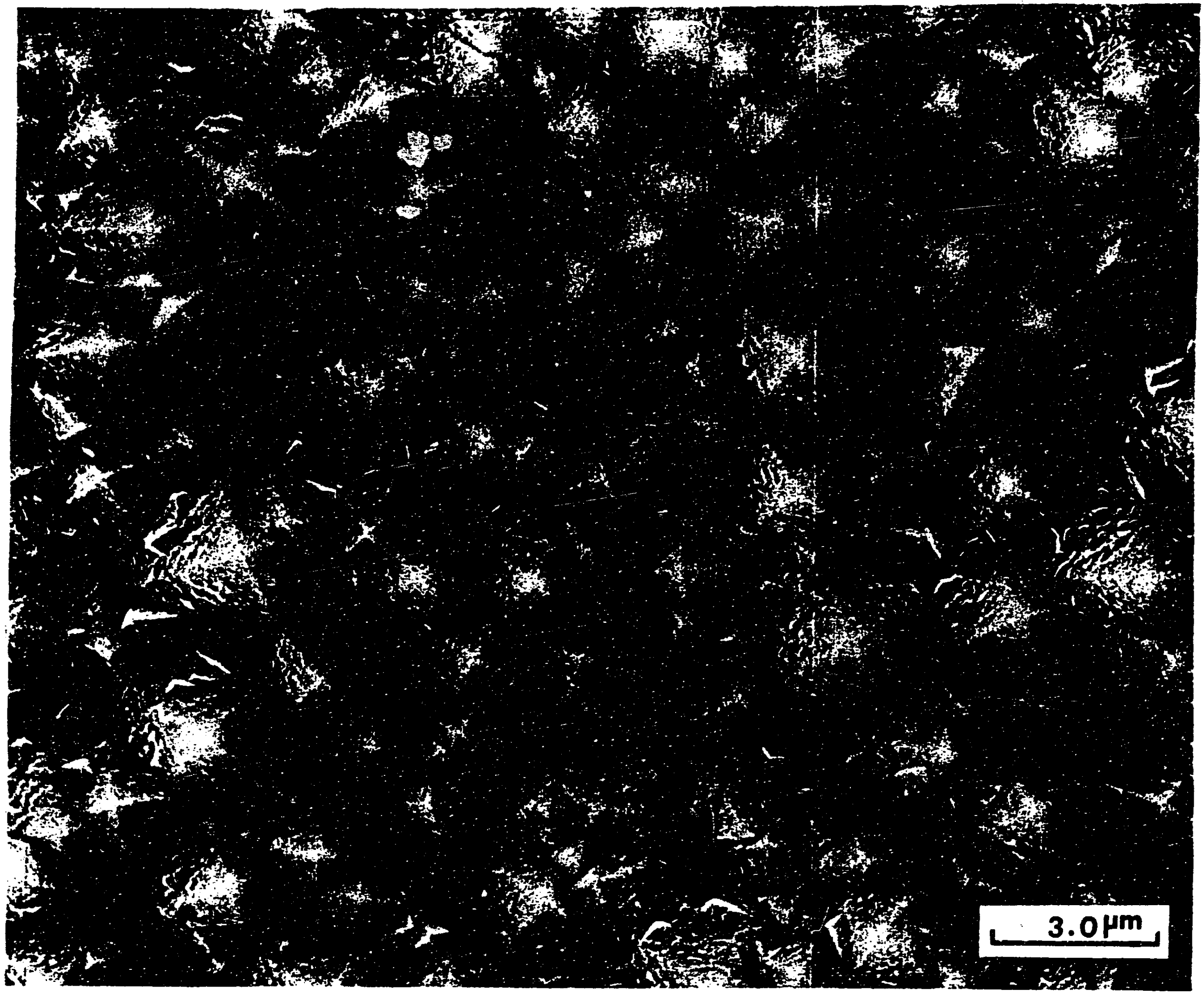
# <100> textured films with (100) facets have smooth surfaces and columnar grains.



YP13223

$R \approx 2.6$

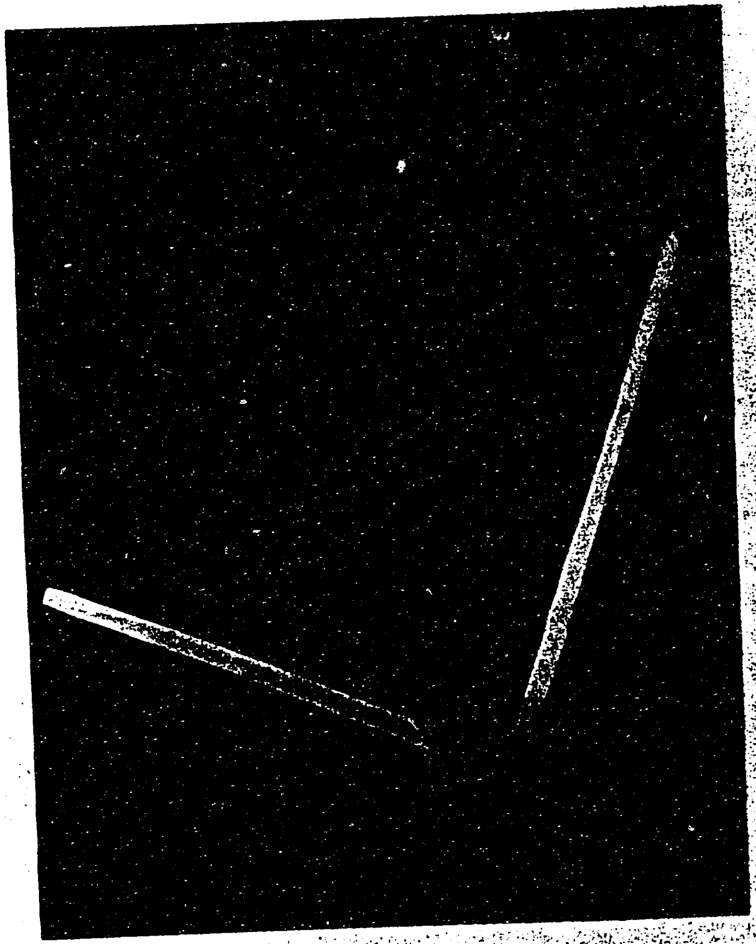
## It is possible to change the growth conditions to produce a <100> texture with (111) facets.



ornl

YP10177

# CVD DIAMOND GROWTH CONDITIONS CAN BE CONTROLED TO PRODUCE THE FULL RANGE OF CRYSTAL HABITS



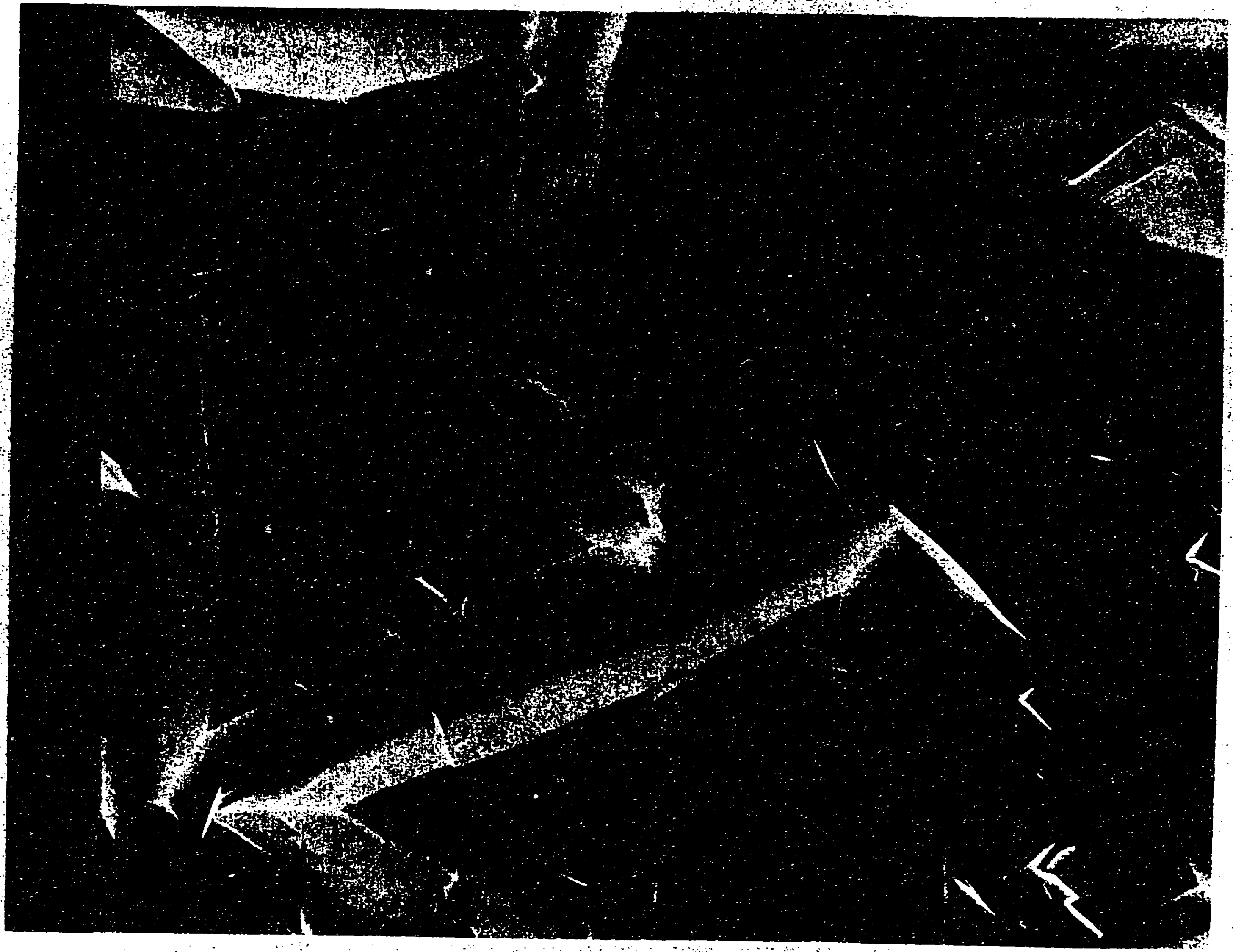
R=0.6

R= 1.7

ornl

YP11988

# FILMS CAN BE GROWN WITH A <111> TEXTURE AND LARGE {111} FACETS PARALLEL TO THE SUBSTRATE.



ornl

YP11992

# FILMS GROWN WITH THE RATIO OF GROWTH RATES OF THE <100>/<111> NEAR 0.6 PRODUCE <111> 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.

