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U.S. ARMY APPLICATIONS FOR DIAMOND AND DIAMONDLIKE MATERIALS

NOVEMBER 1989

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U.S. ARMY RESEARCH OFFICE WORKSHOP
CHAPEL HILL, NC
JUNE 13-14, 1989

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The Materials Science Division of the U.S. Army Research Office Sponsored a one and one-half day workshop in June 1989 to review the status of diamond-related research in the U.S., and to identify Army system requirements that potentially could be met by this technology. Fourteen invited speakers provided an overview of diamond-related research in the U.S., and identified the particular applications where this technology could make a significant contribution to future Army missions. Applications that deserve increased attention include: erosion-resistant broad-band missile domes and detector windows, corrosion-and tribological-resistant coatings, thermal heat dissipating structures, and high-strength ceramics/composites. Working discussions were then convened to determine whether there were specific recommendations which would promote the Army's implementation of this technology.

The general conclusions of the panel were three fold: First, there was general agreement that the mechanisms controlling the nucleation and growth of CVD-deposited (over)

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Dr. John T. Prater

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919-549-0641

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diamond films were not well understood and that continued research in this area was essential to development of high quality films. It was also recognized that the bulk of the existing U.S. research effort was narrowly focussed on the development of electronic material by CVD processes. A broadening of the research to support high-risk, high-payoff studies on alternative avenues of diamond synthesis was strongly encouraged. Finally, it was felt that an eye on the eventual need to scale the process for production was frequently being ignored. Issues relating to scale-up should be addressed from the beginning to promote rapid transition into production.

ARMY APPLICATIONS FOR DIAMOND AND DIAMONDLIKE MATERIALS

U.S. Army Research Office Workshop
June 13-14, 1989
Chapel Hill, NC

EXECUTIVE SUMMARY

The Materials Sciences Division of the U.S. Army Research Office sponsored a one and one-half day workshop in June 1989 to review the status of diamond-related research in the U.S., and to identify Army system requirements that potentially could be met by this technology. Fourteen invited speakers provided an overview of diamond-related research in the U.S., and identified the particular applications where this technology could make a significant contribution to future Army missions. Working discussions were then convened to determine whether there were specific recommendations which would promote the Army's implementation of this technology.

At present, the majority of federally funded research in diamond is very narrowly focussed on the CVD deposition of single crystal films for electronic applications. This is a formidable task. The numerous experiments performed to date have yielded diamond crystals but most generally as highly defective, polycrystalline films. It is anticipated that continual progress will be made toward the achievement of high value added electronic components. There are many low cost Army applications outside of electronics that are extremely important. From an Army perspective this indicates that a more balanced research initiative is appropriate. Applications that deserve increased attention include: erosion-resistant broad-band missile domes and detector windows, corrosion- and tribological-resistant coatings, thermal heat dissipating structures, and high-strength ceramics/composites.

Diamond has a unique combination of physical properties that distinguishes it as the ideal material for fulfilling a broad variety of material applications in optics, electronics and tribology. Originally, its exceptional hardness led to the wide use of natural and man-made diamonds in machining and polishing operations. The advent of diamond films now expands the potential utility of diamond to a much broader spectrum of technologies, see Table 1.

The exceptional strength and thermal shock resistance of diamond sets it apart as being the ultimate material of choice for the construction of parts that will undergo extremely demanding thermal and mechanical loading cycles. Of special interest to the Army is the fact that diamond has an exceptionally high phonon velocity; the velocity of sound in diamond actually exceeds conventional detonation velocities. This makes it a unique candidate material for penetrators.

Table 1. ARMY APPLICATIONS FOR DIAMOND

ELECTRONIC

REFRACTORY SEMICONDUCTORS FOR HIGH POWER DEVICES
HEAT CONDUCTION AND PACKAGING
INSULATING SUBSTRATES AND SUPPORT STRUCTURES FOR RF AND MICROWAVE DEVICES- e.g. TWTs
RADIATION HARDENED DEVICES

OPTICAL

IR DOMES
LASER WINDOWS/OPTICAL COMPONENTS
LASER HOST MATERIAL
PROTECTIVE COATINGS FOR OPTICAL COMPONENTS
HERMETIC COATINGS FOR OPTICAL FIBERS
RADIATION DETECTORS

MECHANICAL

TRIBOLOGICAL AND LOW FRICTION COATINGS
MACHINING AND POLISHING
CORROSION RESISTANT COATINGS
ORDNANCE/ARMOR
VIBRATING CANTILEVERS AND DIAPHRAMS
COMPOSITES

MISCELLANEOUS

HEAT EXCHANGERS

Diamond has exceptionally good thermal conductivity. Where cost is not a factor it is the material of choice for heat dissipation applications ranging from electronic packaging to heat exchangers in space. One area of critical importance to the Army is the application of diamond as protective windows/coatings for optical systems. Diamond can be prepared so as to be transparent over virtually any part of the electromagnetic spectrum, from the UV to mm wave. In combination with its excellent erosion resistance, thermal conductivity and shock resistance, stability and strength, diamond represents the ideal material for IR domes and optical components or host media for lasers.

The exceptional promise that diamond has in the area of advanced electronics has been recognized. Diamond is unique in that it has outstanding thermal conductivity and low electrical conductivity (high electrical resistance). It can be doped to produce a semiconductor which has very respectable electronic and outstanding hole mobilities. This combination of properties makes diamond the ideal substrate material for fabricating high-power, high-frequency electronic devices. However, this application requires that the growth of single crystal material be perfected, a notable difficult undertaking.

Finally, the promise of exceptional stability makes diamond a potentially important material for service in a variety of unusually harsh chemical, tribological and radiation-intense environments.

Unfortunately, the properties of the diamond films currently available are not yet suitable for most of the applications of interest. Costs are also extremely high. Films with improved microstructures that lead to better film adherence, lower defect densities, and improved optical and electronic properties, are clearly needed. Judging from previous investigations, this will be a formidable task; the numerous experiments performed to date have only yielded highly defective, polycrystalline films. A much better understanding of the nucleation and growth of diamond films is required to facilitate these improvements. There is an urgent need to continue the multistep process of carefully characterizing the film structure and properties, correlating these with the deposition parameters, and finally establishing techniques for improving the quality of the deposited films and their physical properties.

The general conclusions of the panel were three fold: First, there was general agreement that the mechanisms controlling the nucleation and growth of CVD-deposited diamond films were not well understood and that continued research in this area was essential to development of high quality films. It was also recognized that the bulk of the existing U.S. research effort was narrowly focussed on the development of electronic material by CVD processes. A broadening of the research to support high-risk, high-payoff studies on alternative avenues of diamond synthesis was strongly encouraged. Finally, it was felt that an eye on the eventual need to scale the process for production was frequently being ignored. Issues relating to scale-up should be addressed from the beginning to promote rapid transition into production.

Fundamental studies on the nucleation and growth of diamond films is critically needed. A number of analytical techniques, both ex situ and in situ, were identified for characterizing diamond growth. It was generally agreed that particular emphasis should be placed on identifying: 1) the gaseous precursor species, 2) the effects of impurities (particularly H2, O2 and the halogens), and 3) the growth mechanism. Without an improved understanding of these issues, advances in promoting 2-D growth of low defect diamond films will be slow. Novel approaches to control nucleation with ion or laser beams should be explored. CVD reactor modelling studies should be encouraged as part of this task.

There was general consensus that a broadening of the research on diamond would be beneficial. Some research is addressing shaping and etching of diamond for electronic applications. Additional research is required for special needs for these areas and adhesion stemming from optical applications. Research on developing post-processing treatments to provide better film morphologies, fewer defects and improved adhesion to the substrate would also be useful.

