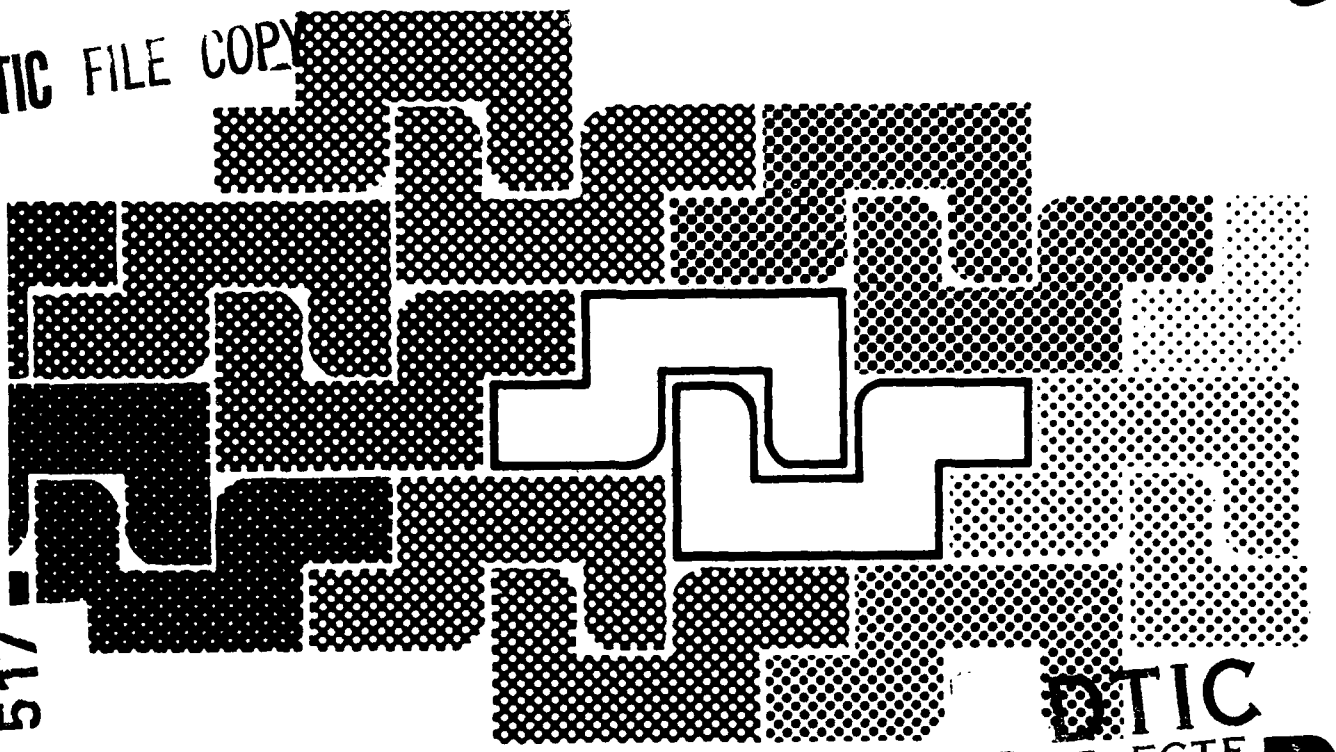
6375-715-02

DTIC FILE COPY



AD-A225 517

DTIC
ELECTE
AUG22 1990
S & E D

NATO-ADVANCED STUDY INSTITUTE

DIAMOND AND DIAMOND-LIKE FILMS AND COATINGS

IL CIOCCO, CASTELVECCHIO PASCOLI, ITALY

JULY 22 - AUGUST 3, 1990

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

90 08 17 071

MAJOR SPONSOR

Scientific Affairs Division, North Atlantic Treaty Organization

CO-SPONSORS

Metals and Ceramics Division, Oak Ridge National Laboratory, USA

National Science Foundation, USA

Fraunhofer Institut für Angewandte Festkörperphysik, FRG

Consorzio Instituto Nazionale Fisica della Materia, Italy

Politecnico di Torino, Italy

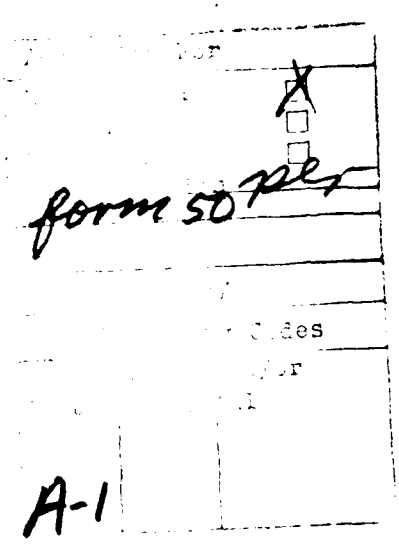
Office of Naval Research, USA

Crystallume, Inc., USA

Nano Instruments, Inc., USA

European Research Office, United States Army

Applied Science and Technology, Inc.



DIRECTORS

Robert E. Clausing	Oak Ridge National Laboratory Oak Ridge, TN, USA
John C. Angus	Case Western Reserve University Cleveland, OH, USA
Peter Koidl	Fraunhofer Institut für Angewandte Festkörperphysik Freiburg, FRG

ORGANIZER

Carl J. McHargue	Oak Ridge National Laboratory, USA

INTERNATIONAL ADVISORY COMMITTEE

Y. Catherine	University of Nantes, France
F. Demichelis	Politecnico di Torino, Italy
A. H. Lettington	Royal Signals & Radar Establishment, UK
N. Setaka	National Institute for Researches in Inorganic Materials, Japan
M. R. Wertheimer	Ecole Polytechnique, Canada

LECTURERS

J. C. Angus	Case Western Reserve University, USA
T. R. Anthony	General Electric Company, USA
P. K. Bachmann	Philips Research Laboratories, FRG
Y. Catherine	University of Nantes, France
J. W. Coburn	IBM Almaden Research Center, USA
J. E. Field	Cambridge University, UK
M. Frenklach	Pennsylvania State University, USA
P. Koidl	Fraunhofer Institut für Angewandte Festkörperphysik, FRG
A. H. Lettington	Royal Signals & Radar Establishment, UK
J. Robertson	Central Electicity Research Laboraotory, UK
N. Setaka	National Institute for Research in Inorganic Materials, Japan
R. Smith	University of Technology, UK
J-E. Sundgren	Linköping University, Sweden

NATO-ADVANCED STUDY INSTITUTE ON DIAMOND AND DIAMOND-LIKE FILMS

The primary objectives of an Advanced Study Institute (ASI) are to contribute to the dissemination of advanced knowledge not yet available in standard university courses and the formation of contacts among scientists from different countries.