ornl

# 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.

ornl

# 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

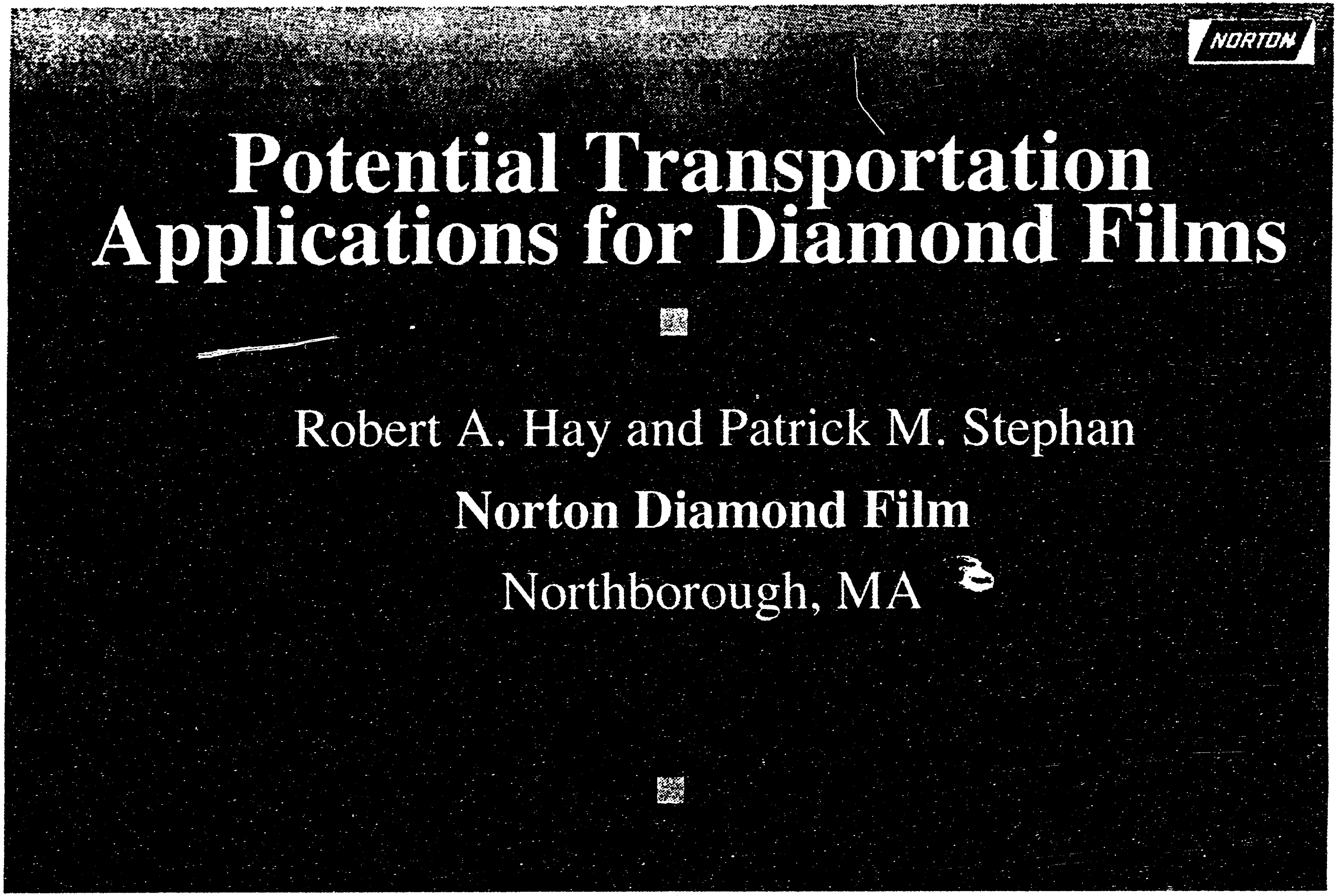
# SUMMARY

- 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.