Current programs have focussed primarily on electronic applications. The Army also has high priority needs in tribology and optics. The extension of diamond processing techniques to other materials such as C3N4, the diamondlike family of materials (including the hydrogen-free compositions), BN and BSiN should be pursued.

Many of the Army applications require that the material be cheap and plentiful. In this respect, exploratory research on alternative processing techniques to CVD would be both warranted and prudent. The expansion of the research base to include feasibility studies on alternative avenues of diamond synthesis such as low temperature, low pressure growth from the liquid, explosive growth, and combustion flame synthesis should be encouraged. Again to promote rapid transition into production, it was stressed that issues relating to scale-up should be addressed from the beginning.

Robert R. Reeber

John T. Prater

TABLE OF CONTENTS

	PAGE
AGENDA	1
ABSTRACTS OF THE ORAL PRESENTATIONS	3
The Advantages of Diamond in Electronics and Electro-Optics (Max N. Yoder)	5
Deposition Methods/Parameters/Processes in Diamond Films (Russell Messier)	7
Microstructure and Properties of Diamond and Diamondlike Thin Films (Jagdish Narayan)	8
Atomic Hydrogen in CVD Diamond Growth (Thomas R. Anthony)	11
Diamond and Diamondlike Materials (John C. Angus)	13
Chemical Studies of Diamond CVD (James E. Butler)	15
Ion Beam Processing of Diamond(like) Films—A Review (James K. Hirvonen)	17
Diagnostics of Sputter Deposition Discharges and Potential Application to Diamond-Like Film Growth (Carolyn R. Aita)	19
Characterization of Growth Processes of Diamond Thin Films by Raman Spectroscopy (Robert J. Nemanich)	21
Nuclear Reaction Analysis of Hydrogen in Materials (William A. Lanford)	23
Army Applications for Diamond and Diamondlike Thin Films (Robert R. Reeber and John T. Prater)	25
Optical Applications for Diamond (Daniel C. Harris)	27
Applications of Diamond-Like Carbon in Infrared Optics (Richard L. C. Wu)	29
SUMMARY OF THE PANEL DISCUSSIONS	33
Characterization of Diamond and Diamond-Like Films (Henry W. White)	35
Modifications of Diamond and Diamondlike Films (James K. Hirvonen)	39
List of Attendees	43

AGENDA

WORKSHOP ON ARMY APPLICATIONS FOR DIAMOND AND DIAMONDLIKE MATERIALS

13-14 June 1989
Siena Hotel, Chapel Hill, N.C.
Chairmen: Drs. J. Prater and R. Reeber

Tuesday, June 13

8:50 Welcome	Dr. J. Prater Dr. R. Reeber (ARO)
9:00 The Advantages of Diamond in Electronics and Electro-Optics	Mr. M. Yoder (ONR)
9:45 Deposition Methods/Parameters/Processes in Diamond Films	Prof. R. Messier (Penn St.)
10:30 Break	
10:45 Microstructure and Properties of Diamond and Diamondlike Thin Films	Prof. J. Narayan (N.C. St.)
11:30 Atomic Hydrogen in CVD Diamond Growth	Dr. T. Anthony (General Electric)
12:15 Break for Lunch	
1:15 Diamond and Diamondlike Materials	Prof. J. Angus (Case-Western)
2:00 Chemical Studies of Diamond CVD	Dr. J. Butler (NRL)
2:45 Break	
3:00 Ion Beam Processing of Diamond(like) Films - A Review	Dr. J. Hirvonen (Spire)
3:35 Diagnostics of Sputter Deposition Discharges and Potential Application to Diamondlike Film Growth	Prof. C. Aita (U. Wisc.-Mil.)

4:10	Characterization of Growth Processes of Diamond Thin Films by Raman Spectroscopy	Prof. R. Nemanich (N.C. St.)
4:45	Nuclear Reaction Analysis of Hydrogen in Materials	Prof. W. Lanford (N.Y. St.-Albany)
5:15	Adjourn	

Wednesday, June 14

8:30	Army Applications for Diamond and Diamondlike Thin Films	Dr. R. Reeber Dr. J. Prater (ARO)
9:00	Optical Applications for Diamond	Dr. D. Harris (Naval Weapons Ctr)
9:15	Applications of Diamondlike Carbon in Infrared Optics	Dr. R.L.C. Wu (Univ. Energy Sys./MTL)
9:30	Panel Discussions on Research Needs:	
	Characterization of Diamond and Diamondlike Films	Prof. H. White (U. Missouri)
	Modifications of Diamond and Diamondlike Films	Dr. J. Hirvonen (Spire)
11:00	Adjourn	

ABSTRACTS
OF THE
ORAL PRESENTATIONS

The Advantages of Diamond in Electronics and Electro-Optics

by

Max N. Yoder
Electronics Division
Office of Naval Research

The saturated charge carrier velocities (both holes and electrons) of diamond exceed those of any other semiconductor. The hole mobility of diamond is exceeded only by that of germanium. While the electron mobility of diamond exceeds that of silicon, it is substantially less than that of most III-V materials; nevertheless, innovative device design approaches have accrued that effectively circumvent the relative lack of electron mobility. Diamond has no known shallow substitutional donor. Recent investigations have found that hydrogen is a shallow donor, but its location is not known. Lithium (a group I element like hydrogen) is known to be a shallow interstitial donor. Recent investigations have found its diffusivity to be nil at temperatures as high as 1000 Celsius.

The optical properties of diamond render it a superlative material in virtually every respect excepting for those requirements requiring nonlinearity. These superlative optical properties must be considered with its mechanical properties for most applications. Paramount among them is the shock resistance parameter wherein diamond excels by orders of magnitude. Also relevant are the tensile strength, thermal conductivity, Young's modulus, Poisson's ratio, and related mechanical characteristics. These are particulary relevant when diamond is considered as a laser host or a material for mirrors, windows, and lenses in extremely high power lasers. Although conventional lenses may be difficult to fabricate in diamond, Fresnel lenses are considered not only possible, but capable of being designed and fabricated with unique properties.

The acoustic properties of diamond render it the material exhibiting the highest elastic wave velocity of any material. This also accounts for the unsurpassed thermal conductivity of diamond. While the thermal conductivity of diamond is impressive, its exploitation must be carefully considered in view of the Kapitsa anomoly and the matching of characteristic acoustic impedance; nevertheless, it can be effectively exploited both for electronic and optical applications.

QUESTIONNAIRE

Name: Max N. Yoder
Affiliation: Office of Naval Research
Address: Code 1114
Arlington, VA 22217
Phone Number: 202-696-4218

Title of Presentation: THE ADVANTAGES OF DIAMOND IN ELECTRONICS & ELECTRO-OPTICS

Presentation is relevant to:

a. Electronic Packaging & Devices	X
b. Optical Windows	X
c. Erosion & Corrosion-Resistant Coatings	
d. Composites	

Briefly state what new approaches to research are presented, discussed or suggested:

1. Roles of hydrogen, oxygen, & halogens
2. Thermal impedance mismatch
3. Free surface energy

Key references (please list one to three):

1. R.W. Keyes; Proc. IEEE, 60, 225 (1972).
2. A.R. Johnson, RCA Review, 26, 163 (1965)
3.

What neglected or developing areas of research, analysis or characterization should be strengthened by future research?

The role of oxygen, hydrogen, and the halogens in nucleating diamond.