An Advanced Study Institute is a high level teaching activity at which a carefully defined subject is presented in a systematic and coherently structured program. The subject is treated in considerble depth by lecturers eminent in their fields, and of international standing. The presentations are made to students who are scientists already specialized in the field, or possessing an advanced general scientific background.

The lectures provide the basis for seminar discussions and the presentation and examination of recent research findings. The presentation of the latest research results of the participants should, however, not dominate an ASI.

The goal of this NATO-Advanced Study Institute is to bring together scientists and engineers from various disciplines to discuss and clarify our current understanding of (1) the growth of diamond and diamond-like films, (2) the characterization of these materials, (3) the optical, physical, and mechanical properties of these films, (4) the relationship of these properties to structure and processing, and (5) to indicate the current and potential technological applications of these new diamond and diamond-like materials.

NATO-ASI
DIAMOND AND DIAMOND-LIKE FILMS AND COATINGS

GENERAL INFORMATION

Place: Il Ciocco International Tourist and Conference Center
Castelvecchio Pascoli (Lucca), Italy

Date: 22 July - 3 August 1990

HOTEL INFORMATION

TV in all rooms with CNN and other foreign networks
Refrigerators/Minibars in rooms
Hair Dryers in rooms

Rates: (Full Board)

Double occupancy	82 800 I. Lire	per person per day
Single occupancy	107 800 " "	per day
Children in room with parents:		
under 1 year in age	free	
1 to 3 years	41 400 I.L. per day	
3 - 10 years	66 240 I.L. per day	
10+	full rate	

Activities

Swimming pool	no charge	
Nominal charge for deck chairs etc		
*Tennis	8 000 lire per hour	- day
	12 000 " " "	- lighted
*Horseback riding	25 000 " " "	- with guide
*Body-building	8 000 " " "	
*Gym	no charge	
(volleyball, basketball, etc)		
Game room - billards, ping pong, electronic games		
Disco - nightly as you please		
*Baby sitting	8 000 lire per hour	

*Arrange at reception desk

Note: Two professional football (soccer) teams will be training at Il Ciocco during the Institute. There should be opportunities to attend practice or exhibition games.
Week 1. Glasgow Rangers
Week 2. Sampdoria Genoa

Dress:

In keeping with the ASI traditions, dress at the Institute will be informal. However, remember that many of the religious sites to be visited on the excursions have dress codes.

Transportaion:

Bus transportation to Pisa will be provided on Saturday, August 4. We will arrange the time of departure during the meeting since people's departure times will be known then.

NON-TECHNICAL PROGRAM

The following events will be covered by the registration fee:

Welcome drink and reception	Monday, July 23
Wine and Cheese Party	Tuesday, July 24
Half day excursion to Pisa	Wednesday, July 25
Barbecue	Thursday, July 26
Picnic	Tuesday, July 31
Half day excursion to Lucca	Wednesday, August 1
Gala dinner	Thursday, August 2
(followed by dancing to orchestra)	

Full day excursions are planned for Saturday and Sunday. We will offer these at cost--estimated at $25 to $30 per person for both.