ornl

# 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.



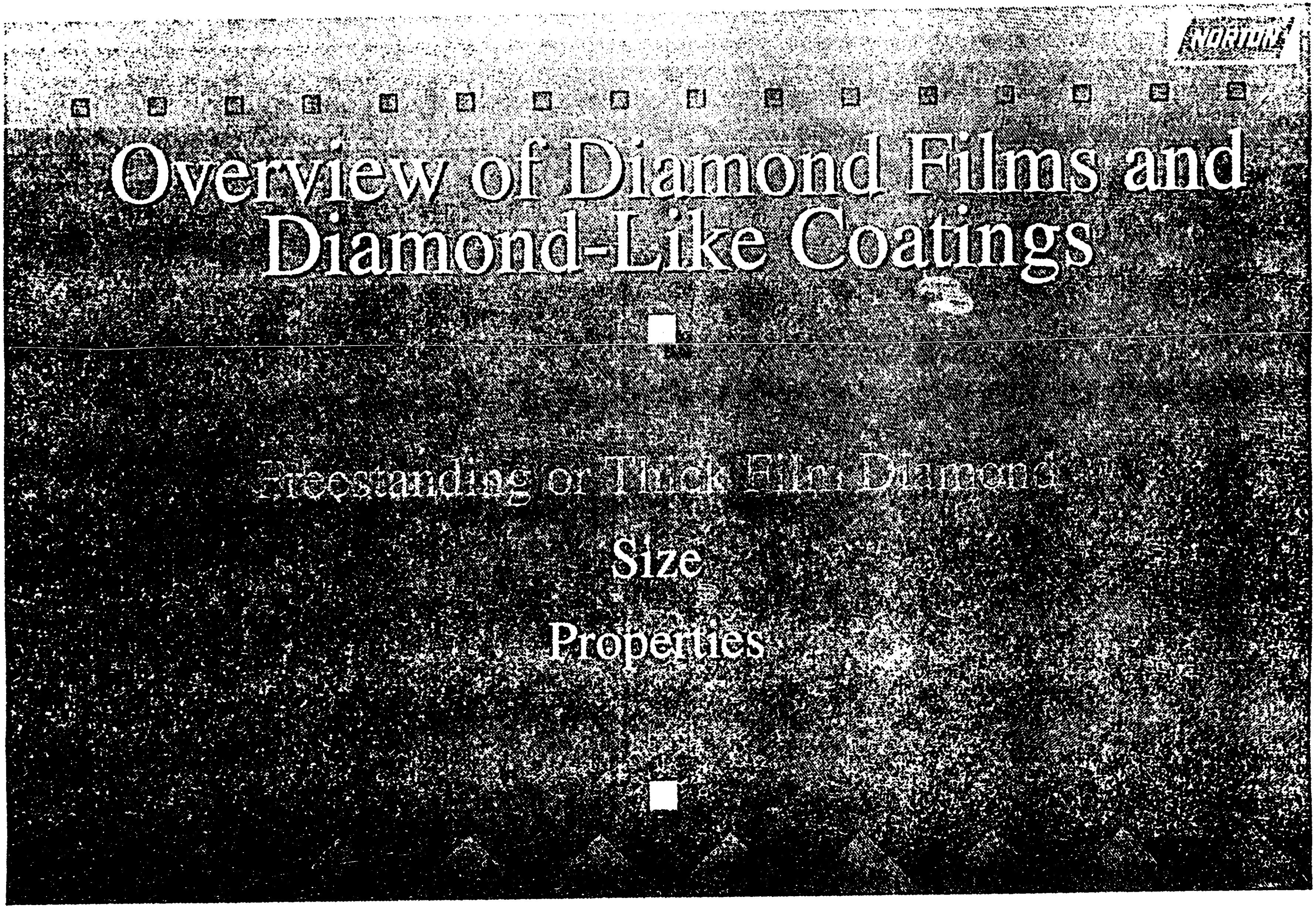
NORTON

# Potential Transportation Applications for Diamond Films

Robert A. Hay and Patrick M. Stephan

**Norton Diamond Film**

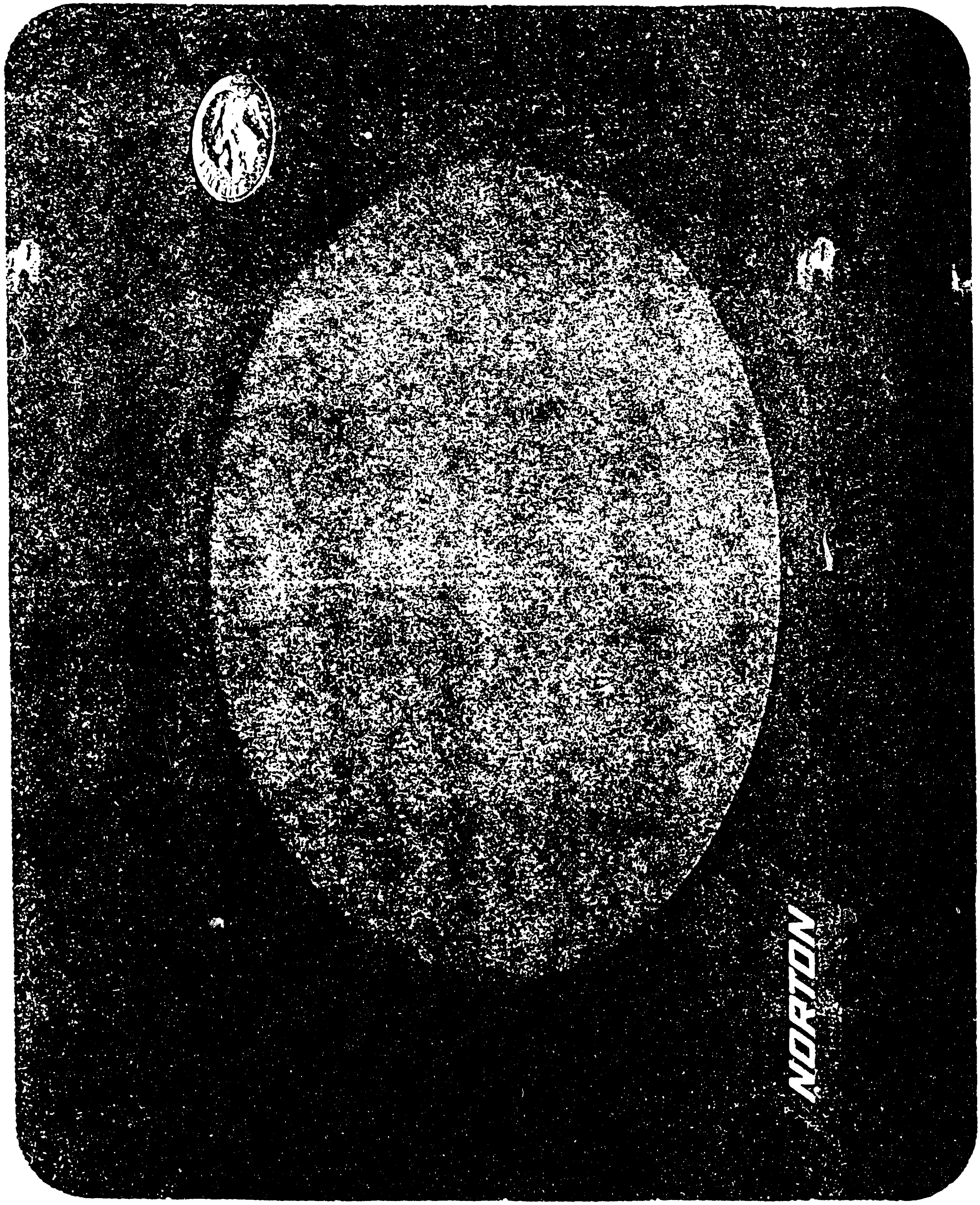
Northborough, MA

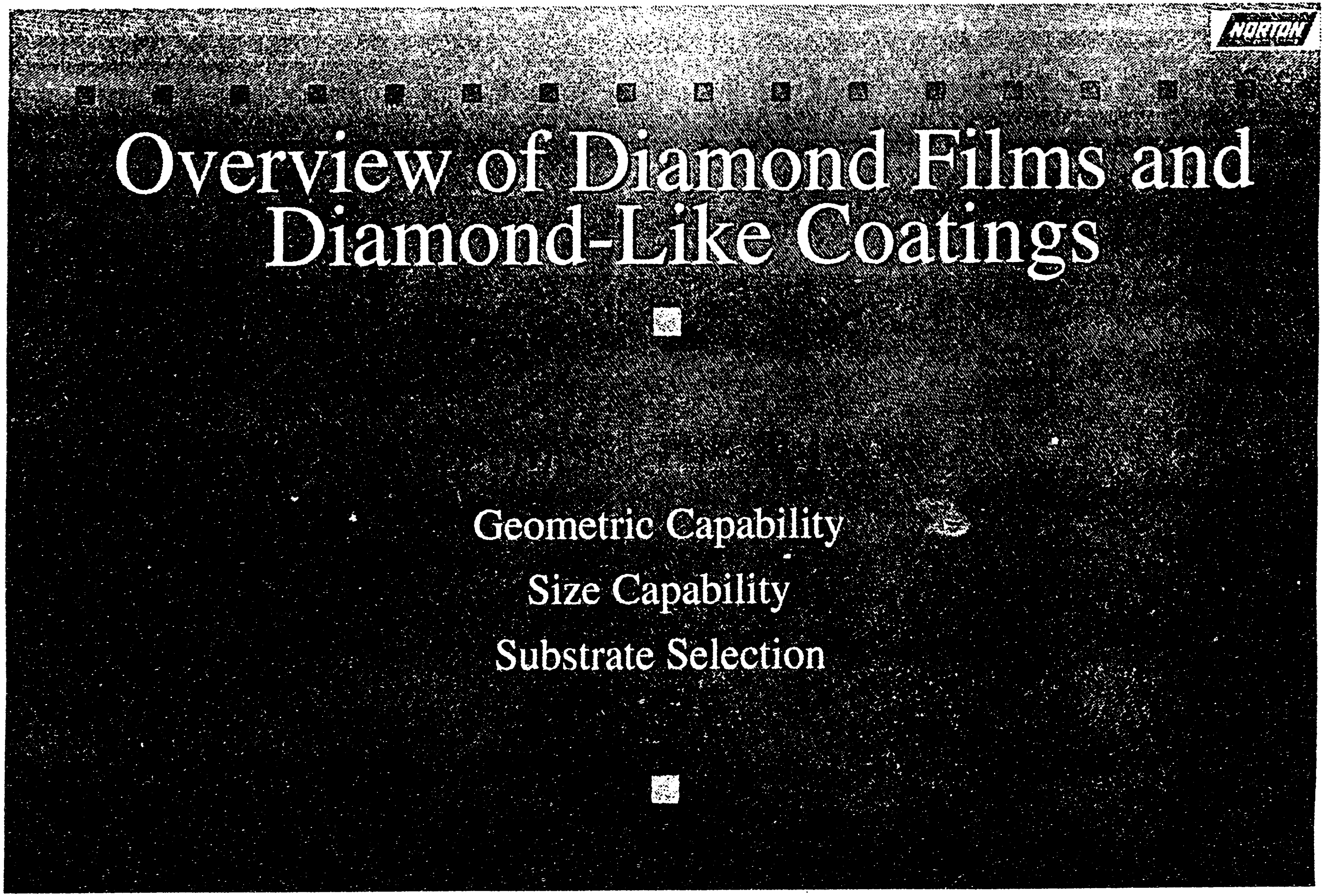


NORTON

# Overview of Diamond Films and Diamond-Like Coatings

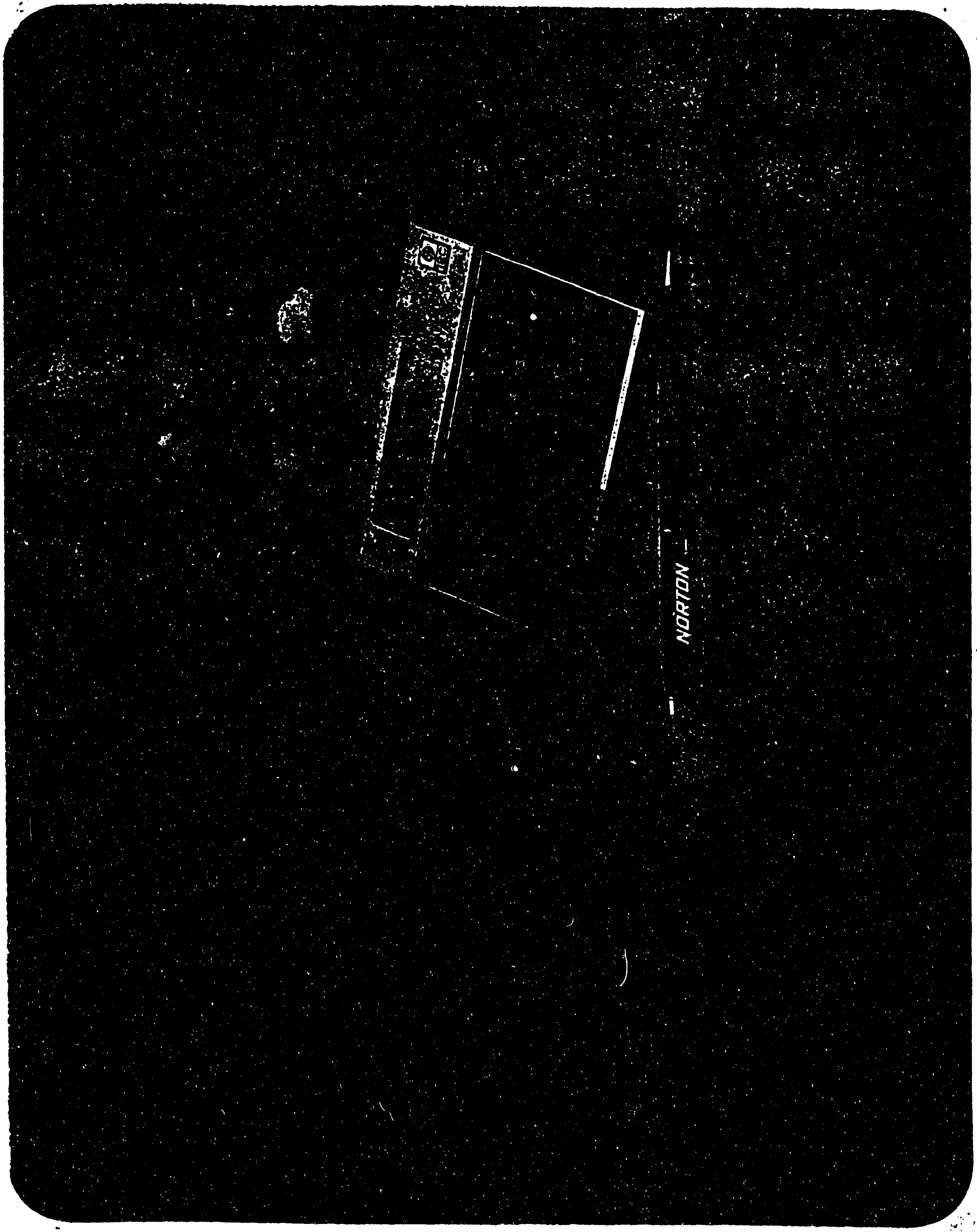
- Freestanding or Thick Film Diamond
  - Size
  - Properties