DEPOSITION METHODS/PARAMETERS/PROCESSES IN DIAMOND FILMS

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

Whereas ion bombardment is the dominant general deposition process for preparing the class of diamond-like materials which include dense carbons and dense hydrocarbons, it is highly selective chemical processes which control the growth of essentially single-phase, polycrystalline diamond films. Within the last decade a number of thin film chemical vapor deposition (CVD) techniques have been developed for the preparation of diamond at practical rates. These methods can be grouped in three areas: thermally assisted CVD, plasma assisted CVD, and combustion flames as well as combinations of these. In all techniques a high supersaturation of atomic hydrogen is created along with a supersaturation of carbonic species and a substrate temperature in the range of 700-1000°C. Other similarities include process parameters of gas pressure (~10 mbar - 1 bar) and percentage of hydrogen to the total gas pressure (~95-99.9%), and the resulting film morphology.

However, there are a number of other specific process parameters which are considerably different from technique to technique. For instance, the conditions for and mode of gas activation are different for cold plasma and thermal plasma CVD, and, in turn, both are considerably different from combustion flame deposition. These process parameters lead to differences in the energy partitioning in the deposition process, the deposition efficiency, deposition rate, and film uniformity to name just some of the more important ones.

Such a detailed comparison would be a formidable, and possibly worthwhile task, but is not the object of this study. Instead, the focus will be on a single deposition technique, microwave plasma assisted CVD (MPACVD), which is one of the most commonly employed methods to grow diamond films and has been studied by a number of other groups. Even within a specific plasma based deposition method, the exact geometry and materials used in a particular plasma reactor are important, and thus precise comparisons of parameters from one deposition system to another are difficult.

In this paper a consistent set of experiments will be presented in which the growth rate, morphology (as indicated by scanning electron microscopy) and structure (as indicated by Raman spectroscopy) are measured for a range of critical deposition parameters. The investigated experimental parameters are: methane concentration in hydrogen (CH_4%), substrate temperature (T), total gas flow rate (V), total gas pressure (P), and substrate position (distance). The goal of this talk is not to simply establish the optimum set of conditions for highest quality diamond deposition (that is already known, in general, for the type of conditions chosen), but rather to generate data with which we can begin to understand the more fundamental deposition processes of the kinetics and mechanisms of growth.

This work was supported in part by the Office of Naval Research (with funding from the Strategic Defense Initiative Organization's Office of Innovative Science and Technology) under contract no. N00014-86-K-0443 and The Diamond and Related Materials Consortium at The Pennsylvania State University. The specific contributions of W. Zhu, A.R. Badzian, S. Woodrow, D. Pickrell, D. Knight, E. Plesko, A. Inspektor and W. Yarbrough are gratefully acknowledged.

MICROSTRUCTURE AND PROPERTIES OF DIAMOND AND DIAMONDLIKE THIN FILMS

J. Narayan and J. Krishnaswamy
Materials Science and Engineering
North Carolina State University
Raleigh, NC 27695-7916

Abstract

We have investigated characteristics of polycrystalline diamond thin films formed by plasma-enhanced chemical vapor deposition method on silicon substrates using Raman spectroscopy, analytical and high-resolution transmission electron microscopy techniques. Grains with average size 1 μm in diameter were observed in these films. The Raman spectra from these films contain the strongest peak at 1335 cm^{-1}, providing the characteristics signature for sp^3 (diamond) bonding. The broad peak centered around 1550 cm^{-1} is believed to be due to some graphitic bonding. From detailed high-resolution images and microdiffraction, films were characterized to be cubic diamond with a lattice parameter 3.56Å. Diamond crystallites with fivefold external morphologies were also observed. The large crystallites in the films exhibited preferential texture in ⟨011⟩ type orientations. These crystallites were found to be twinned in {111} planes. The large ⟨011⟩ crystallites exhibited matching in {111} or {200} lattice planes of diamond with {022} planes of silicon. This is in agreement with our previous work on the growth of Ni on MgO, which showed that textured growth can occur by matching a set of lattice planes in the absence of matching of lattice constants.

The HRTEM micrographs clearly show that fivefold symmetry in diamond microcrystallites results from twinning in {111} planes, in agreement with

electron diffraction data. The five ⟨110⟩ oriented microcrystallites that provide fivefold symmetry are enclosed by {111} planes. The angles between various planes in these microcrystallites can be directly measured in HRTEM micrographs. The angles between {111} planes are found to vary from 70.5° (ideal) to as much as 74° for some microcrystallites. The boundaries of microcrystallites contain coherent twins with only occasional presence of dislocations to accommodate the misfit. We propose a model for nucleation and formation of fivefold diamond microcrystallites. The proposed model, based upon the presence of a/2 ⟨110⟩{001} edge dislocations or surface steps, is found to be consistent with HRTEM observations.

A new laser ablation and plasma hybrid technique has been developed for depositing thin diamond-like carbon (DLC) films on Si ⟨100⟩ substrates at room temperature and at 100°C with improved optical and mechanical properties. The technique involves coupling of laser energy (λ = 0.308 μm, pulse duration = 40 ns, and power 125 MW/cm^2) to a graphite target and superimposing capacitively stored energy (2 - 3 J at 3 kV) to laser ablated spot. The laser-and plasma-deposited diamond-like carbon films were analyzed by spectroscopic ellipsometry and microhardness measurements. These films showed considerable improvements in both uniformity and homogeneity. Optical properties and hardness of the films deposited by this technique closely match the DLC films. We discuss possible causes of improvements in the above properties of these films.

QUESTIONNAIRE

Name: J. Narayan and J. Krishnaswamy
Affiliation: North Carolina State University
Address: Materials Science and Engineering
Raleigh, NC 27695-7916
Phone Number: 919-737-7874

Title of Presentation: "Microstructure and Properties of Diamond and Diamondlike Thin Films"

Presentation is relevant to:

a. Electronic Packaging & Devices ___
b. Optical Windows X
c. Erosion & Corrosion-Resistant Coatings X
d. Composites ___

Briefly state what new approaches to research are presented, discussed or suggested:

Epitaxial Growth Issues in Diamond Films, Novel Methods for Producing Diamondlike Films

Key references (please list one to three):

1. Appl. Phys. Lett. 53, 1823, (1989)
2. Appl. Phys. Lett. 54, 1661, (1989)
3. Appl. Phys. Lett., (June 5, 1989)

What neglected or developing areas of research, analysis or characterization should be strengthened by future research?

Nucleation and Growth Problems, Epitaxial Considerations, Unseeded Crystallizations Morphologies

Fundamental Issues in the Formation of Diamonlike Films

ATOMIC HYDROGEN IN CVD DIAMOND GROWTH

Thomas R. Anthony
General Electric Corporate Research & Development Center
River Road, Schenectady, New York, 12309
(518) 387-6160

Atomic hydrogen serves several critical roles in CVD diamond growth, namely:

1. Stabilization of the Diamond Surface
2. Reduction of the Size of the Critical Nucleus
3. "Dissolution" of Carbon in the Gas
4. Production of Carbon Solubility Minimum
5. Generation of Condensable Carbon Radicals
6. Abstraction of Hydrogen from Hydrocarbons Attached to the Surface
7. Production of Vacant Surface Sites

Atomic hydrogen satisfies these seven functions and induces CVD diamond growth because of favorable bond energetics. Its compatibility with normal containers, substrates, plasma generators and gas heaters is also important from a practical standpoint.

Nevertheless, the quality of diamond crystals chemically vapor deposited with atomic hydrogen has not improved much over the last seven years. Because many applications such as lasers and semiconductor devices require better crystal quality, alternative low-pressure processes for making diamond must be developed. A first step in this direction is to substitute other elements or compounds for atomic hydrogen. Potential atomic hydrogen substitutes include fluorine, chlorine, bromine, iodine, oxygen, nitrogen, various compounds containing these elements and some metals, as both gases and liquids.