Saturday	Florence
Sunday	Siena - San Gimignano

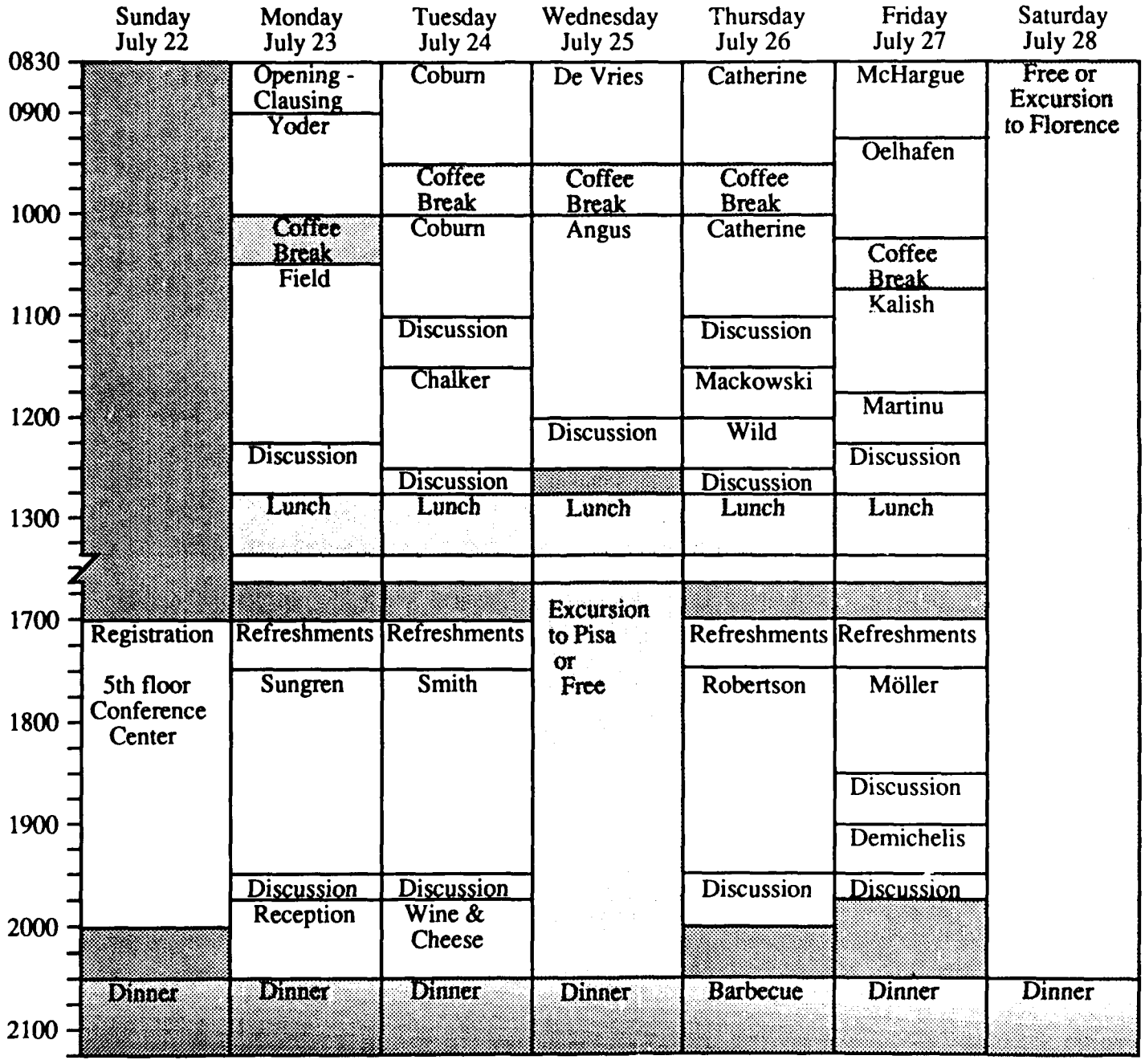
Accompanying Persons

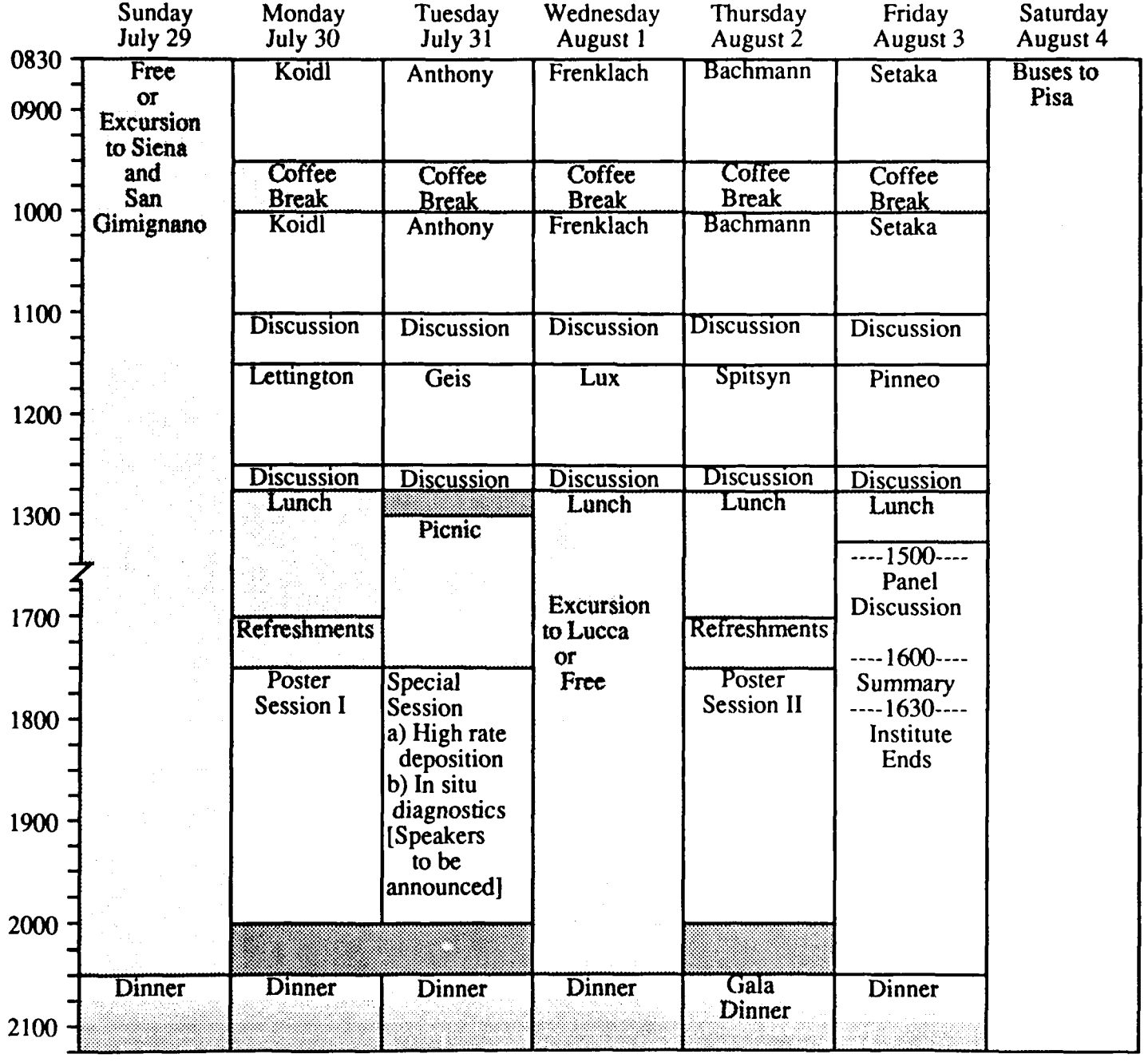
A registration fee of $50 will be charged. If there is interest, we will offer other activities on a cost-sharing basis. Information and sign-up sheets are located in the Institute registration area.

REGISTRATION FEES

Industrial and government employees	$300
University faculty and staff	150
University students	50
Accompanying person	50

Fees may be waived upon application to the Organizing Committee.