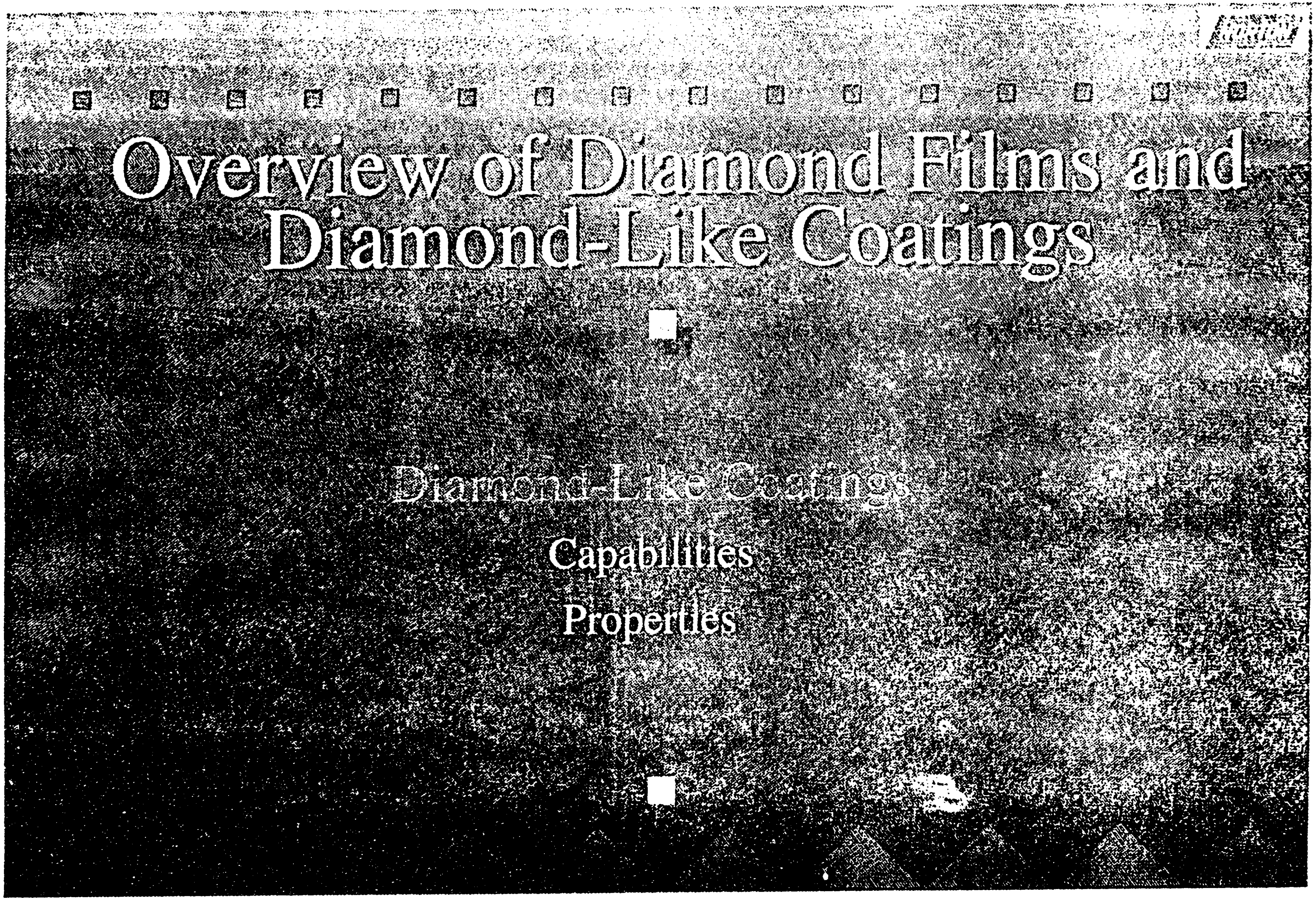

NORTON



# Overview of Diamond Films and Diamond-Like Coatings

- Geometric Capability
- Size Capability
- Substrate Selection


NORTON

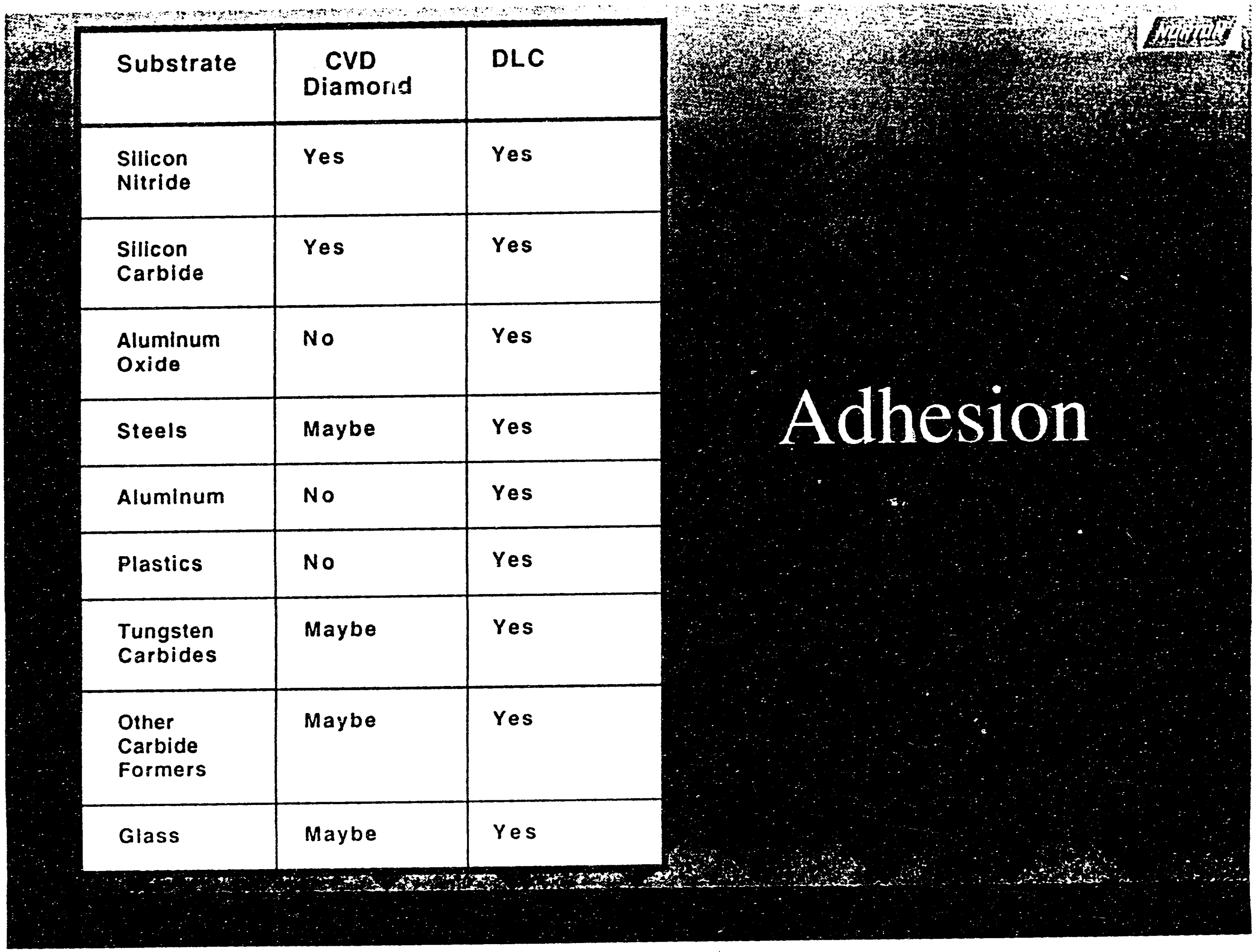


# Overview of Diamond Films and Diamond-Like Coatings

## Diamond-Like Coatings

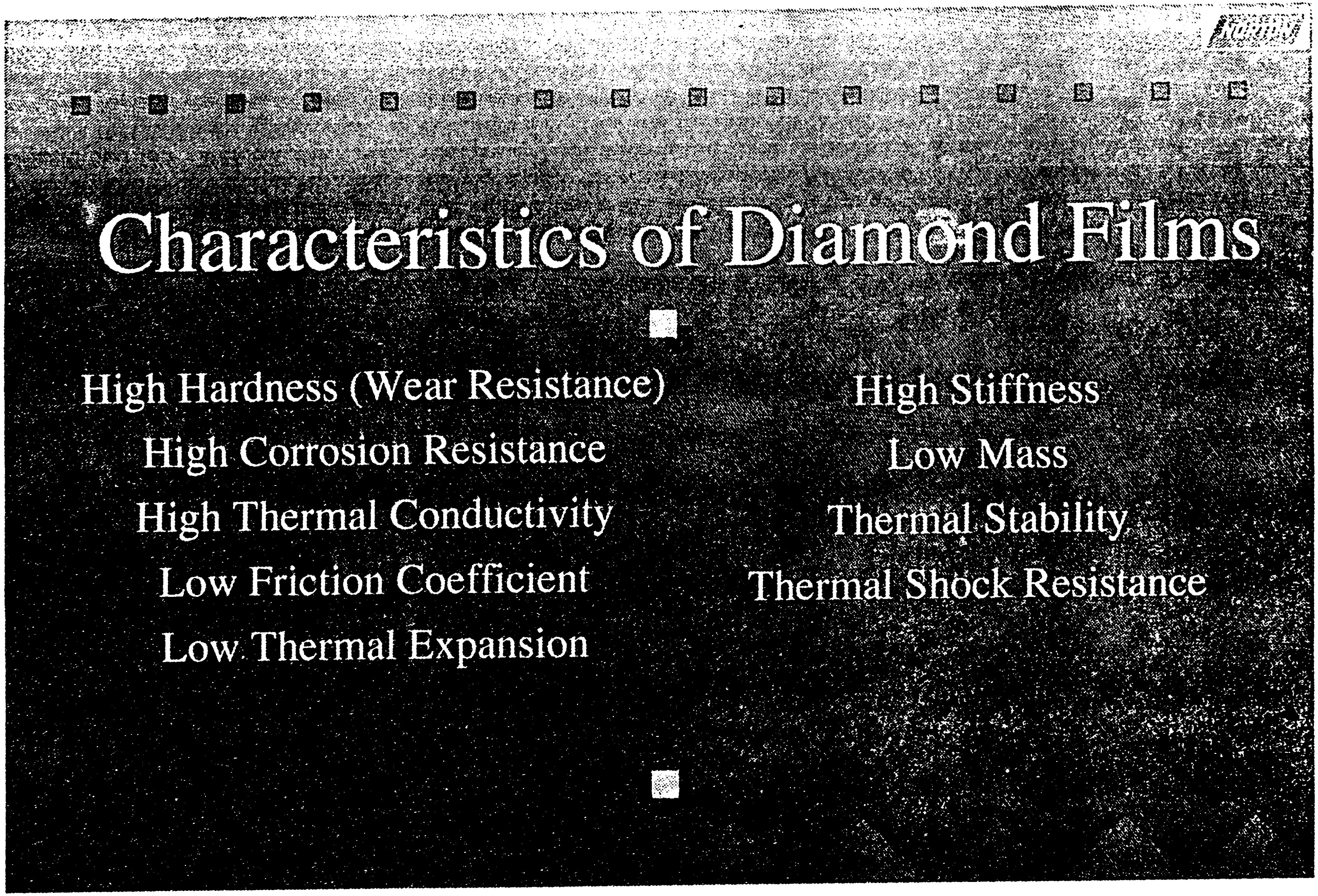
Capabilities

Properties



# Adhesion

| Substrate | CVD Diamond | DLC |
|---|---|---|
| Silicon Nitride | Yes | Yes |
| Silicon Carbide | Yes | Yes |
| Aluminum Oxide | No | Yes |
| Steels | Maybe | Yes |
| Aluminum | No | Yes |
| Plastics | No | Yes |
| Tungsten Carbides | Maybe | Yes |
| Other Carbide Formers | Maybe | Yes |
| Glass | Maybe | Yes |



# Characteristics of Diamond Films

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

NORTON

# Properties

| Properties | Natural Diamond | CVD Diamond | PCD | DLC | Tungsten Carbide (ISO K10) |
|---|---|---|---|---|---|
| Hardness GPa | 56-102 | 70-100 | 50-80 | 25-50 | 18 |
| Young's Modulus GPa | 400-1000 | 1000 | 840 | - | 630 |
| Thermal Conductivity W/m K | 600-2000 | 600- 1400 | 560 | - | 110 |
| Temperature Limit Deg. C | 600-650 | 700 | 600 | 200-400 | 600 |