QUESTIONNAIRE

Name: Thomas R. Anthony
Affiliation: GE R&D Center
Address: River Road
Schenectady, NY 12309
Phone Number: 518-387-6160

Title of Presentation: "Atomic Hydrogen in CVD Diamond Growth"

Presentation is relevant to:

a. Electronic Packaging & Devices	X
b. Optical Windows	X
c. Erosion & Corrosion-Resistant Coatings	
d. Composites	

Briefly state what new approaches to research are presented, discussed or suggested:

See abstract

Key references (please list one to three):

1.

2.

3.

What neglected or developing areas of research, analysis or characterization should be strengthened by future research?

1) new methods of synthesis

2) better crystal quality

DIAMOND AND DIAMONDLIKE MATERIALS

John C. Angus
Dept. of Chemical Engineering
Case Western Reserve University
Cleveland, OH 44106

The ability to deposit diamond at low pressures may be one of the most significant new materials technologies of the past several decades. There has been a continuing, rapid increase in both the number of papers and the number of corporate and government laboratories initiating work in this field. However, despite considerable progress, significant electronic and optical applications of CVD diamond still have not been achieved. The defect density, optical absorption and surface roughness of current diamond films preclude their use in these applications. The major obstacle remains the inability to understand and to control the nucleation and growth processes, especially the initial nucleation events. Independent nucleation of new diamond crystals now limits the ability to grow hetero-epitaxial diamond films.

Diamondlike films are extremely smooth and can be applied at low substrate temperatures. They have found application as optical coatings, e.g., on germanium infrared optical coatings. Their properties are, however, inferior to crystalline diamond. There appear to be two types of diamondlike films, hydrogenated and non-hydrogenated. The structure of the former appears to be reasonably well understood. However, the non-hydrogenated diamond films are not yet well characterized. They may, in some cases, be microcrystalline diamond.

New methods of structural characterization, to supplement the information obtained by Raman spectroscopy, are required to understand both diamond and diamondlike films. Electron energy loss spectroscopy (EELS) is very useful in this regard. The mechanical properties (modulus, adhesion, hardness etc.) are very important for applications and require further study.

Additional attention should be paid to the engineering and design of deposition systems and to relating deposition parameters to the properties and structure of the deposit. Emphasis should also be placed on novel deposition methods as well as comparative economic and technical analyses of alternative diamond deposition processes. Synthesis of novel composite structures using vapor-grown diamond also have considerable technological potential.

QUESTIONNAIRE

Name: Prof. John C. Angus
Affiliation: Case Western Reserve University
Address: A.W. Smith Bldg.
Cleveland, OH 44106
Phone Number: (216) 368-4133

Title of Presentation: Diamond and Diamondlike Materials

Presentation is relevant to:

a. Electronic Packaging & Devices X
b. Optical Windows X
c. Erosion & Corrosion-Resistant Coatings X
d. Composites X

Briefly state what new approaches to research are presented, discussed or suggested:

1. Nucleation mechanisms
2. Characterization of diamond and diamondlike carbons by EELS.
3. Comparative economic and technical analysis of deposition methods.

Key references (please list one to three):

1. J.C. Angus and C.C. Hayman, Science 241, 913-21 (1988)
2. J.C. Angus and F. Jansen, J. Vac. Sci. and Tech. A6, 1778-82 May/June (1988).
3.

What neglected or developing areas of research, analysis or characterization should be strengthened by future research?

1. Fundamental mechanisms of nucleation and growth.
2. Structure and properties of non-hydrogenated diamondlike films.
3. Fundamentals of reactor engineering including: plasma physics, chemical kinetics, fluid mechanics, comparative analysis of reactor types.

CHEMICAL STUDIES OF DIAMOND CVD

James E. Butler
Gas/Surface Dynamics Section
Code 6174
Naval Research Laboratory
Washington, DC

ABSTRACT:

It is now well established that in the region of its thermodynamic metastability, diamond can be synthesized by a variety of techniques. This presentation will cover an overview of these techniques, some of the motivations behind diamond research, applications which are already appearing for CVD diamond, and challenges facing the technology. The filament-assisted CVD and combustion flame growth techniques in use at NRL will be described. The use of micro-Raman analysis of diamond deposited in flames and the results of insitu laser spectroscopic analysis of the filament-assisted diamond growth environment will be presented. We have employed tunable IR diode laser, Resonant enhanced multi-photon ionization, and laser induced fluorescence spectroscopies to detect CH_3, C_2H_2, C_2H_4, H, and C_3 during the hot filament-assisted CVD of diamond from CH_4 in H_2. Simple models of the chemistry of diamond CVD are discussed.

QUESTIONNAIRE

Name: J. E. Butler
Affiliation: Code 6174
Address: Naval Research Lab.
Washington, DC 20375
Phone Number: 202-767-1115

Title of Presentation: "Chemical Studies of Diamond CVD"

Presentation is relevant to:

a. Electronic Packaging & Devices X
b. Optical Windows X
c. Erosion & Corrosion-Resistant Coatings X
d. Composites X

Briefly state what new approaches to research are presented, discussed or suggested:

Diagnostics are applied to Diamond CVD environment and a simple model of gaseous processes is developed.

Key references (please list one to three):

1. Appl. Phys Lett, 52, 2043 (1988)
2. Appl. Phys Lett, 54, 1031 (1989)
3. Mat. Lett, 7, 289 (1989)

What neglected or developing areas of research, analysis or characterization should be strengthened by future research?

Understanding of gaseous and surface processes in homo-epi of diamond and nucleation of diamond. Modelling of these processes.

ION BEAM PROCESSING OF DIAMOND(LIKE) FILMS-A REVIEW

J. K. Hirvonen
Spire Corporation
Patriots Park
Bedford, MA 01730

Since the early 1970's various ion beam processes have been used to deposit diamond(like) coatings. This talk will concentrate on the use of directed ion beams versus plasma assisted processes for diamond (like) formations. Ion beam processes being used include: i) ion beam deposition of a carbon containing molecular species ion beam (e.g., CH_4^+), ii) ion beam depositions of a mass separated, low energy C^+ ion beam, and iii) the simultaneous physical vapor deposition of carbon atoms accompanied by simultaneous bombardment with energetic ions.

The basic physics of energetic ion/solid interactions will be briefly reviewed and related to nucleation, and subsequent film growth. Several ion based techniques used in these studies will be reviewed and the characteristics of coatings prepared by them will be compared. The evolution and present status of the ion beam, based techniques will be discussed and compared to plasma based processes. Finally, some recent work investigating the use of ion beams for the production of cubic boron nitride, having a diamond structure, will be presented.

QUESTIONNAIRE

Name: James K. Hirvonen
Affiliation: Spire Corp.
Address: Patriots Park
Bedford, MA 01730
Phone Number: 617-275-6000

Title of Presentation: "Ion Beam Processing of Diamond (like) Films - A Review"

Presentation is relevant to:

a. Electronic Packaging & Devices ___
b. Optical Windows ___
c. Erosion & Corrosion-Resistant Coatings X
d. Composites X

Briefly state what new approaches to research are presented, discussed or suggested:

A review giving history and present status of Ion beam based techniques for diamond (like) formation.

Key references (please list one to three):

1. Ion-Beam Deposition of Thin Films of Diamondlike Carbon, S. Aisenberg and R. Chabot, Journ. Appl. Physics, 42(7) June 1971

2. Preparation and Structure of Carbon Film Deposited by A Mass-Separated C^+ Ion Beam, Miyazawa et. al. Journ. Appl. Physics 55(1), January 1984.