Sunday July 22
Monday July 23
Tuesday July 24
Wednesday July 25
Thursday July 26
Friday July 27
Saturday July 28
0830
0900
1000
1100
1200
1300
1700
1800
1900
2000
2100
Registration
5th floor Conference Center
Opening - Clausing
Yoder
Coffee Break
Field
Discussion
Lunch
Refreshments
Sungren
Discussion
Reception
Dinner
Coburn
Coffee Break
Coburn
Discussion
Chalker
Discussion
Lunch
Refreshments
Smith
Discussion
Wine & Cheese
Dinner
De Vries
Coffee Break
Angus
Discussion
Lunch
Excursion to Pisa or Free
Dinner
Catherine
Coffee Break
Catherine
Discussion
Mackowski
Wild
Discussion
Lunch
Refreshments
Robertson
Discussion
Barbecue
McHargue
Oelhafen
Coffee Break
Kalish
Martinu
Discussion
Lunch
Refreshments
Möller
Discussion
Demichelis
Discussion
Dinner
Free or Excursion to Florence
Dinner


Sunday July 29
Monday July 30
Tuesday July 31
Wednesday August 1
Thursday August 2
Friday August 3
Saturday August 4
0830
0900
1000
1100
1200
1300
1700
1800
1900
2000
2100
Free or Excursion to Siena and San Gimignano
Koidl
Anthony
Frenklach
Bachmann
Setaka
Buses to Pisa
Coffee Break
Discussion
Lettington
Geis
Lux
Spitsyn
Pinneo
Lunch
Picnic
Refreshments
Poster Session I
Special Session
a) High rate deposition
b) In situ diagnostics
[Speakers to be announced]
Excursion to Lucca or Free
Poster Session II
----1500----
Panel Discussion
----1600----
Summary
----1630----
Institute Ends
Dinner
Gala Dinner

PROGRAM

NATO-ASI DIAMOND AND DIAMOND-LIKE FILMS AND COATINGS

Sunday, July 22

1700 - 2000 Registration Desk Open--5th Floor Conference Center
2030 Dinner

Monday, July 23

0830 - 0900 Opening of Institute - Robert E. Clausing
0900 - 1000 Introduction and Overview - Max N. Yoder
1000 - 1030 Coffee Break

PART I. FUNDAMENTAL CONCEPTS

Discussion Leader - Michael R. Wertheimer

1030 - 1215 Natural Diamond-The Standard - John E. Field
1215 - 1245 Discussion
1245 Lunch

1700 - 1730 Refreshments
1730 - 1930 Physics of Plasmas and Plasma/Surface Interactions During Thin Film Growth - Jan-Eric Sungren
1930 - 1945 Discussion
1945 - 2030 Welcome Drink and Reception
2030 Dinner

Tuesday, July 24

Discussion Leader - Michael R. Wertheimer

0830 - 0930 Reactive Gas Glow Discharges - John W. Coburn
0930 - 1000 Coffee Break
1000 - 1100 Coburn (Continued)
1100 - 1130 Discussion
1130 - 1230 Techniques for Characterization of Diamond and Diamond-Like Films - Paul R. Chalker
1230 - 1245 Discussion
1245 Lunch

1700 - 1730 Refreshments
1730 - 1930 Modelling and Simulation of Particle-Surface Interactions Roger Smith
1930 - 1945 Discussion
1945 - 2030 Wine and Cheese on the Terrace
2030 Dinner

Wednesday, July 25

0830 - 0930 Review of Diamond-Related Materials - Robert C. DeVries
0930 - 1000 Coffee Break

PART II. DIAMOND-LIKE FILMS AND COATINGS

Discussion Leader - Robert E. Clausing

1000 - 1200 Diamond-Like Hydrocarbon and Carbon Films - An Introduction John C. Angus
1200 - 1230 Discussion
1245 Lunch
1400 Excursion to Pisa or Free
2030 Dinner

Thursday, July 26

Discussion Leader - Robert E. Clausing

0830 - 0930 Preparation Techniques for Diamond-Like Carbon
Yves Catherine
0930 - 1000 Coffee Break
1000 - 1100 Catherine (Continued)
1100 - 1130 Discussion
1130 - 1200 Correlation Between Precursor Gas and Structure
J-M Mackowski
1200 - 1230 Characterization of a-C:H Plasma Deposition - Ch. Wild
1230 - 1245 Discussion
1245 Lunch

1700 - 1730 Refreshments
1730 - 1930 Electronic Structure and Properties of Diamond-Like Carbon
John Robertson
1930 - 2000 Discussion
2030 Barbecue

Friday, July 27

Discussion Leader - John Angus

0830 - 0915 Mechanical Property Determinations of Thin Films and Hard Materials - Carl J. McHargue
0915 - 1015 In Situ Characterization of a-C:H Films and Film/Substrate Interfaces by Photoelectron Spectroscopy - Peter Oelhafen
1015 - 1045 Coffee Break
1045 - 1145 Post-Deposition Treatments and Stability of Diamond-Like Films - Rafael Kalish
1145 - 1215 Aging Processes in Diamond-Like Carbon and Carbon/Metal Films
Ludvik Martinu
1215 - 1245 Discussion
1245 Lunch

1700 - 1730 Refreshments
1730 - 1830 Computer Modeling of C:H Film Growth - Wolfhard Möller
1830 - 1900 Discussion
1900 - 1930 Gap States and Electron Spin Resonsnce in Amorphous Carbon and Hydrogenated Amorphous Carbon - Francesca Demichelis
1930 - 1945 Discussion
2030 Dinner

Saturday, July 28

Full-day excursion to Florence or Free

Sunday, July 29

Full-day excursion to Siena and San Gimignano or Free

Monday, July 30

Discussion Leader - John Argus

0830 - 0930	Characterization and Properties of Diamond-Like Films Peter Koidl
0930 - 1000	Coffee Break
1000 - 1100	Koidl (Continued)
1100 - 1130	Discussion
1130 - 1230	Applications of Diamond-Like (Hard Carbon) Films Alan Lettington
1230 - 1245	Discussion
1245	Lunch
1700 - 1730	Refreshments
1730 - 2000	Poster Session 1 Papers P 1 to P 16
2030	Dinner