NORTON

# Potential Transportation Applications

▨

Automotive

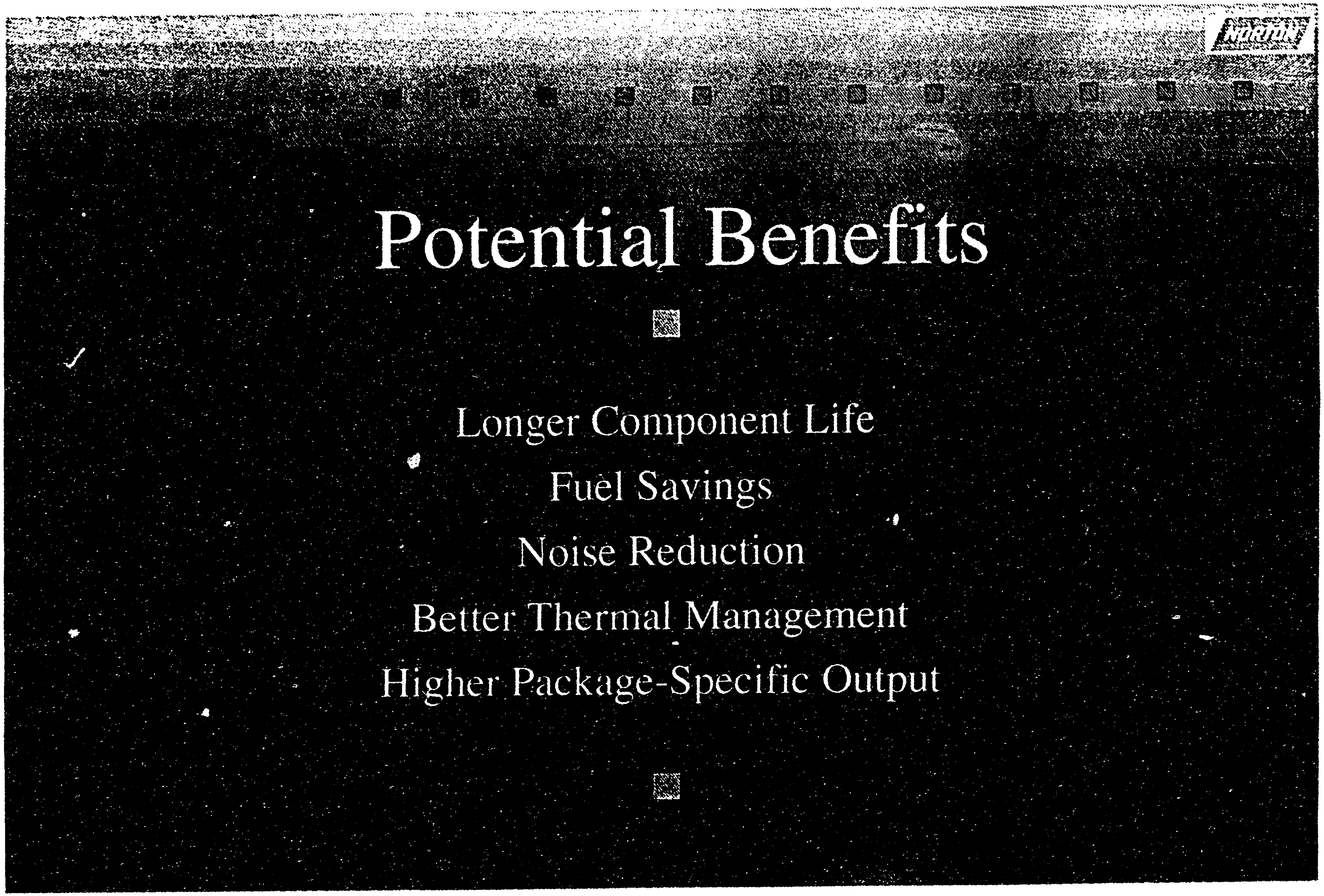
Aeronautics

Space

Rail

Special Defense Needs

▨



# Potential Benefits

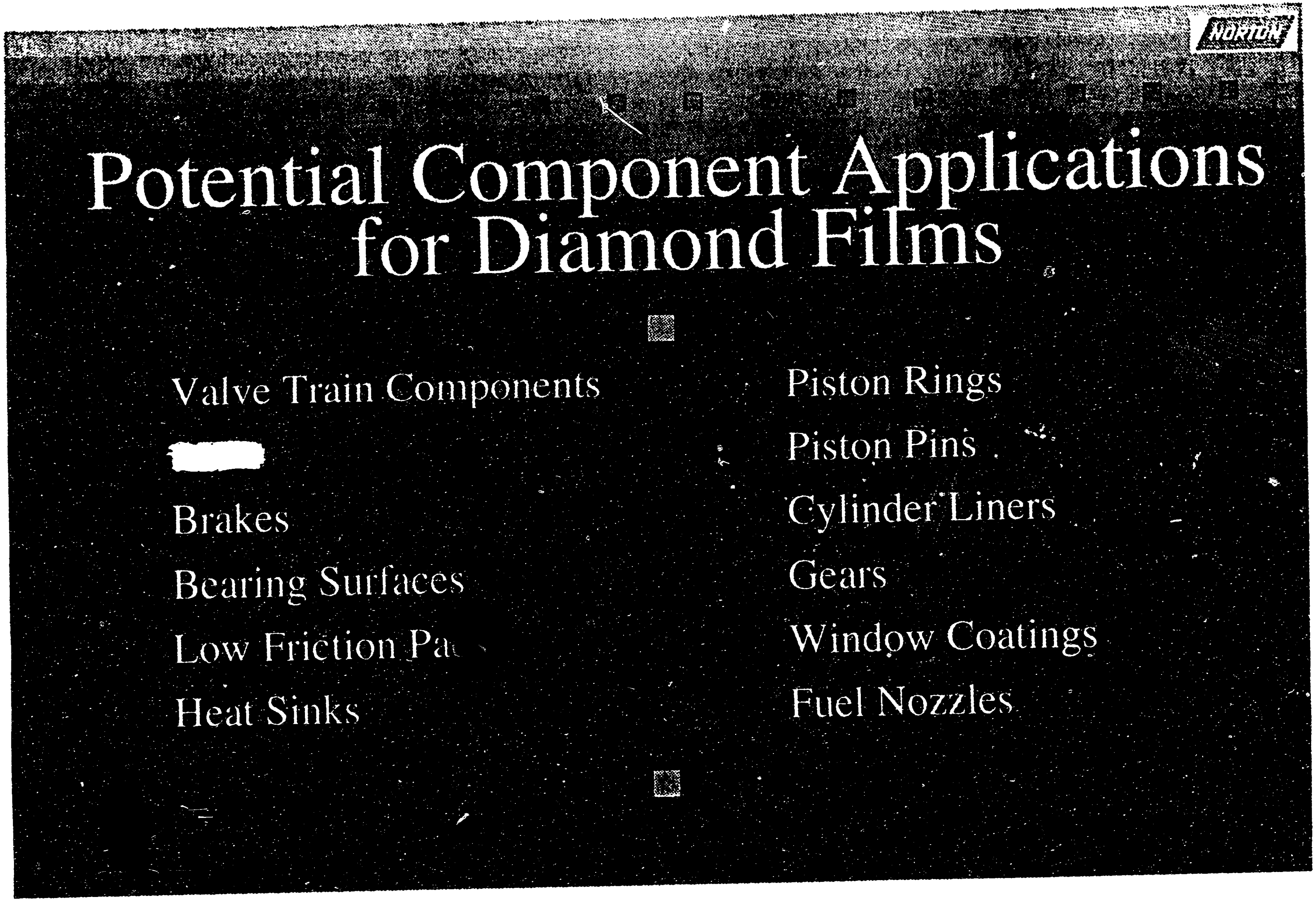
Longer Component Life

Fuel Savings

Noise Reduction

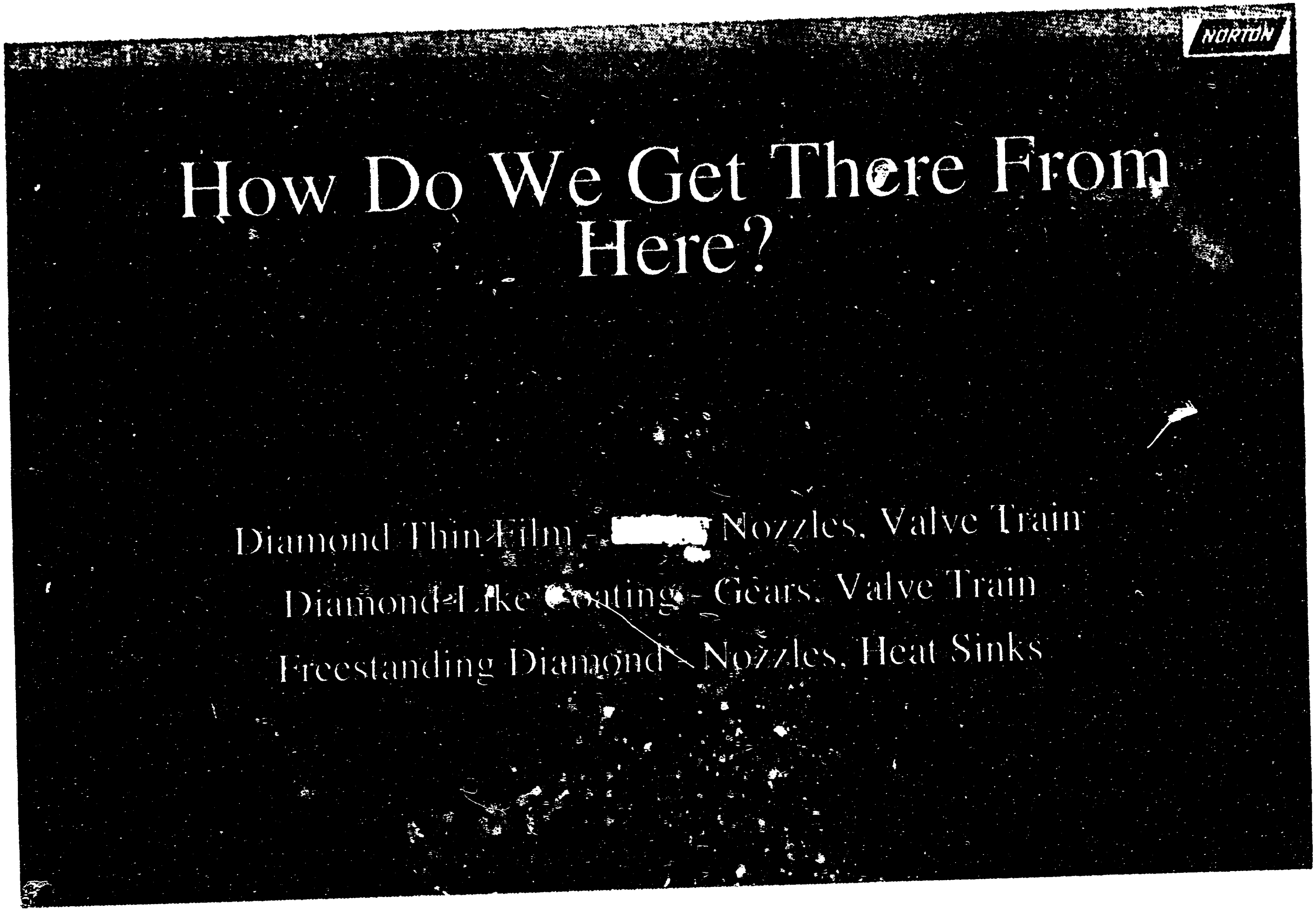
Better Thermal Management

Higher Package-Specific Output



# Potential Component Applications for Diamond Films

- Valve Train Components
- [redacted]
- Brakes
- Bearing Surfaces
- Low Friction Pa
- Heat Sinks
- Piston Rings
- Piston Pins
- Cylinder Liners
- Gears
- Window Coatings
- Fuel Nozzles



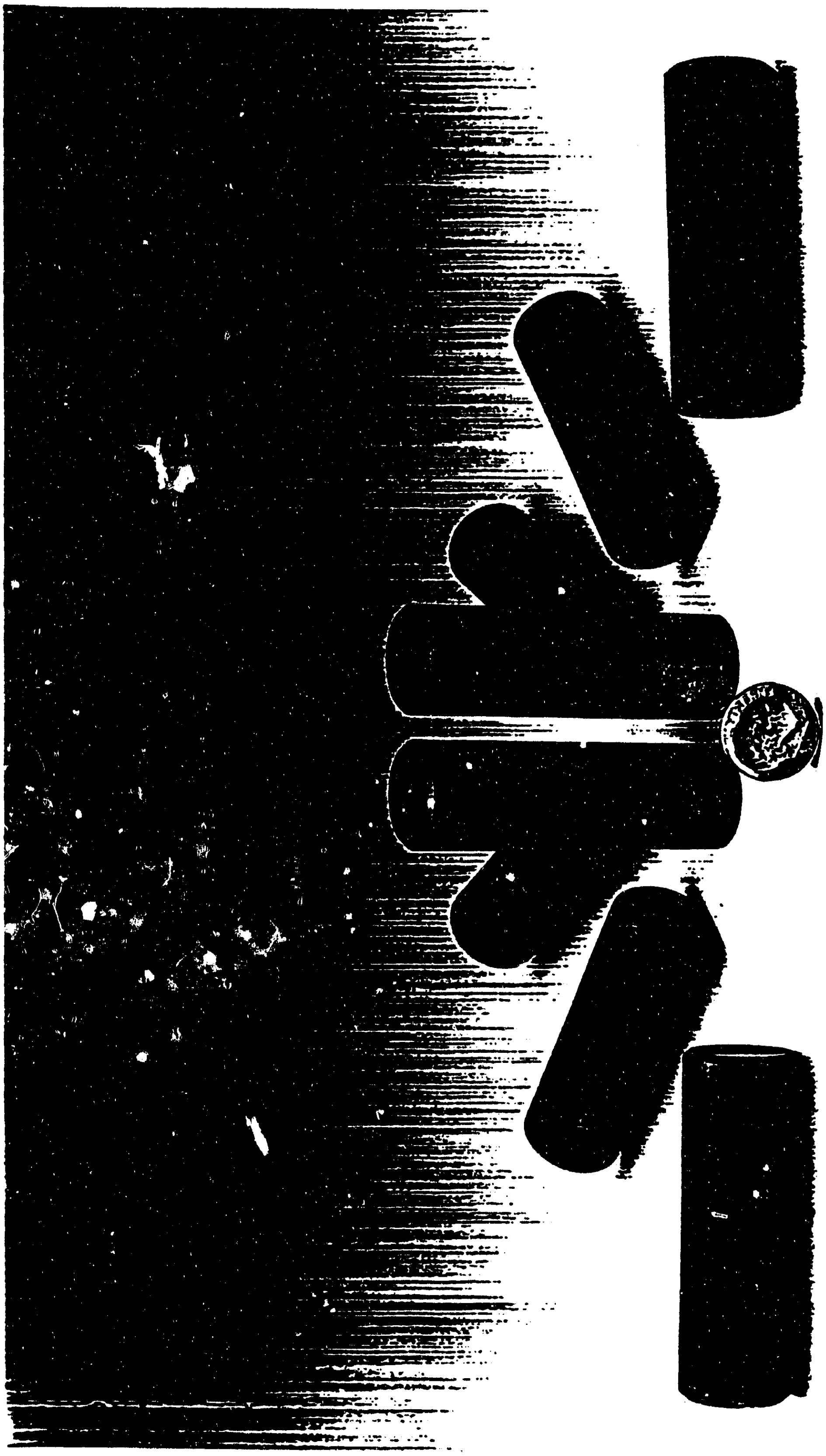
NORTON

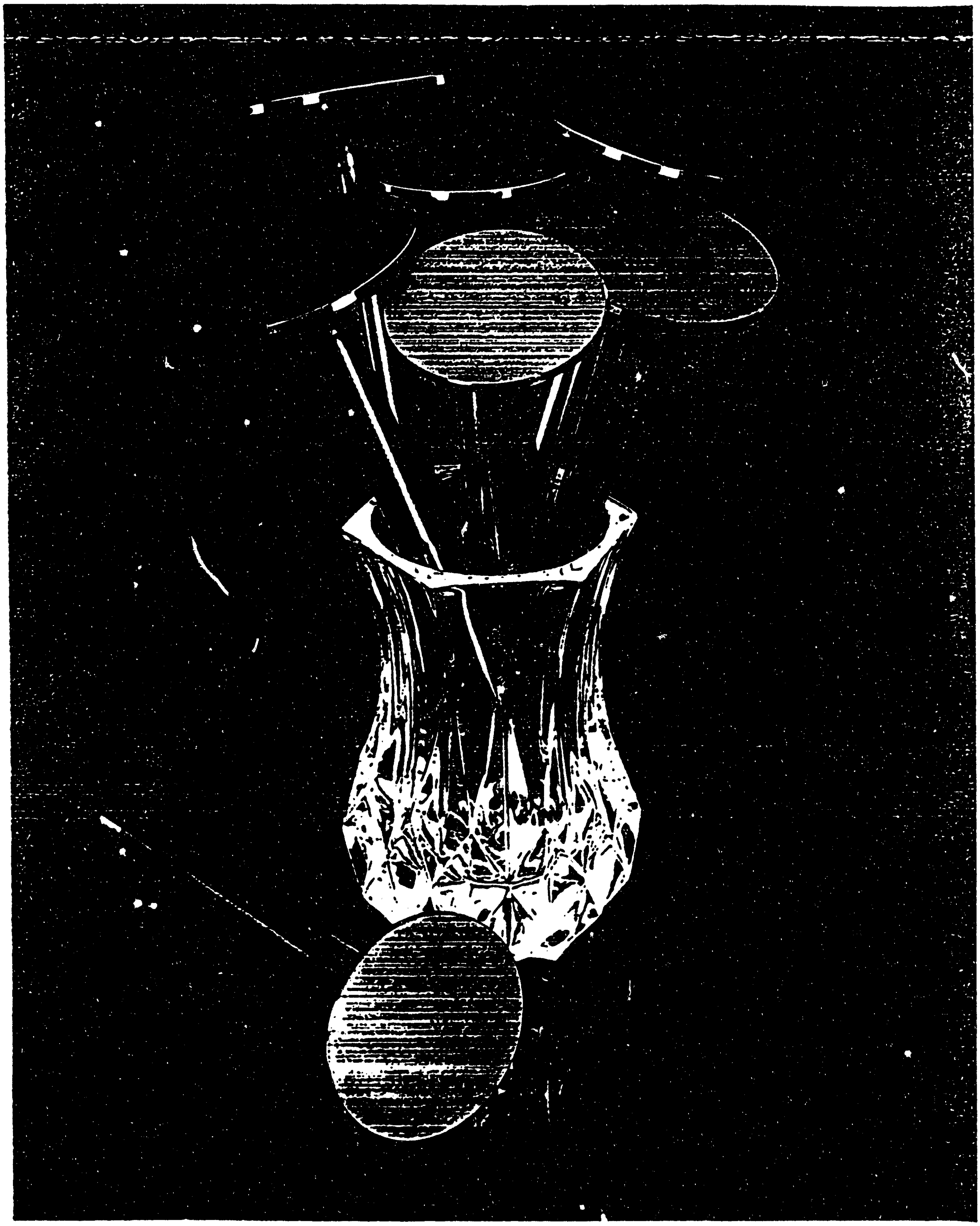
# How Do We Get There From Here?