What neglected or developing areas of research, analysis or characterization should be strengthened by future research?

Determine feasibility of growth rates competitive with CVD using ion based process.

DIAGNOSTICS OF SPUTTER DEPOSITION DISCHARGES AND POTENTIAL APPLICATION TO DIAMOND-LIKE FILM GROWTH

Carolyn Rubin Aita
Materials Department and the Laboratory for Surface Studies
University of Wisconsin-Milwaukee
P.O. Box 784
Milwaukee, Wisconsin 53201
aita@csd4.milw.wisc.edu

ABSTRACT

This presentation is concerned with plasma diagnostics used for in situ monitoring and control of the sputter deposition process with an eye towards application to the growth of diamond-like films.

Sputter deposition is a useful method for near-room temperature synthesis of high temperature/high pressure phases of insulating materials. A feature of the process is that the growing film is in contact with a low pressure, weakly ionized glow discharge. In situ real-time plasma diagnostics is therefore essential to determine process parameter-growth environment-film property relationships for a particular materials system.

This presentation is structured as follows. The electrical, space-charge, and light emission features of the sputter deposition discharge are first briefly reviewed. Independent process parameters are defined, and effect of changing these parameters on discharge characteristics is discussed. Next, optical (1) and mass spectrometry (2) specifically related to monitoring the flux and energy of non-electronic species in sputter deposition discharges are described. It is shown how these techniques yield complementary information. Last, the literature on sputter deposition of diamond-like films is reviewed (3-5). These films are grown by sputtering a graphite target in an Ar plasma, where H is not a factor in stablilzing sp^3 bonding. The degree of three-to-four fold C coordination was found to depend upon the discharge power, which led to the proposal (5) that the ratio of Ar^+/C species arriving at the growth interface is the critical factor in determining C coordination in the film. We finish by formulating questions raised by the few published reports of diamond-like film growth by sputter deposition, and outline experiments in plasma diagnositics that hopefully will provide the answers.

1. J.E. Greene, J. Vac. Sci. Technol. 15, 1718 (1978).
2. C.R. Aita, J. Vac. Sci. Technol. A 3, 6225 (1985).
3. N. Savvides, J. Appl. Phys. 58, 518 (1985).
4. N. Savvides and B. Window, J. Vac. Sci. Technol. A 3, 2386 (1985).
5. N. Savvides, J. Appl. Phys. 59, 4133 (1986).

QUESTIONNAIRE

Name: Prof. Carolyn Rubin Aita
Affiliation: Materials Department and the Laboratory for Surface Studies
Address: University of Wisconsin-Milwaukee
Milwaukee, Wisconsin 53201
Phone Number: (414) 229-4733

Title of Presentation: Diagnostics of Sputter Deposition Discharges and Potential Application to Diamond-Like Film Growth

Presentation is relevant to:

a.	Electronic Packaging & Devices	x
b.	Optical Windows	x
c.	Erosion & Corrosion-Resistant Coatings	x
d.	Composites	

Briefly state what new approaches to research are presented, discussed or suggested:

Development of process parameter-growth environment-film property relationships for the sputter deposition of diamond-like coatings, using in situ discharge diagnostics for plasma monitoring and control.

Key references (please list one to three):

1. N. Savvides, J. Appl. Phys. 59, 4133 (1986).

2. C.R. Aita, J. Vac. Sci. Technol. A 3, 6225 (1985).

3. J.E. Greene, J. Vac. Sci. Technol. 15, 1718 (1978).

What neglected or developing areas of research, analysis or characterization should be strengthened by future research?

The formation of diamond-like coatings by sputter deposition, and monitoring and control of the process by complementary mass and optical spectrometric techniques.

CHARACTERIZATION OF GROWTH PROCESSES OF DIAMOND THIN FILMS BY RAMAN SPECTROSCOPY

R.J. Nemanich, Y. M. LeGrice, R.E. Shroder and J.T. Glass

DEPARTMENT OF PHYSICS
AND DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING
NORTH CAROLINA STATE UNIVERSITY
RALEIGH, NC 27695-8202

Recent advances of CVD techniques have demonstrated the growth of crystalline diamond carbon films. The growth processes involve activated CVD deposition from methane or other hydrocarbon diluted in hydrogen. For these and other activation methods it has been found that for concentrations of ~1 % methane in hydrogen, the films exhibit a high percentage of diamond crystalline structures. While the CVD techniques show diamond structures which are characterized by sp^3 carbon bonding, sp^2 structures which are characteristic of graphite are also observed. In this study, Raman spectroscopy is applied to characterize carbon films produced under various CVD growth conditions, and from the observations, models for the growth processes are suggested.

One of the major emphasis of the characterization process is to identify the particular structures in the film and to quantitatively estimate the amount of diamond in the film. An analysis of the different Raman spectra has been carried out for graphite, microcrystalline graphite, amorphous sp^2 materials and amorphous sp^3 bonded structures. Thus by comparison to these measurements, the sp^2 and sp^3 carbon bonded structures can be identified.

The Raman spectra of films grown with different methane show several spectral features which are associated with the different possible structures. These results demonstrate the composite nature of the films. The aspects of optical characterization of films composed of highly absorbing graphite and transparent diamond are explored. For reference, composite samples are prepared from powders of graphite and diamond. The results demonstrate that the scattering from the films is dependent on the crystalline domain sizes of the various composites. Analysis of the linewidth of the diamond Raman peak is presented as a characterization of the diamond domain size.

The initial stages of film growth often involve nucleation on a surface. In the case of diamond film growth, luminescence results indicate that a surface layer forms before nucleation of diamond regions. A feature that prove most interesting in the Raman spectra is the broad component at 1140cm^{-1} which has been attributed to disordered sp^3 bonded carbon. This feature is most evident at conditions where the 1332 cm^{-1} diamond feature is weakly observed. It is also much weaker for films examined just after nucleation of the film growth process. Thus this feature seems most evident at the onset of diamond nucleation. It is suggested that the disordered sp^3 structures form as precursors to the nucleation of crystalline diamond structures.

Acknowledgement: We gratefully acknowledge R. Rudder and R. Markunas of RTI, and K. Kobashi of Kobe Steel, Ltd for helpful discussions and for supplying some of the samples used in this study. This work is supported in part by the SDIO/IST through the Office of Naval Research under contract N00014-86-K-0666.

QUESTIONNAIRE

Name: R. J. Nemanich
Affiliation: North Carolina State University
Address: Department of Physics
Raleigh, NC 27695-8202
Phone Number: 919-737-3225 FAX 737-7331

Title of Presentation: "Characterization of Growth Processes of Diamond Thin Films by Raman Spectroscopy"

Presentation is relevant to:

a.	Electronic Packaging & Devices	X
b.	Optical Windows	X
c.	Erosion & Corrosion-Resistant Coatings	
d.	Composites	X

Briefly state what new approaches to research are presented, discussed or suggested:

1) Dependence of optical characterization on domain sizes.

2) Relation of Raman-luminescence to diamond growth processes.

Key references (please list one to three):

1. R. J. Nemanich et. al. J. Vac. Sci. & Technol.

2. R. E. Shroder et. al. SPIE Symposium on Diamond Optics

3.

What neglected or developing areas of research, analysis or characterization should be strengthened by future research?

NUCLEAR REACTION ANALYSIS OF HYDROGEN IN MATERIALS

W. A. Lanford
Physics Department
SUNY Albany
Albany, New York 12222

Hydrogen plays a variety of important roles in the science of packaging, surface coating and passivation. First, in the general area of surface corrosion, usually reactions with atmospheric water are of key concern and it is necessary to have a method with which to measure the penetration of hydrogen (from water) into surfaces in order to determine the mechanism of corrosion. Second, when thin-film coating are applied, interface hydrogen (present as a contaminant) can have large effects on the adhesion of the coating to the substrate. Third, many (most) of the thin-film coatings (e.g. carbon, silicon nitride,...) tend to contain large amount of hydrogen which can have large effects on film properties (density, stress, index, hardness, chemical durability...); hence, it is important to have a method for characterizing the hydrogen content of these coatings.