Tuesday, July 31

PART I.I. DIAMOND FILMS

Discussion Leader - Max N. Yoder

0830 - 0930	Techniques for the Growth of Diamond - Tom R. Anthony
0930 - 1000	Coffee Break
1000 - 1100	Anthony (Continued)
1100 - 1130	Discussion
1130 - 1230	Device Applications for Diamonds - Michael W. Geis
1230 - 1245	Discussion
1300 - 1700	Picnic
1730 - 2000	Special Sessions on: (a) High-rate Deposition, and (b) In-situ Diagnostics [Speakers to be announced]
2030	Dinner

Wednesday, August 1

Discussion Leader - Max N. Yoder

0830 - 0930	Theory and Models for Nucleation of Diamond Michael Frenklach
0930 - 1000	Coffee Break
1000 - 1100	Frenklach (Continued)
1100 - 1130	Discussion
1130 - 1230	Nucleation and Growth of Low Pressure Diamond - B. Lux
1230 - 1245	Discussion
1245	Lunch
1400	Excursion to Lucca or Free
2030	Dinner

Thursday, August 2

Discussion Leader - Peter Koidl

0830 - 0930 Characterization and Properties of Artificially Grown Diamond
Peter K. Bachmann
0930 - 1000 Coffee Break
1000 - 1100 Bachmann (Continued)
1100 - 1130 Discussion
1130 - 1230 Emergence and Development of Science and Technology of Diamond Films in the USSR - B. V. Spitsyn
1230 - 1245 Discussion
1245 Lunch

1700 - 1730 Refreshments
1730 - 2000 Poster Session 2
Papers P 17 - p 39
2030 Gala Dinner followed by dancing

Friday, August 3

Discussion Leader - Peter Koidl

0830 - 0930 Critical Assessment of State-of-the-Art of Diamond Growth
Nobuo Setaka
0930 - 1000 Coffee Break
1000 - 1100 Setaka (Continued)
1100 - 1130 Discussion
1130 - 1230 Applications of Diamond Films - J. Michael Pinneo
1230 - 1245 Discussion
1245 Lunch

1500 - 1600 Panel Discussion: Where are we? Where are we going?
1600 - 1630 Summary and Closing

2030 Dinner

Saturday, August 4

Buses to Pisa -- Times to be determined

DIAMOND: POTENTIAL AND STATUS

M. N. Yoder
Electronics Division
Office of Naval Research
800 North Quincy Street
Arlington, VA 22217 USA

While many of the physical characteristics of diamond have been known for decades, the electrical characteristics were generally determined during the 1970s. Even then, there was no viable means of synthesizing diamond films for electrical and electronic applications. During the early 1980s artificial diamond polycrystalline films were grown with respectable quality. In the past few years, free-standing "water clear" polycrystalline films of up to 75 mm in diameter have emerged. Single crystalline films have also been grown homoepitaxially and with characteristics exceeding those of the underlying natural diamond substrate.

A proliferation of growth techniques has recently ensued; each seem to have some advantages, but none are optimum for each application. High quality diamond particles have been grown at room temperature and high quality films have been grown as low as 300°C. The use of oxygen in the feed stock has generally relaxed the temperature as well as the gas flow rates and mixtures that can be used to grow diamond. Water clear artificial diamond films generally require oxygen in the feed stock and are grown in the 550-750°C range. More recent experiments have demonstrated the efficacy of halogens and solid phase epitaxy.

As research and development activity in the field grows, so do the potential applications of diamond. Applications exploiting the hardness of diamond are most numerous at this time although tribological applications and optical applications are becoming more extensive. Electronic appliations await the first successful and economical heteroepitaxy.

Examples of the latest approaches to nucleation, growth, and applications will be presented.

NATURAL DIAMOND

J. E. Field
Cavendish Laboratory
University of Cambridge
Madingley Road, Cambridge CB3 OHE, UK

The extreme rigidity of the diamond lattice is the key to many of its exceptional properties. This review first discusses the main physical properties of diamond including its structure, stability, the impurities diamonds contain and their effect on its thermal, optical, and electrical behavior. With this as background, recent results and data are then presented on the elastic, cleavage, strength, fracture, hardness, frictional and wear properties of diamond.

Introduction

Diamond is an exciting material with many outstanding properties. It is pre-eminent as a gemstone, an industrial tool, and as a material for solid state research. Since natural diamonds grow deep below the earth's surface before their ejection to mineable levels, they also contain valuable information for geologists. The key to many of diamond's properties is the rigidity of its structure which explains, for example, its exceptional hardness and its high thermal conductivity. Since 1953 it has been possible to grow synthetic diamond. Techniques are now available to grow gem quality synthetic diamonds greater than 1 carat (0.2 gm). However, the costs are high, and the largest commercially available industrial diamonds are about 0.01 carat in weight or about 1 mm in linear dimension. The bulk of synthetic diamonds used industrially are 600 μm or less. Over 75% of diamond used for industrial purposes today is synthetic material. A recent development has been the production of composites based on diamond; these materials have a significantly greater toughness than diamond while still maintaining very high hardness and reasonable thermal conductivity. The facility to grow synthetic diamond of chosen size, morphology, and impurity content has further added to the versatility of the material.

Diamond Stability

Diamond and graphite are both forms of carbon. In 1955, Berman and Simon considered the thermodynamics of the phase change and obtained the diamond/graphite equilibrium diagram. Subsequent recalculation, using improved data, for specific heats, molar volumes and compressibilities has modified the line slightly above pressures 40 kbar (0.4 GPa). It is important to appreciate that although the line marks the boundary between regions of thermodynamic stability it says nothing quantitatively about the rate of change from one phase to another. Diamond, it will be noted, is <u>not</u> the stable form under normal environmental conditions though experience suggests that the transformation to graphite must be a slow process. Similarly, when synthesizing diamond, it is not sufficient to simply take graphite to a P/T point above the Berman/Simon line; if this were so, many of the early attempts at diamond synthesis would have been successful.