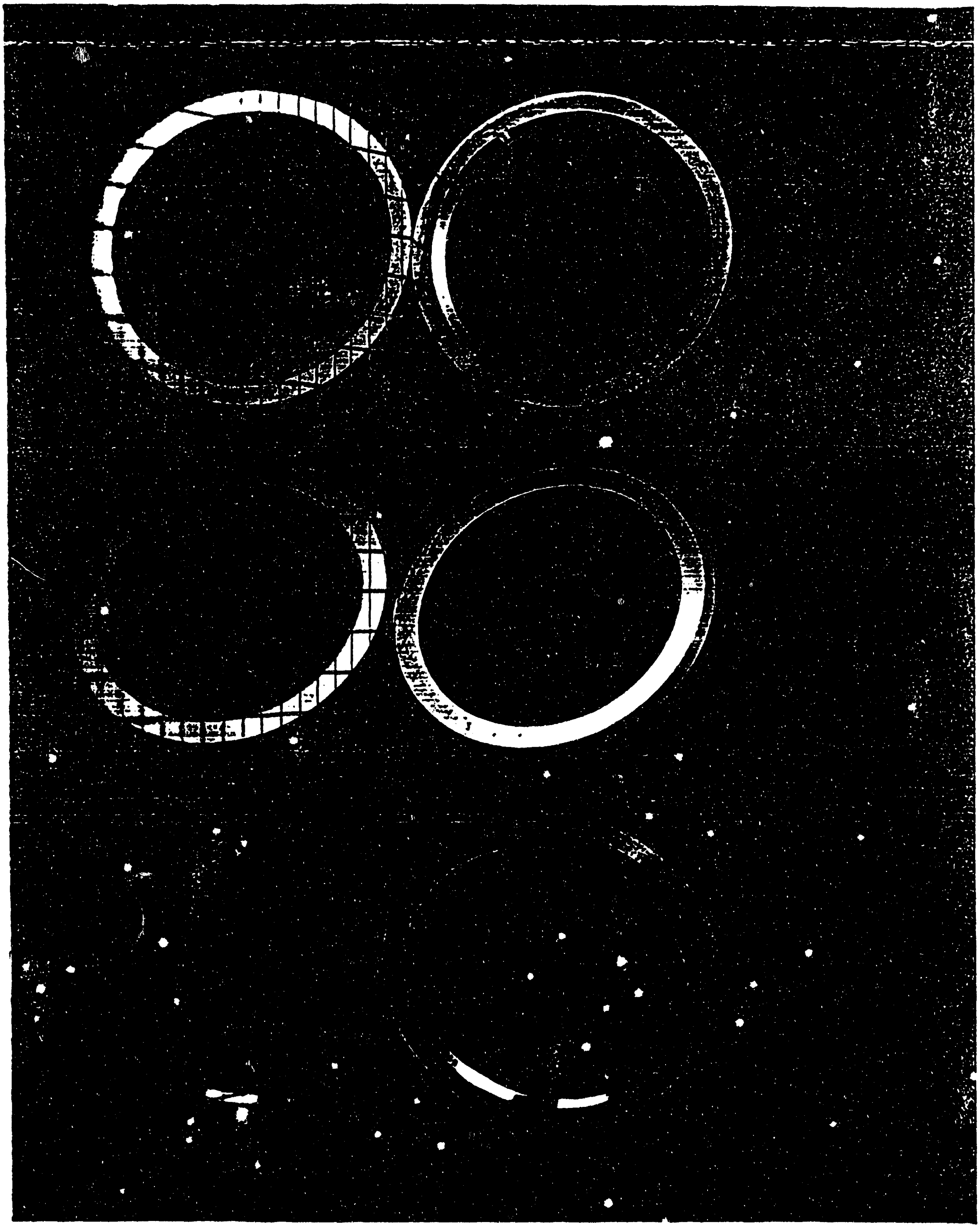
Diamond Thin Film - [illegible] Nozzles, Valve Train

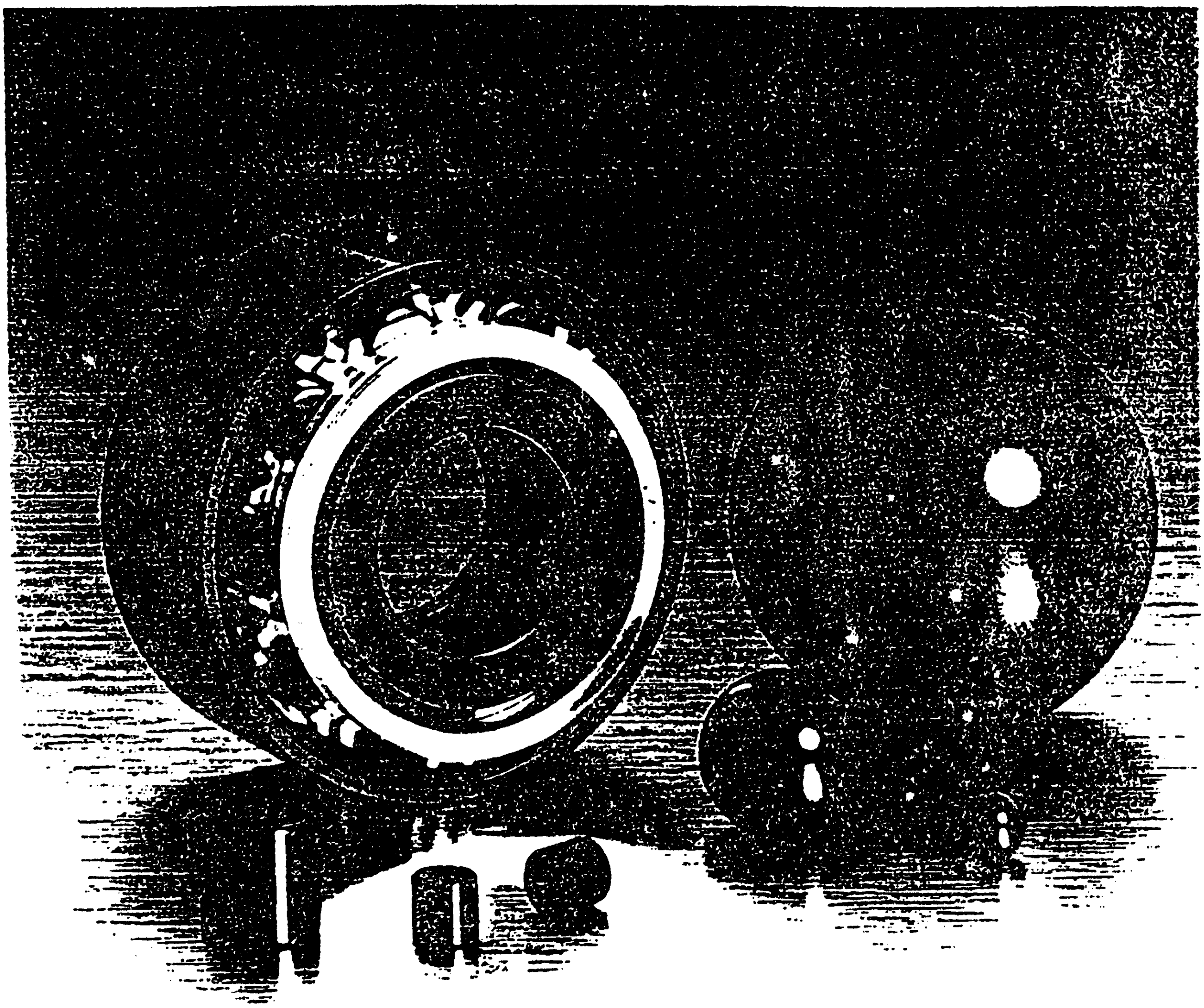
Diamond-Like Coating - Gears, Valve Train