Nuclear reaction analysis for hydrogen will be briefly discussed in the context of thin-film coatings. The application of plasma enhanced CVD carbon films as coatings on long wavelength transmitting zirconium fluoride glasses will be briefly discussed.

QUESTIONNAIRE

Name: William A. Lanford
Affiliation: Physics Department
Address: SUNY at Albany
Albany, NY 12222
Phone Number: 518-442-4480

Title of Presentation: "Nuclear Reaction Analysis of Hydrogen in Materials"

Presentation is relevant to:

a. Electronic Packaging & Devices X
b. Optical Windows X
c. Erosion & Corrosion-Resistant Coatings X
d. Composites ___

Briefly state what new approaches to research are presented, discussed or suggested:

Use of nuclear reaction analysis for hydrogen will be discussed in the context of corrosion studies, thin film collision, and properties of thin films.

Key references (please list one to three):

1. "Hydrogen in Thin Films", W. A. Lanford, Diagnostic Techniques for Semiconductor Materials and Devices, T. J. Shaffner and D. K. Schroeder, editor, Electrochemical Society Proceeding 88-20 (1988) 27.

2. "Interface Self-Cleaning by Partially Ionized Beam Deposition", A. S. Yapsir et.al., A.P.L. 52 (1988) 1962.

What neglected or developing areas of research, analysis or characterization should be strengthened by future research?

ARMY APPLICATIONS FOR DIAMOND AND DIAMONDLIKE THIN FILMS

John T. Prater, Robert R. Reeber and CPT William A. Herman (USAR)

Materials Sciences Division
U.S. Army Research Office,
Research Triangle Park, NC 27709

Recent accomplishments in synthesizing diamond and diamondlike films has generated a high level of interest within industry and government. Its unique combination of physical properties distinguishes diamond as the ideal material for fulfilling a broad variety of material needs. Originally, its exceptional hardness led to the wide use of natural and man-made diamonds in machining and polishing operations. The advent of diamond films now expands the potential utility of diamond to a much broader spectrum of new technologies. The unsurpassed thermal conductivity of diamond makes it the material of choice for heat dissipation applications ranging from electronic packaging to heat exchangers in space. In conjunction with its high electrical resistivity and the demonstrated ability to dope diamond to produce a semiconductor with very repectable carrier mobilities, diamond has outstanding potential for fabricating high-temperature, high-power electronic devices. This will, however, require the development of techniques for growing single-crystal films. Another area of great importance to the Army is the application of diamond as protective windows/coatings for optical systems. Diamond can be prepared so as to be transparent over virtually any part of the electromagnetic spectrum, from the UV to mm wave. In combination with its excellent erosion resistance, thermal shock resistance, stability and strength, diamond represents the ideal material for radomes and optical components for lasers. Likewise, its exceptional strength and thermal shock resistance makes diamond a potentially important material for the construction of parts that will undergo extremely demanding thermal and mechanical loading cycles. Finally, the exceptional stability of diamond makes it a potentially important material for service in unusually harsh chemical, tribological and radiation-intense environments.

QUESTIONNAIRE

Name: John T. Prater, Robert R. Reeber and CPT William A. Herman
Affiliation: U.S. Army Research Office
Address: P.O. Box 12211
Research Triangle Park, NC 27709-2211
Phone Number: 919-549-0641

Title of Presentation: "Army Applications for Diamond and Diamondlike Thin Films"

Presentation is relevant to:

a. Electronic Packaging & Devices X
b. Optical Windows X
c. Erosion & Corrosion-Resistant Coatings X
d. Composites X

Briefly state what new approaches to research are presented, discussed or suggested:

The properties of diamond films and areas of potential application are discussed.

Key references (please list one to three):

1.

2.

3.

What neglected or developing areas of research, analysis or characterization should be strengthened by future research?

Complete correlation relating deposition conditions/film microstructure/physical properties is required.

Mechanisms for film nucleation must be clearly established.

OPTICAL APPLICATIONS FOR DIAMOND

Daniel C. Harris
Naval Weapons Center
Code 3853
China Lake, California 93555

Diamond is a potentially useful material for infrared-transmitting missile domes. Such domes must have high transmission and low emission at elevated temperatures of operation. The material should also resist erosion from collisions with rain and dust and must tolerate extreme thermal shock. Diamond is unique among materials that could be used for domes. It is extremely hard and strong, with very high thermal conductivity and low thermal expansion. It is a good transmitter in the 8-14 um atmospheric window and has the added bonus of being a good transmitter of millimeter wavelengths. Two approaches for near term use of diamond in the area of infrared domes are (1) to cost existing materials such as ZnS and (2) to produce bulk diamond hemispheres. One limitation of diamond is that oxidation occurs in the air at 700-800 C. Technical issues related to diamond dome applications include: (1) incompatibility of sulfide dome materials with diamond deposition plasmas; (2) poor adherence of diamond to many substrates; (3) need for an infrared-transmitting buffer layer to promote diamond-substrate adherence and match thermal expansions; (4) development of anti-reflection and anti-oxidation coatings for diamond; and (5) development of polishing techniques for diamond.

QUESTIONNAIRE

Name: Daniel C. Harris
Affiliation: Naval Weapons Center
Address: Code 3854
China Lake, CA 93555
Phone Number: 619-939-1649
AV 437-1649

Title of Presentation: OPTICAL APPLICATIONS FOR DIAMOND

Presentation is relevant to:

a.	Electronic Packaging & Devices	___
b.	Optical Windows	X
c.	Erosion & Corrosion-Resistant Coatings	X
d.	Composites	___

Briefly state what new approaches to research are presented, discussed or suggested:

Infrared transmission of diamond films

Air oxidation of diamond films

Key references (please list one to three):

1.

2.

3.

What neglected or developing areas of research, analysis or characterization should be strengthened by future research?

Adhesion of diamond to other materials

Oxidative protection of diamond at elevated temperature

Polishing of diamond surface

Growth of stress-free bulk diamond (1 mm thick)

APPLICATIONS OF DIAMOND-LIKE CARBON IN INFRARED OPTICS*

Richard L. C. Wu
Universal Energy Systems, Inc.
4401 Dayton-Xenia Road
Dayton, Ohio 45432

Diamond-like carbon coatings have been deposited on several infrared (IR) transmitting substrates using the ion-beam technique. These IR materials of interest are silicon, olycarbonates, fused silica, zinc sulfide, zinc selenide, BK-7, KG-3 glass, and heavy metal fluoride. Optimum deposition parameters have been determined as a function of source gas composition (CH_4/H_2), source pressure, ion-impact energy (500 ~ 1000 eV), substrate materials and cleaning procedures.

Extensive characterization of the DLC films was performed. Rutherford backscattering and proton recoil techniques were used to analyze carbon and hydrogen content and impurities. These films contains 70% atomic carbon and 30% atomic hydrogen. Auger electron spectroscopy showed a trace (<0.2 at.%) of nitrogen. Transmission electron microscopy was used to analyze the crystallinity, void structure and surface microstructure of the DLC film, which were found to be amphorous, dense and pinhole free. The Knoop hardness of the DLC was measured to be 1508 ± 173 kg/mm^2 using a 10 g load. The IR and visible transmission and IR reflectance of DLC coated and uncoated optical substrates were measured. The transmission of the DLC coated substrate is the same or better than the uncoated substrate between 1 μm to 15 μm. The index of refraction was measured by ellipsometry and was determined to be 1.91 ± 0.02 with an extinction coefficient <0.001 at 10.6 μm. The absorption coefficient of the DLC was measured using adiabatic laser calorimetry and found to be 189 ± 10 cm^{-1}.