Crystallographic Structure

Diamond has tetrahedral, covalent bonds between each atom and its four nearest neighbors. In diamond, the commonest way of linking the tetrahedral units into a three-dimensional structure is the cubic form. An alternative structure is the hexagonal würtzite lattice which was predicted as a possible polymorph of diamond by Ergun and Alexander. Bundy has synthesized this form in the laboratory and it has now also been produced in various shock loading experiments. The cubic form of diamond occurs most commonly in nature as octahedra with {111} planes or in dodecahedra with {110} planes as a dissolution form. The simple cube with {100} planes is relatively rare with natural diamonds, but is common synthetically if particular conditions of T and P have been used in the growth capsule. Diamonds invariably contain an individual and complex internal structure which reflects the growth conditions, impurity content and any deformation while at high P and T.

Impurities: Inclusions

The observed properties of diamonds show unambiguously that elements other than carbon must be present in the diamond lattice. Much of recent diamond research has had the objectives of identifying these elements, their chemical relationship, their effect on optical, electrical, thermal and mechanical properties and their geochemical significance. The major impurity in diamond is nitrogen but recent research has shown that there are significant amounts of oxygen and hydrogen both in the bulk and at the surface of diamond.

Diamond Types: The Role of Nitrogen

Measurements of the adsorption of diamond in the infrared, visible and ultra-violet has led to a classification into types I and II. Most natural diamonds are type I and have their adsorption edge at ca. 330 nm, while a much smaller group, type II, have this edge at ca. 220 nm. As would be expected from the size of the band gap, most diamonds are good insulators. However, a small proportion of type II diamonds are semiconductors (type IIb). The major factor in explaining the adsorption spectra of diamond is the presence of nitrogen in amounts up to ca. 0.3%. The conductivity, and blue coloration of some diamonds is due to boron impurities which act as acceptors.

Thermal Properties

The very high thermal conductivity of diamond is a major factor in explaining its performance in many technological applications. As is well known, diamond is frequently used in processes such as machining, grinding, cutting, and polishing which generate high temperatures at the work interface. It is paradoxical that a material which graphitizes in air at ca. 900 K should survive such conditions. The answer is the thermal conductivity which has a value at room temperature about five

times greater than that of copper. The heat is conducted by phonons so that the rigidity of the lattice which gives diamond its great hardness also favors a high conductivity.

Cleavage Plane

The dominant cleavage plane is the (111) though others have been observed. Diamonds can be readily cleaved along this plane. The wear of diamond, which depends markedly on the crystal face and direction of motion, has been explained in terms of micro-cleavage with the (111) planes dominating. The cleavage energy for the (111) plane has been measured by an indentation technique at 5.50 ± 0.15 Jm^{-2} which is close to the theoretical value. This suggests that little, if any, dislocation motion takes place at the crack tip during cleavage growth at room temperature. Indentation methods have also been used to measure the tensile strength properties of diamond.

Plastic Flow

Diamond has the greatest resistance to plastic flow of any material. Its exceptional yield strength arises essentially for two reasons: the first is that the theoretical strength is high because of the high density of strong atomic bonds; and secondly, because the strongly directional nature of the bonding only allows the presence of narrow dislocations which are difficult to move. There has been considerable interest in determining the conditions under which flow is possible. Recent research using diamond anvils to generate high pressures has led to a deeper understanding of the ultimate compressive and shear strength of diamond.

Friction

The friction of diamond depends on the crystal face and orientation. On the octahedral face the friction is low and there is practically no anisotropy. On the cube face, polished in the <100> direction there is four-fold symmetry in the friction. The lowest friction is along the <011> or cube diagonal direction; the highest along the <100> or cube edge direction. If the cube face is polished in the <110> direction, the four-fold symmetry is replaced by two-fold symmetry. In some situations, repeated traversal over the same track on the cube face of diamond reverses the order of frictional anisotropy. After a few hundred traversals the friction is higher in the <011> direction and low in the <100> direction. For diamond sliding on diamond under vacuum conditions, the friction can reach a high value (μ~1). The high friction is accompanied by a very high wear rate.

PHYSICS OF PLASMAS AND PLASMA/SURFACE INTERACTIONS DURING THIN FILM GROWTH

J-E. Sundgren
Department of Physics
Linköping University
S-581 83 Linköping, Sweden

Glow discharge plasmas have played an increasingly important role during the last decades for materials analyses and processing. A glow discharge plasma can be defined as a partially ionized low pressure gas in a quasi-neutral state sustained by the presence of energetic electrons. The character and the properties of such a plasma is basically a consequence of the mass difference between the electrons and the ions. For example, when an electric field is applied to such an ionized gas, energy is transferred more rapidly to the electrons than to the ions resulting in a large energy difference between electrons and ions in the plasma. The nature of a glow discharge plasma also depends on the interaction between the charged particles and electromagnetic fields present. The purpose of this paper is to discuss the generation of these charged and excited (radicals, etc.) particles, their collective nature and their interaction with surfaces immersed in the plasma. Particular emphasis will be placed on the role of low-energy ions in controlling and altering the nucleation and growth kinetics of thin films grown from the vapor phase.

The first part of the paper is a brief review of the features of glow discharge plasmas including particle motions, ionization and excitation events, energy contents and energy distributions of the species in the plasma as well as collective phenomena in plasmas. In this section also various types of glow discharge plasmas are summarized. Especially the magnetic field configuration in magnetically sustained glow discharges is discussed. By altering the magnetic field configuration thin film growth can be achieved with a varying amount of ion or electron fluxes impinging on the growing film surface. For example, arrival ratios of the ion flux to neutral deposition flux larger than five can be achieved in unbalanced magnetron discharges.