Freestanding Diamond - Nozzles, Heat Sinks

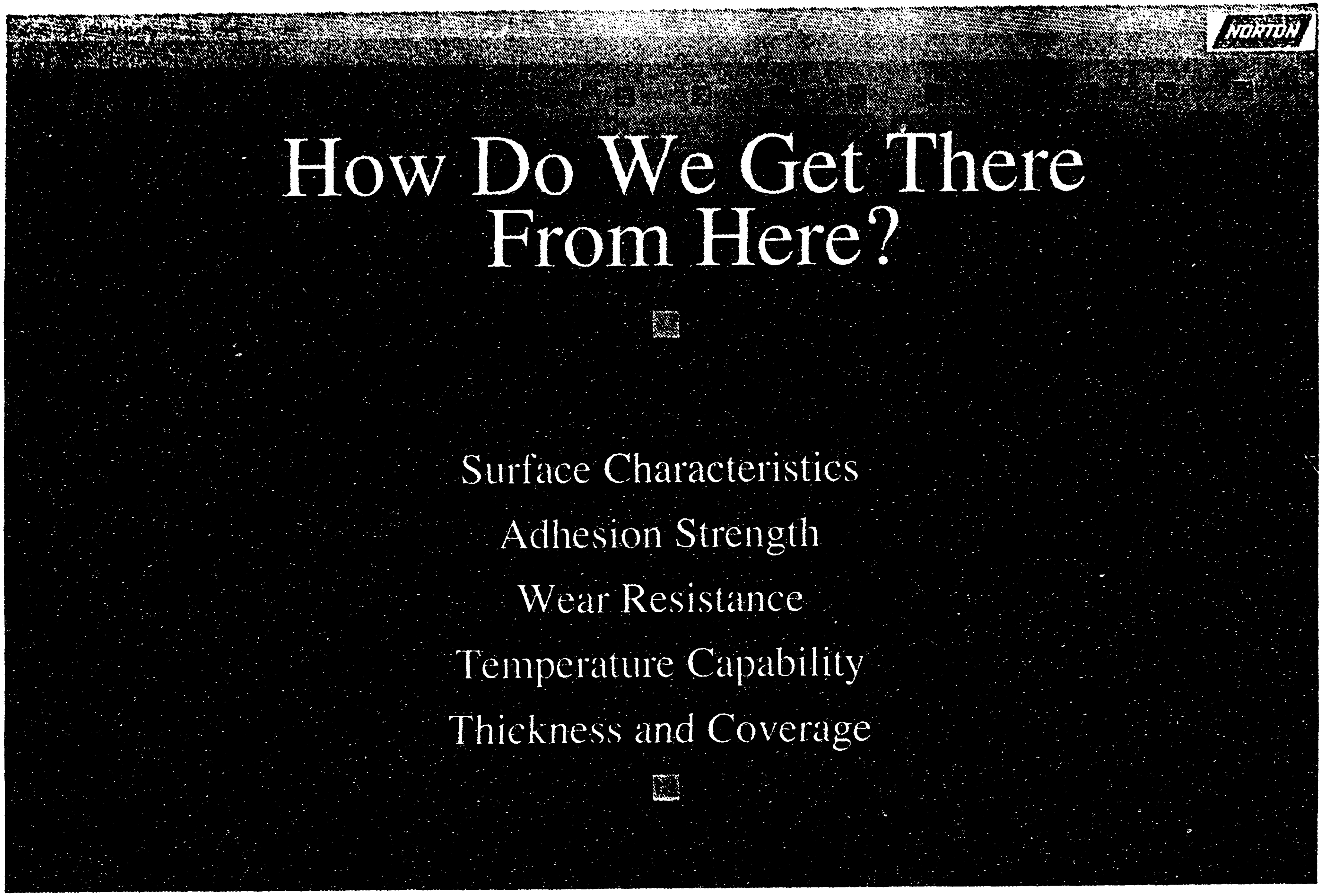








NORTON



# How Do We Get There From Here?

Surface Characteristics

Adhesion Strength

Wear Resistance

Temperature Capability

Thickness and Coverage

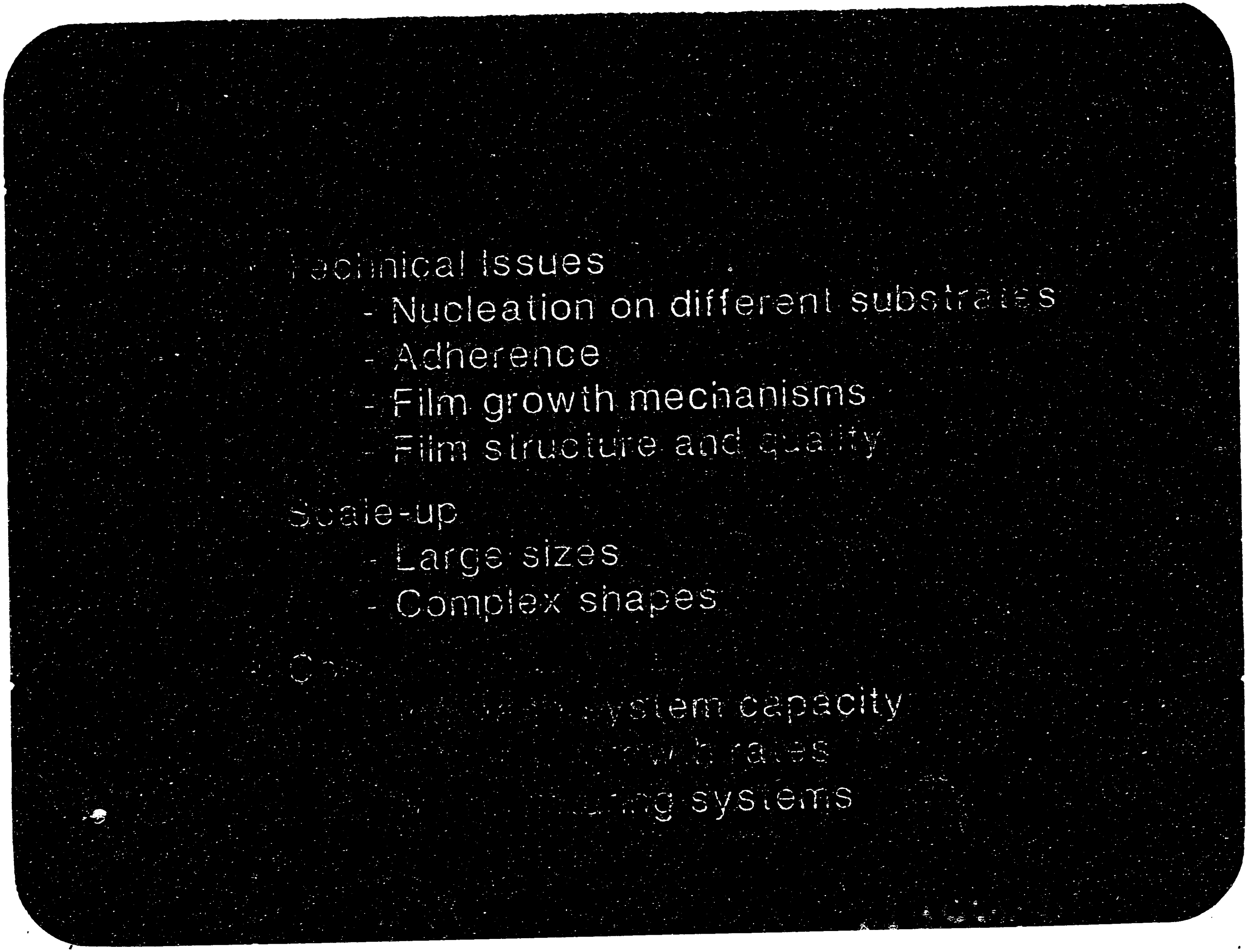
# How Do We Get There From Here?

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

[illegible]
  - [illegible] system capacity
  - [illegible] growth rates
  - [illegible] systems

# Conclusions

- Three Viable Technologies –
  Needs Considerable Amount of Development
  Near-Term Commercial Applications

# 4.0 REPORTS FROM WORKING PANELS

## 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 | National 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 III: Comparative Limitations**

| | | PCDs | DLCs |
|---|---|---|---|
| A | substrate preparation (nucleation) | x | |
| B | growth rates | x | x |
| C | component size | x | |
| D | substrate temperature | x | |
| E | cost | x | ? |
| F | surface finish | x | |
| G | maximum coating thickness | | x |
| H | adhesion | x | ? |
| I | grain-size, crystallites, heteroepit. | x | N/A |
| J | thermal conductivity | | x |
| K | geometry | x | x |
| L | thermal oxidation | | x |

**TABLE IV: Ranking of Diamond-Deposition Processes**

|  | **Thrml-Mngmnt** |  | **Optics** |  | **Tribology*** |  | **Sensors** |  |
|---|---|---|---|---|---|---|---|---|
|  | (B, D, E, J, L) |  | (F, G, H, I) |  | (C, D, F, H, K, L) |  | (H, J, L) |  |
|  | Prvn** | Pot** | Prvn | Pot | Prvn | Pot | Prvn | Pot |
| LA-CVD | – | – | – | – | – | – | – | * |
| HF-CVD | 3 | – | 3 | – | 3 | – | 2 | – |
| PA-CVD | 2 | + | 1,2 | – | 1 | c–BN | 1 | – |
| hal-CVD | – | + | – | + | – | low–$T_s$ | – | – |
| FLAME | – | – | – | + | – | + | – | – |
| Arc-Jet | 1 | + | 1,2 | – | 2 | – | – | – |

*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**

| | Thrml-Mngmnt | | Optics | | Tribology | | Sensors | |
|---|---|---|---|---|---|---|---|---|
| | (B, D, E, J, L) | | (F, G, H, I) | | (C, D, F, H, K, L) | | (H, J, L) | |
| | Prvn | Pot | Prvn | Pot | Prvn | Pot | Prvn | Pot |
| EB-PVD | 0* | 0 | – | – | 1 | – | 0 | 0 |
| SPT-PVD | 0 | 0 | 1 | – | 1 | – | 0 | 0 |
| CVD | 0 | 0 | – | – | 1 | – | 0 | 0 |
| LA-PVD | 0 | 0 | – | – | – | ** | 0 | 0 |
| IBD | 0 | 0 | – | – | 1 | – | 0 | 0 |
| IAD | 0 | 0 | 2, 3 | [a] | 1 | – | 0 | 0 |
| PA-PVD | 0 | 0 | 2,3[b] | – | 1 | – | 0 | 0 |

*A '0' denotes these techniques should **not** be considered.

**Refers to technologies that have potential.

[a] Protective coatings for low-heat-load windows.

[b] IR 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:

1. 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]

2. 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]

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

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

5. 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:

| Subject | No. of Votes |
|---|---|
| 1. friction | 13 |
| 2. wear | 13 |
| 3. better surface-morphology characterization | 10 |
| 4. rolling-contact-fatigue characterization | 5 |
| 5. lubrication of D/DLCF | 4 |
| 6. scuffing-reduction properties | 3 |

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

| Subject | No. of Votes |
|---|---|
| 1. adhesion | 15 |
| 2. hardness | 8 |
| 3. residual stress | 4 |
| 4. fracture toughness | 3 |
| 5. elastic properties | 2 |

## 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 data base.

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. *What* 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 $sp^2/sp^3$ 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

↔

- surface
- film
- interfaces
- substrate

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 | Sundstrand Aerospace |
| Rabi Bhattacharya | Universal Energy Systems, Inc. |
| Bharat Bhushan | Ohio State University |
| Dennis Blunier | Caterpillar, Inc. |
| Bruce Boardman | Deere & Co. |
| Larry Brombolich | Compu-Tec Engineering |
| Jim Davidson | Vanderbilt University |
| Mike Graham | Northwestern University |
| Nabil Hakim | Detroit Diesel Corporation |
| Keith Harris | Dubbeldee Harris Diamond Corp. |
| Rob Hay | Norton Diamond Film |
| Leonard Herk | Southwest Research Institute |
| Henry Hojnacki | Intelligent Structures Incorporated |
| Roy Kamo | Adiabatics, Inc. |
| Bill Nieman | Allied-Signal Inc., R&T |
| Dave O'Neill | 3M |
| Marshall B. Peterson | Wear Sciences |
| Gene Pfaffenberger | Allison Gas Turbine |
| Roger W. Pryor | Wayne State University |
| Dave Rourk | Intelligent Structures Incorporated |
| Jim Russell | Superconductivity Publications, Inc. |
| Walter Syniuta | Advanced Mechanical Technology, Inc. |
| Mike Tamor | Ford Motor Co. |
| Ted Vojnovich | USDOE |
| Wally Yarbrough | Penn State University |
| Charles S. Yust | 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.

### 3. 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 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.

# Diamond and Diamond-Like-Carbon Films Workshop Attendees

Ajayi, Oyelayo O.
Argonne National Laboratory
MCT/212
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-4976
FAX: 708-252-4798

Anthony, Thomas Richard
GE Research & Development Center
Rm. 1C30, Bldg. K-1
River Road
Schenectady NY 12309
Phone: 518-387-6160
FAX: 518-387-7563

Au, Joseph J.
Sundstrand Aerospace
Materials Science & Engineering
4747 Harrison Avenue
Rockford IL 61125
Phone: 815-226-2921
FAX: 815-226-7488

Barber, Gary Charles
Detroit Diesel Corporation
Tribology
13400 Outer Drive
Detroit MI 48239
Phone: 313-592-5145; 370-2184
FAX: 313-592-7888

Bartelt, Paul F.
Deere & Co.
Metals Research
3300 River Dr.
Moline IL 61265
Phone: 309-765-3854
FAX: 309-765-3807

Baughman, Ray H.
Allied-Signal
Forward Research
Research and Technology, PO Box N2112
Morristown NJ 07962
Phone: 201-455-2375
FAX: 201-455-5991

Benson, David K.
National Renewable Energy Lab.
Basic Sciences Div.
1617 Cole Blvd.
Golden CO 80401
Phone: 303-231-7000, X1162
FAX: 303-231-1381

Bhat, Deepak Govind
GTE Valenite Corporation
Materials Research & Development
1711 Thunderbird St.
Troy MI 48084
Phone: 313-589-6656
FAX: 313-362-3534

Bhattacharya, Rabi
UES, Inc.
4401 Dayton-Xenia Road
Dayton OH 45432
Phone: 513-426-6900
FAX: 513-426-5718

Bhushan, Bharat
Ohio State University
Mechanical Engineering
206 W. 18th Avenue
Columbus OH 43210
Phone: 614-292-0651
FAX: 614-292-3163

Blau, Peter J.
Oak Ridge National Laboratory
Metals and Ceramics Division
PO Box 2008
Oak Ridge TN 37831-6063
Phone: 615-574-5377
FAX: 615-574-6918

Blunier, Dennis L.
Caterpillar Inc.
Advanced Materials Technology
PO Box 1875
Peoria IL 61601
Phone: 309-578-6619
FAX: 309-578-2953

Boardman, Bruce E.
Deere & Co.
Metals Research
3300 River Dr.
Moline IL 61265
Phone: 309-765-3814
FAX: 309-765-3807

Brombolich, Lawrence Joseph
Compu-Tec Engineering
1415 Elbridge Payne
Chesterfield MO 63017
Phone: 314-532-4062
FAX: 314-532-1999

Chang, R. P. H.
Northwestern University
Materials Science & Engineering Department
2145 Sheridan Road
Evanston IL 60208
Phone: 708-491-3598
FAX: 708-491-4181

Chen, Yu-Lin
Allison Gas Turbine Division, GM
Materials and Processes
PO Box 420 -- W5
Indianapolis IN 46206
Phone: 317-230-3797
FAX: 317-230-2866

Clausing, Robert E.
ORNL
Metals & Ceramics Division
Box 2008
Oak Ridge TN 37831-6093
Phone: 615-574-5084
FAX: 615-574-7721

Cooper, Clark V.
United Technologies Research Center
Materials Technology
400 Main Street
East Hartford CT 06108
Phone: 203-727-7138
FAX: 203-727-7879