The environmental resistance of the DLC was performed using various acids and solvents. The adhesion of the films was tested after exposure to different environments by the Scotch tape and rubber wear test (MIL-C-48497A). The coating adhesion was not affected by these tests. Also, the DLC adhesion was not affected by exposure to high humidity and severe temperature cycling of -196°C and 98°C. The effect of high ion energy radiation on DLC film was studied using 1 MeV gold, 6.4 MeV fluorine and 300 KeV oxygen. The radiation resistance of these films was high. The potential applications of the DLC film in infrared optics for antireflection, abrasion and corrosion resistant coatings will be presented and discussed.

*The author wishes to thank the Army Materials Technical Laboratories, Watertown, MA for their support under Contract No. DAAL04-86-C-0030.

QUESTIONNAIRE

Name: Dr. Richard L.C. Wu
Affiliation: Universal Energy Systems, Inc.
Address: 4401 Dayton-Xenia Road, Dayton, Ohio 45432

Phone Number: (513) 426-6900

Title of Presentation: Applications of Diamond-like Carbon in Infrared Optics

Presentation is relevant to:

a. Electronic Packaging & Devices ____
b. Optical Windows X
c. Erosion & Corrosion-Resistant Coatings X
d. Composites ____

Briefly state what new approaches to research are presented, discussed or suggested:

Diamond-like carbon has been coated on several infrared transmitting optics using high energy ion beam technique. The depositing technique is a low temperature process with the improvement of adhesion between the substrate and DLC film. These DLC films can be used in the abrasion and corrosion resistant and antireflection coatings for IR optics.

Key references (please list one to three):

1. R.L.C. Wu and John A. Woollam, UES Final Report, U.S. Army Materials Technology Laboratory, Contract No. DAAL04-86-C-0033, 1988.
2. R.L.C. Wu, "Synthesis and Characterization of Diamond-like Carbon Films Using Ion Beam Technique, Proceedings of Materials Research Society (Spring), 1989.
3. J. T. Keeley and R.L.C. Wu, "Diamond-like Carbon Films as a Protective Coating forZnS and ZnSe," Proceedings of First International Symposium on Diamond and Diamond-like Films, 1989.

What neglected or developing areas of research, analysis or characterization should be strengthened by future research?

Nuclear magnetic resonance is a valuable tool for studies of local atom bonding interaction in materials. The NMR study of DLC film can yield the type of bonding between hydrogen and carbon in the film. The present study was not successful in obtaining this information due to a signal-to-noise ratio problem.

SUMMARY OF THE PANEL DISCUSSIONS

Panel Discussion of Research Needs

Characterization of Diamond and Diamond-Like Films

H. W. White, Panel Moderator
University of Missouri-Columbia

Questions addressed by the panel were: (1) What is the current status of characterization and growth of diamond and diamond-like films? and (2) Which future directions for research are most important?

A recurring comment heard throughout the conference and in the panel discussion was the critical need for a better understanding of the mechanism of nucleation. We know little about chemical precursors to diamond growth on diamond or foreign substrates. We understand very little about the kinetics and growth mechanisms in CVD diamond or diamond-like films. As a consequence, we do not know how to achieve high 2-D growth rates. There are few scientific papers published on fundamental studies of the interface region; hence, the lack of understanding is not surprising. As a consequence, fundamental work is needed to enhance our knowledge of the basic mechanisms of nucleation and growth.

A number of tools have been used to characterize both diamond and diamond-like films w/wo hydrogen as well as the film substrate interface. In situ techniques are especially valuable in that they allow the interface region to be monitored during the actual growth process. Listed below are some of the proven in situ characterization techniques as well as several that are just now beginning to be explored. There are a number of other techniques that probably can and will be used for in situ measurements. The list is not intended to be exhaustive.

- IRAS (Infrared Reflectance Absorption Spectroscopy), for identification of surface species.
- Raman Spectroscopy, for identification of crystal structure and bonding.
- SHG (Second Harmonic Generation), an interface-specific probe which is undergoing rapid development.
- CARS, which is a valuable technique for profiling the plasma temperature.
- Ellipsometry which provides invaluable information on the optical constants of the growing film.
- Mass spectrometry.

Other techniques are required for careful characterization of film and crystal properties. These include:

- o TEM (Transmission Electron Microscopy) which provides high-resolution structure information.
- o SEM (Scanning Electron Microscopy).
- o XRD (X-Ray Diffraction Spectroscopy), for structural information.
- o Auger Spectroscopy, for elemental analysis and XPS for chemical bonding.
- o RBS (Rutherford Back Scattering).
- o ^{15}N Neutron Reaction Spectroscopy, for analysis of hydrogen.
- o Direct Ion Scattering.
- o Neutron Spectroscopy (lattice dynamics).
- o PET (Position Emission Tomography), for the study of voids.
- o EELS (Electron Energy Loss Spectroscopy), for surface analysis.
- o HREELS (High Resolution EELS), for surface analysis.
- o Microluminescence, for impurity studies.
- o STM (Scanning Tunneling Microscopy), for atomic resolution surface morphology.

There is a continuing and critical need of modeling of the gas phase, as well as crystal-growth mechanisms, and defect formation/annihilation. The gas phase is very complex with many ionized species. Work on developing gas-phase and crystal-growth theories should utilize to the extent possible previous work that has been done to characterize natural diamonds and for MOCVD, MBE combustion and reactor modeling, growth techniques.

There are several areas of research where characterization techniques mentioned previously will prove useful in advancing our understanding of the growth of diamond and diamond-like films.

- o More work needs to be done on homoepitaxy. As an understanding of homoepitaxy is gained, there could be a systematic transition to the study of more complex heteroepitaxy systems.
- o Efforts should continue to determine the immediate chemical precursors to diamond and diamond-like film growth. Several studies on the major

molecular species occurring in the gas phase are in progress. Greater control of diamond growth may be gained through ion-flux control techniques, e.g., hydrogen beams. Such studies would also contribute to our understanding of precursor chemistry.

- It is important to understand the role of trace additions in the gas phase and on the reaction surface. The chemistry is very complex. The best optical diamond to date has been made with addition of a small amount of oxygen to the gas feed stock (e.g., by incorporating CO gas).

- Additional modeling and data are needed on the rate and energetics of defects and void formation in the initiation and growth process. Better potentials and additional work in the use of potentials and electronic bond structure calculations are needed to model growth patterns, electronic properties, and structure of films.

- Most of the films have significant strain. We need quantitative tools to relate strain to growth conditions. X-ray, ellipsometry and Raman are good candidates.

- Additional work is needed in the area of high-temperature processing. Fabrication of devices is very dependent on the etching/cutting/polishing process. Such studies are rather recent in the U.S. As a related issue we need to understand how halogens terminate the diamond surface.

- Improved adhesion of diamond and diamond-like carbon films to various substrates is a broad and continuing need. A number of systems which should be investigated include metal-diamond interfaces, ohmic contacts and the possibility of using special interfaces such as plasma polymerized films or ion bombarded surfaces.

- Diamond and diamond-like carbon films have, in general, poor annealing properties. Can novel treatments i.e. (high pressure/temperature) techniques be developed that will yield special film properties?