The second part of the paper concerns sputtering, i.e., ejection of surface atoms due to energetic particle bombardment, that occurs at the cathode surface in a glow discharge providing that the energy of the incident particles is high enough. The physical understanding of sputtering mechanisms, sputtering yields, and distributions of sputtered particles from elemental targets are briefly reviewed. In the ion-solid collision process not only sputtering occurs but a fraction of the impinging ions are also elastically reflected. For ion-solid combinations in which the impinging ions have a considerably lower mass compared to the solid, the flux of the reflected energetic neutrals (the ions will be neutralized just prior to collision) can in fact be so high that it dominates the nucleation and growth kinetics during thin film growth by sputter deposition. Since the backscattered species are neutralized their flux and energy when impinging on the growing film surface can only be affected by changing the mass of the impinging ions or by changing the number of collisions in the gas phase. The latter

can be done by altering the pressure and/or the target-to-substrate distance.

The last part of the paper deals with the role of low-energy (<500 eV) particle bombardment on the nucleation and growth kinetics of thin films. Examples will be given from a diverse number of material systems. During the nucleation stage of thin film growth low-energy ion interaction can lead, in addition to sputter cleaning of the substrate, to fundamental changes in the nucleation kinetics. Examples of irradiation-induced effects include the production of defects in the substrate surface which can act as preferential adsorption sites, trapping of the incident species in the near-surface region, dissociation of small clusters, enhanced adatom diffusivities, and local electrical field effects due to charging. Also local atomic rearrangement can occur allowing atoms to relax into lower energy sites in turn resulting in, e.g., reduced epitaxial temperatures. Also the growth kinetics will be modified by energetic particle bombardment. In areas such as optical and wear-protective films, the application of ion irradiation to densify and increase the internal strength of the layers as well as to increase the film/substrate adhesion is already a prerequisite to commercial success. However, energetic particle irradiation during growth can also be disadvantageous for certain applications due to, e.g., the generation of very high compressive stress levels in the films.

It will also be demonstrated in this paper how low-energy ion irradiation can be used during film growth to controllably alter the composition of as-deposited films. Examples include preferential sputtering during alloy and compound deposition, enhanced reactive-gas incorporation during deposition of compounds and increased dopant incorporation during semiconductor growth. However, also potential deleterious effects such as rare-gas incorporation in sputter-deposited films can also occur. Mechanisms associated with particle/surface interactions leading to changes in incorporation probabilities range from pure physical effects such as implantation and recoil processes to irradiation-assisted chemistry. Finally, examples will also be given where ion-bombardment is used to form a variety of thermodynamically metastable phases including diamond and diamond-like films.

REACTIVE GAS GLOW DISCHARGES

J. W. Coburn
IBM Almaden Research Center
650 Harry Road, San Jose, CA 95120-6099 USA

Low-pressure glow discharges of reactive molecular gases are being used more and more frequently for etching solids, for depositing thin films and for modifying the properties of existing surfaces. Application areas include microelectronics, magnetic and optical recording, photovoltaics, machine tool hardening, fabrication of solar absorbers and optical filters, to name a few. The primary reasons for the growing use of reactive gas glow discharges are the ability to deliver relatively intense and uniform fluxes of both energetic positive ions and thermal energy neutral atoms or radicals to surfaces. The surfaces being processed can be electrically conducting or insulating and can be at any desired temperature. In some applications only the energetic ion bombardment is required, in others only the atom/radical fluxes are important, but in more and more cases it is the combination of energetic ions and reactive atoms/radicals which are responsible for the unique surface processing capabilities of reactive gas glow discharges. It is difficult to find a better way of generating this combination of particle fluxes than with a reactive gas glow discharge.

Whereas the apparatus associated with a reactive gas glow discharge can be very simple, the reactive gas glow discharge itself is enormously complex. The parameter space associated with the apparatus is very large and the gas phase and plasma-surface interactions of importance are not well understood. This situation has resulted in a high degree of empiricism in the development of equipment and processes with little assurance that optimization has been achieved. The science associated with materials processing in reactive gas glow discharges can be divided into three categories: plasma science (species generation), plasma diagnostics (species measurement), and plasma-surface interactions (species reaction).

Plasma Science

The most important collisional process in the gas phase is, of course, between energetic electrons and the feed gas molecules. These collisions generate the important ions and atoms/radicals by ionization and dissociation processes respectively. In almost all cases it is believed that the desired surface chemistry is accomplished by these species. Electron-molecule collisions also impart internal energy to the discharge species in the form of electronic, vibrational and rotational excitation. Although internal energy is known to influence the reactivity of species with surfaces, it is suspected that in the glow discharge these species do not contribute in a major way to the surface reactions of interest. The optical emission, emitted as electronically excited species de-excite, is probably the most useful diagnostic for species measurement. Secondary reactions between the ions, atoms, radicals and neutral molecules are also very important in this complex environment. The consequences of these secondary processes can be both deleterious (i.e., loss of active species by atom-atom

recombination) or beneficial (i.e., fine-tuning of radical or atom concentrations by the addition of radical/atom scavengers). These secondary processes can occur in the gas phase or on surfaces and in general are very poorly understood.

There is a rapidly increasing data base for the cross-sections of importance in these systems and much activity is being directed towards developing predictive computer-based models of the gas phase processes. A key problem is the lack of information concerning the electron energy distribution in the discharge. It is not trivial to measure this energy distribution and it will depend on most of the parameters of the system.

The entire problem is complicated by the almost unlimited number of geometrical/electrical configurations used to establish these reactive gas glow discharges. The technological applications began in very simple tubular reactors (often called "barrel" systems), progressed to the widely used planar geometry (most often powered with 13.56 MHz excitation) and recently attention has been directed to higher density discharges based on magnetrons, microwave-electron cyclotron resonance configurations or multipolar geometries.