Davidson, Jim Lee
Vanderbilt University
Electrical Eng.
Box 99-B (400 24th Ave, S. 37212)
Nashville TN 37235
Phone: 615-343-7804
FAX: 615-343-6702

Davis, Frank Guy
Allied-Signal Aerospace Company
Government Program Office
7550 Lucerne Dr., Suite 203
Middleburg Hts. OH 44130
Phone: 216-826-0330
FAX: 216-826-0333

Deming, Shu
Argonne National Laboratory
APS/Experimental Facilities Division
9700 S. Cass Avenue (Bldg. 362)
Argonne IL 60439
Phone: 708-252-4684
FAX: 708-252-3222

Diamond, Sid
U.S. Department of Energy
Department of Transportation Materials
1000 Independence Avenue
Washington DC 20585
Phone: 202-586-8032
FAX: 202-586-7114

Dugger, Michael T.
Sandia National Laboratories
Division 1832
PO Box 5800
Albuquerque NM 87185-5800
Phone: 505-844-1091
FAX: 505-844-1543

Erck, Robert A.
Argonne National Laboratory
MCT/212
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-4972
FAX: 708-252-4798

Erdemir, Ali
Argonne National Laboratory
MCT/212
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-6571
FAX: 708-252-4798

Feldman, Albert
Natl. Inst. of Standards and Technology
Ceramics Division
Bldg. 223, Room B328
Gaithersburg MD 20899
Phone: 301-975-5740
FAX: 301-990-8729

Fenske, George R.
Argonne National Laboratory
MCT/212
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-5190
FAX: 708-252-4798

Freedman, Andrew
Aerodyne Research Inc.
45 Manning Road
Billerica MA 01821
Phone: 508-663-9500, X296
FAX: 508-663-4918

Gat, Roy
Case Western Reserve University
Chemical Engineering
Cleveland OH 44106
Phone: 216-308-2189
FAX: 216-308-3016

Glass, Jeffrey T.
North Carolina State University
Dept. of Materials Science & Engineering
Box 7919
Raleigh NC 27695-7919
Phone: 919-515-2867
FAX: 919-515-3419

Graham, Michael E.
Northwestern University
BIRL
1801 Maple Avenue
Evanston IL 60201
Phone: 708-491-5436
FAX: 708-467-1022

Gruen, Dieter M.
Argonne National Laboratory
Materials Science Divisiohn/Bldg. 200
9700 South Cass Avenue
Argonne IL 60439
Phone: 708-252-3513
FAX: 708-252-9555

Hakim, Nabil S.
Detroit Diesel Corporation
Materials Engineering
13400 W. Outer Drive
Detroit MI 48239
Phone: 313-592-7455
FAX: 313-592-5906

Harris, Keith
Dubbeldee Harris Diamond Corp.
100 Stierli Ct.
Mt. Arlington NJ 07856
Phone: 201-770-1420
FAX: 201-770-1549

Hay, Robert A.
Norton Diamond Film
Northboro Research Center
Goddard Rd.
Northboro MA 01532
Phone: 508-351-7864
FAX: 508-351-7788

Herk, Jr., Leonard F.
Southwest Research Institute
Detroit Office
26100 American Drive #603
Southfield MI 48034
Phone: 313-353-2550
FAX: 313-353-2666

Hojnacki, Henry Edward
Intelligent Structures Incorporated
6933 Pittsford
Canton MI 48187
Phone: 313-459-3773
FAX:

Hsieh, Jang-Hsing
Argonne National Laboratory
MCT/212
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-6911
FAX: 708-252-4798

Kamo, Roy
Adiabatics, Inc.
3385 Commerce Dr.
Columbus IN 47201
Phone: 812-372-5052
FAX: 812-372-4470

Kelly, Michael A.
Stanford University
Materials Science
Peterson Lab.
Stanford CA 94305-2205
Phone: 415-723-2617
FAX: 415-854-0281

Kim, George Arthur
Edge Technologies, Inc.
4455 West 62nd
Indianapolis IN 46268
Phone: 317-293-2165
FAX: 317-293-2185

Kleiner, Rick
Coors Ceramics Company
Department 660/Corporate Technology
4545 McIntyre Street
Golden CO 80403
Phone: 303-277-4739
FAX: 303-277-4595

Kuzay, Tuncer M.
Argonne National Laboratory
APS/362
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-3084
FAX: 708-252-3222

Larsen-Basse, Jorn
National Science Foundation
Surface Engineering and Tribology Program
1800 G Street, NW #1108
Washington DC 20550
Phone: 202-357-9542
FAX: 202-357-0167

Lawler, James E.
University of Wisconsin
Dept. of Physics
1150 University Avenue
Madison WI 53706
Phone: 608-262-2918
FAX: 608-265-2334

Lawton, Emil A.
JPL/Caltech
125/224
4800 Oak Grove
Pasadena CA 91109
Phone: 818-354-2128
FAX:

Lee, Richard H.
Argonne National Laboratory
MCT/212
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-7927
FAX: 708-252-4798

Lindsey, Jr., Paul Carpenter
Crystalline Materials Corporation
2411-A Old Crow Canyon Rd.
San Raman CA 94583
Phone: 510-831-8689
FAX: 510-831-9557

Liu, Yung Y.
Argonne National Laboratory
MCT/212
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-5127
FAX: 708-252-4798

McGuire, Neal R.
Caterpillar
Advanced Materials Technology
PO Box 1875
Peoria IL 61656-1875
Phone: 309-578-4004
FAX:

McHargue, Carl J.
Univ. of Tennessee-Knoxville Campus
College of Engr./Ctr. for Materials Processing
121 Perkins Hall
Knoxville TN 37996-2000
Phone: 615-974-7680
FAX: 615-974-2669

Messier, Russell F.
Penn State University
Materials Research Laboratory
265 MRL
University Park PA 16802
Phone: 814-865-3704
FAX: 814-865-2326

Morrison, Jr., Philip Walter
Advanced Fuel Research
87 Church Street
East Hartford CT 06108
Phone: 203-528-9806
FAX: 203-528-0648

Nagle, Dennis C.
Martin Marietta Labs
Coatings and Structures
1450 South Rolling Rd.
Baltimore MD 21227
Phone: 301-247-0700
FAX: 301-247-4939

Nichols, Fred A.
Argonne National Laboratory
MCT/212
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-8292
FAX: 708-252-4798

Nieman, Bill
Allied-Signal Inc., R&T
Modeling & Manufacturing Systems
50 E. Algonquin Rd.
Des Plaines IL 60201
Phone: 708-391-3508
FAX: 708-391-3653

Nobel, Gary L.
John Crane, Inc.
Product Development
6400 W. Oakton St.
Morton Grove IL 60053
Phone: 708-967-2414
FAX: 708-967-3086

O'Neill, David G.
3M
Corporate Research
Bldg. 219-1S-01
St. Paul MN 55144
Phone: 612-733-9896
FAX: 612-736-7037

Ostrowski, Michael H.
John Crane, Inc.
Business Development
6400 Oakton St.
Morton Grove IL 60053
Phone: 708-967-2423
FAX: 708-967-3086

Outka, Duane A.
Sandia National Laboratories
Division 8342
PO Box 969
Livermore CA 94551-0969
Phone: 510-294-1311
FAX: 510-294-3231

Ovaert, Timothy C.
Penn State University
Mechanical Engineering
313-B Reber
University Park PA 16802
Phone: 814-865-3160
FAX: 814-863-4848

Pan, Xianzheng
Argonne National Laboratory
MCT/212
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-4074
FAX: 708-252-4798

Peebles, Diane E.
Sandia National Laboratories
Division 1834
PO Box 5800
Albuquerque NM 87185-5800
Phone: 505-845-8087
FAX: 505-844-1543

Perez, Joseph M.
U.S. Department of Energy
Tribology Program Mgr. CE-34
1000 Independence Ave., SW
Washington DC 20585
Phone: 202-586-2325
FAX: 202-586-7114

Peterson, Marshall
Wear Sciences
925 Mallard Circle
Arnold MD 21012
Phone: 301-261-2342
FAX: 301-757-1953

Pfaffenberger, Eugene E.
Allison Gas Turbine
Mechanical Technology
2001 S. Tibbs Avenue
Indianapolis IN 46241
Phone: 317-230-2187
FAX: 317-230-5100

Pitts, J. Roland
NREL
Photovoltaics Division, Br. 4120
1612 Cole Blvd.
Golden CO 80401
Phone: 303-231-1929
FAX: 303-231-1381

Prunoske, John Patrick
ANL
MCT/212
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-5182
FAX: 708-252-4798

Pryor, Roger W.
Wayne State University
Institute for Manufacturing Research
666 W. Hancock
Detroit MI 48201
Phone: 313-577-0846
FAX: 313-577-7743

Purohit, Ankur
Argonne National Laboratory
EP/MCT
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-6670 (X8619, X5172)
FAX:

Revankar, Gopal Subray
Deere & Co.
Technical Center
3300 River Dr.
Moline IL 61265
Phone: 309-765-3795
FAX: 309-765-3807

Rourk, Dave Robert
Intelligent Structures Incorporated
6933 Pittsford
Canton MI 48187
Phone: 313-459-3773
FAX:

Russell, Jim
Superconductivity Publications, Inc.
Diamond Depositions: Science & Technology
710 Easton Avenue, Suite C
Somerset NJ 08873
Phone: 908-846-2002
FAX: 980-846-2050

Sartwell, Bruce D.
Naval Research Laboratory
Code 4675
Washington DC 20375
Phone: 202-767-4800
FAX: 202-767-5301

Schertz, William W.
Argonne National Laboratory
ES/362
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-6230
FAX: 708-252-4211

Shack, William J.
Argonne National Laboratory
MCT/212
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-5137
FAX: 708-252-4798

Sibold, Jack D.
Coors Ceramics Company
660 - Corporate Technology
4545 McIntyre Street
Golden CO 80403
Phone: 303-277-4441
FAX: 303-277-4595

Stodolsky, Frank
Argonne
Energy Systems Div.
340 L'Enfant Promenade SW, STE 201A
Washington DC 20024
Phone: 202-488-2431
FAX: 202-488-2444

Subramaniam, Vish V.
The Ohio State University
Mechanical Engineering
2087 Robinson Labs., 206 W. 18th Ave.
Columbus OH 43210
Phone: 614-292-6096
FAX: 614-292-3163

Sunkara, Mahendra Kumar
Case Western Reserve University
Chemical Engineering
Dept. of Chemical Engineering, CWRU
Cleveland OH 44106
Phone: 216-368-4255
FAX: 216-368-3016

Syniuta, Walter D.
Advanced Mechanical Technology, Inc.
151 California Street
Newton MA 02158
Phone: 617-964-2042
FAX: 617-964-6234

Tamor, Michael A.
Ford Motor Co.
Research Staff
SRL MD-3028
Dearborn MI 48121-2053
Phone: 313-337-4108
FAX: 313-594-6863

Vojnovich, Ted
U. S. Dept. of Energy
Office of Alternative Fuels
1000 Independence
Washngton DC 20582
Phone: 202-586-8060
FAX: 202-586-8134

Weeks, Richard W.
Argonne National Laboratory
MCT/212
9700 S. Cass Avenue
Argonne IL 60439
Phone: 708-252-4931
FAX: 708-252-4798

Wei, Ronhua
Colorado State University
Mechanical Engineering
Fort Collins CO 80523
Phone: 303-491-8234
FAX: 303-491-8671

Wilbur, Paul James
Colorado State University
Mechanical Engineering
Fort Collins CO 80523
Phone: 303-491-8564
FAX: 303-491-8671

Wong, Ming-Show
Northwestern University
BIRL, Industrial Research Lab.
1801 Maple Avenue
Evanston IL 60201
Phone: 708-491-2796
FAX: 708-467-1022

Woolam, William E.
Southwest Research Institute
Materials Science
1235 Ifferam Davis Highway #1104
Arlington VA 22202-3293
Phone: 703-979-0500
FAX: 703-920-2189

Yarbrough, Walter A.
Penn State University
Ceramic Science & Engineering
149 Materials Research Lab.
University Park PA 16802
Phone: 814-865-7102
FAX: 814-863-7039 or (814-865-2326)

Yust, Charles S.
Oak Ridge National Laboratory
Metals and Ceramics Division
PO Box 2008
Oak Ridge TN 37830
Phone: 615-574-4812
FAX: 615-574-6918

# END

DATE
FILMED

4/16/93