Panel Discussion on Research Needs

Modifications of Diamond and Diamondlike Films

J. Hirvonen, Panel Moderator
Spire Corporation

The successful development of low-cost techniques for preparing high quality diamond and diamondlike materials will be a technological boon for the Army and U.S. industry. However, realization of these potential benefits will require a much better understanding of the nucleation and growth of these materials and the development of new techniques for controlling the growth of these films to improve their properties. This panel sought to identify key research areas that would most benefit the development of this important technology.

The conclusions of the panel were three fold: First, there was general agreement that the mechanisms controlling the nucleation and growth of CVD-deposited diamond films were not well understood and that continued research in this area was essential to development of high quality films. It was also recognized that the bulk of the existing U.S. research effort was narrowly focussed on the development of electronic material by CVD processes. A broadening of the research to support high-risk, high-payoff studies on alternative avenues of diamond synthesis was strongly encouraged. Finally, it was felt that an eye on the eventual need to scale the process for production would be very desirable. Specific recommendations in these areas are listed below.

I. Nucleation and Growth of CVD Diamond Films

- Research on developing a better understanding of the nucleation and growth processes of diamond, which would include studies to:

    a) Identify the gaseous precursor species for film growth. Recommend that organic chemists be consulted to provide insight on synthesis of novel organic precursors?

b) Establish the mechanism of film growth and identify techniques for promoting 2-D growth of diamond and control of film microstructure and properties.

c) Identify the effect of impurities, especially hydrogen, oxygen and the halogens, on film growth and determine methods for controlling impurity levels in diamond films.

d) Investigate the effect of adatom energy on PACVD film growth using a carbon ion source or ECR source.

e) Identify the mechanism of defect generation in diamond and methods for their elimination.

f) Control nucleation with ion or laser beams.

g) Determine growth/etching kinetics for diamond/graphite.

- Characterization of the diamondlike family of materials, including the hydrogen-free compositions, should be pursued.

- CVD reactor modelling studies should be encouraged.

II. Expansion of Research to Include New Areas

- Investigate alternative growth techniques:

  a) Feasibility of low temperature, low pressure growth from the liquid.

  b) Methods of explosive growth.

- Post-processing of diamond to improve film properties:

  a) Contact technology for electronic applications is required.

b) Post-processing treatments to provide better film morphologies, fewer defects and improved adhesion to the substrate.

c) Conversion techniques using pressure/temperature gradients.

- Current programs have focussed primarily on electronic applications. Recognize that the Army also has high priority needs in tribology and optics that are technically less demanding.

- The extension of diamond processing techniques to related materials such as C_3N_4, diamondlike carbon, BN and BSiN.

III. Scale-Up for Specific Applications: Issues relating to scale-up should be addressed from the beginning to promote rapid transition into production.

- New approaches for growth, such as flame synthesis, should address scale-up and versatility issues from the beginning.

- Comparisons with existing technologies can to a limited extent be used to provide a general assessment of capital and production costs.

- Need models of the CVD reactor process and the nucleation and growth process to permit the efficient extrapolation to larger systems. Codes are available to do this with a minimum of rewrite.

- Desirable that communication with the end user be present from the beginning.

IV. General Comments

- Industrial - academic collaborations should be strongly encouraged.

- Collaboration between investigators could be improved through development of a diamond technical database and listing of researcher names, addresses, telephone, fax and E-mail numbers.

LIST OF ATTENDEES

WORKSHOP ON ARMY APPLICATIONS FOR DIAMOND AND DIAMONDLIKE MATERIALS
June 13-14, 1989

Carolyn R. Aita
Materials Department and the
Laboratory for Surface Studies
University of Wisconsin-Milwaukee
P.O. Box 784
Milwaukee, WI 53201
414-229-4733
Fax: 414-229-6958
E-Mail: aita@csd4.milw.wisc.edu

John C. Angus
Department of Chemical Engineering
Case Western Reserve University
A. W. Smith Building
Cleveland, OH 44106-4931
216-368-4133
E-Mail: angus@cwru

Thomas Anthony
General Electric Corporate Research
and Development Center
River Road
Schenectady, NY 12309
518-387-6160
E-Mail: anthony@ge.crd.com

James E. Butler
Naval Research Laboratory
Gas/Surface Dynamics Section
4555 Overlook Avenue, SW
Code 6174
Washington, DC 20375-5000
202-767-1115
Fax: 202-767-1295
E-Mail: butler2@nrl.arpa

Helen M. Dauplaise
U.S. Army Materials Technology
Laboratory
SLCMT-EMS
Watertown, MA 02172-0001
617-923-5383 AV 955-5383
E-Mail: hdaupla@amtl

Robert F. Davis
Materials Science and Engineering
Department
North Carolina State University
Box 7907
Raleigh, NC 27695
919-737-3272
Fax: 919-737-3419

Jeffrey T. Glass
Materials Science and Engineering
Department
North Carolina State University
Box 7907
Raleigh, NC 27695-7907
919-737-7216
Fax: 919-737-3419

Daniel C. Harris
Naval Weapons Center
Optical and Electronic Materials
Code 3854
China Lake, CA 93555
619-939-1649 AV 437-1649

James K. Hirvonen
Spire Corporation
Patriots Park
Bedford, MA 01730
617-275-6000

Jayaram Krishnaswamy
North Carolina State University
Materials Science & Engineering
Box 7916, Burlington Lab
Raleigh, NC 27695-7916
919-737-3555

William A. Lanford
Department of Physics
State University of New York
at Albany
Albany, NY 12222
518-442-4480
Fax: 518-446-4486

LIST OF ATTENDEES (cont.)

William D. Martin
U.S. Army Strategic Defense Command
CSSD-H-VP
P.O. Box 1500
Huntsville, AL 35807-3801
205-722-1533 AV 788-1533

Stoney Massey
U.S. Army Strategic Defense Command
CSSD-H-VE
P.O. Box 1500
Huntsville, AL 35807-3801
205-895-4821 AV 788-4821

James W. Mayer
Department of Materials Science
Cornell University
210 Bard Hall
Ithaca, NY 14853
607-255-7273

Russell Messier
The Pennsylvania State University
265 Materials Research Lab
University Park, PA 16802
814-865-3704

Jagdish Narayan
Materials Science and Engineering
North Carolina State University
Raleigh, NC 27695-7916
919-737-7874 FAX 919-737-7642

Robert J. Nemanich
Department of Physics
North Carolina State University
Box 8202
Raleigh, NC 27695-8202
919-737-3225 FAX 737-7331

Coy Dale Perry
U.S. Army Missile Command
AMSMI-RD-ST-CM
Redstone Arsenal, AL 35898-5247
205-876-1074

John T. Prater
U.S. Army Research Office
Materials Science Division
P.O. Box 12211
Research Triangle Park, NC 27709
919-549-0641 AV 935-3331
Fax: 919-549-9399
E-Mail: prater@aro-emh1.army.mil

Robert R. Reeber
U.S. Army Research Office
Materials Science Division
P.O. Box 12211
Research Triangle Park, NC 27709
919-549-0641 AV 935-3331
Fax: 919-549-9399
E-Mail: reebrr@unc.bitnet
E-Mail: reeber@aro-emh1.army.mil

Alessandro Rengan
Materials Science Department
North Carolina State University
Raleigh, NC 27695
919-737-3535

Henry W. White
Department of Physics and Astronomy
University of Missouri-Columbia
Columbia, MO 65201
314-882-3625

Richard L. C. Wu
Universal Energy Systems, Inc.
4401 Dayton-Xenia Road
Dayton, OH 45432
513-426-6900

Max Yoder
Office of Naval Research
Electronics Division
Code 1114
Arlington, VA 22217
202-696-4218