Plasma Diagnostics

The problems created by the complexities discussed above have led to important developments in the ability to carry out in-situ measurements of species concentrations in reactive gas glow discharges often with spatial resolution. Optical emission spectroscopy (OES) is, in the opinion of this author, by far the most important diagnostic technique for molecular gas glow discharges. Its most important attribute is its ease of implementation. The information is provided by the glow discharge and all that is needed is optical access to the plasma. OES can provide valuable information about a wide variety of species independent of their reactivity. By definition OES is non-invasive and the method provides high sensitivity in many cases. A certain degree of spatial resolution can be realized with OES. The greatest weakness of the method is the lack of information concerning the origin of the emitting species. For example, excited atomic species can be created by the excitation of a ground state atom or the dissociation of a molecule or radical. The proper interpretation of OES data requires a knowledge of the excitation process and misinterpretations can result if this information is lacking. A second characteristic of OES is that the sensitivity of the method depends on all the plasma parameters. Consequently, the emission intensity from a specific specie cannot be assumed to be proportional to the specie density if any plasma parameters are changed (e.g., pressure, power, etc.). A method for calibrating the OES sensitivity, known as actinometry, has been widely used recently. Actinometry involves the injection of a small amount of rare gas (a few percent typically) with the molecular feed gas and monitoring the emission from the rare gas thus providing a measure of the optical emission from a fixed concentration specie.

A more elegant way of overcoming the problems associated with OES is provided by laser-induced fluorescence (LIF). In this technique a

relatively high power pulsed laser is used to excite a specific transition of a well-defined species and the resulting optical emission is monitored. In addition to eliminating the role of the plasma electrons in the excitation process, LIF is capable of much better spatial resolution than is OES. LiF is much more complex experimentally than OES, and the difficulties associated with delivering high fluences of high energy (>10 eV) photons to the plasma complicate the detection of certain species with very high energy excited states (e.g., F atoms). This technique is not widely used yet in process monitoring or even process development but has provided much improved understanding of reactive gas glow discharges. In addition, there are several other laser-based plasma diagnostic methods being applied to the study of reactive gas glow discharges. These include gas phase methods such as laser-optogalvanic spectroscopy and optical absorption spectroscopy as well as methods in which the laser is used to probe the surface being processed (laser-induced photoemission and laser-induced surface photoluminescence).

Mass spectrometry is the other major approach used to monitor the species present in reactive gas glow discharges. Mass spectrometric monitoring of plasmas is limited to the detection of species arriving at a wall. This is not a serious limitation in this application in that it is these species which are responsible for the surface processing. Mass spectrometric monitoring of plasmas can be accomplished in various ways: ion sampling in which ions are extracted from the plasma and directed into the mass spectrometer, molecular beam mass spectrometric sampling in which a beam of the plasma species is modulated mechanically and directed on a line-of-sight into the mass spectrometer and effluent gas analysis in which plasma species are monitored after many collisions with various surfaces. The first two methods, although potentially very useful, are almost always totally incompatible with any realistic plasma apparatus. Effluent gas analysis is incapable of observing highly reactive or condensible species and thus its usefulness is limited. However, this approach is very helpful in leak detection and gas purity verification.

Plasma-Surface Interactions

The vast majority of studies of gas-surface interactions have involved stable molecules. Relatively few studies of atom/radical-surface interactions have been carried out, and it is this topic which is of prime importance in reactive gas glow discharge processing of surfaces. Two approaches to improving our understanding of this area have been taken. One approach is to direct controlled beams of representative particles onto atomically clean surfaces in an ultrahigh vacuum environment and study the resulting chemical reactions with modulated beam mass spectrometry and/or careful surface characterization. The second approach is to vacuum-transfer a surface which has been processed in reactive gas glow discharge into a surface analysis facility which can characterize the processed surface in great detail. These approaches are complimentary and between them have provided some

rudimentary understanding of some phenomena of much importance in this field.

For example, it has been recognized for some time that the reaction probability of some neutral atoms/radicals/molecules with surfaces can be dramatically increased if the surface is subjected to a flux of energetic ions simultaneously with the reactive neutral flux. This phenomenon is responsible for the directionality which can be obtained in some plasma-assisted etching processes. More recently it has been observed that the reaction probability of atomic species with surfaces can be increased by the simultaneous exposure of the surface to a second atomic flux. The situation which has prevailed at least to this time is that the important discoveries are made empirically using reactive gas plasma systems, and the surface science studies have subsequently helped to understand these discoveries.

OVERVIEW OF THE CHARACTERIZATION OF DIAMOND AND DIAMOND-LIKE CARBON FILMS

P. R. Chalker and I. M. Buckley-Golder
Microelectronics Materials Centre
Harwell Laboratory
Oxford, England

The allotropy of carbon and the existence of C:H ceramics give rise to a wide variety of materials which can be prepared in the form of thin films by chemical and physical vapor deposition techniques. These materials exhibit diverse optical, electrical, mechanical and chemical properties, many of which are potentially attractive for engineering and device applications. In order to understand the origin of these properties and to optimize the fabrication procedures, a detailed knowledge of film chemistry, impurities, morphology and microstructure must be investigated to ensure reproducibility.

An overview of the main analytical methods which are available for the characterization of diamond and diamond-like films and coatings will be presented, e.g., XPS, AES, SIMS, EMPA, LRM, XRD, RBS, ERDA, PIXE, TEM, STEM, and SEM. The techniques reviewed fall broadly into the categories: chemical characterization which identify and distinguish different carbon phases, in addition to the role of hydrogen and other dopant impurities; and physical characterization methods which investigate the morphological and microstructural properties of the films, defects, and interfaces.

The fundamental mechanisms of these analytical techniques will be discussed with a view to interpretation of spectroscopic data and the relationship of analytical measurements to the optical, electrical, and mechanical properties of these important classes of materials.

MODELLING AND SIMULATION OF PARTICLE-SURFACE INTERACTIONS

Roger Smith
Department of Mathematical Sciences
Loughborough University
Leicestershire LE11 3TU, UK

This paper will discuss different approaches to modelling the interaction of energetic particles with surfaces and will be divided into two parts. In the first part, the primary focus of the paper will be towards developing models which can explain how surface topography changes on the macroscopic scale both as a result of sputtering (erosion) and deposition or redeposition (growth). The crudest approach will be to model the surface as a moving wavefront[1] whose shape can be determined as the erosion or growth process continues provided the velocity at a point on the surface is known as a function of the beam species, surface orientation, position and time. The non-linearities can give rise to discontinuous solutions (shock waves) which manifest themselves as gradient discontinuities such as points and edges, and these can even arise as a result of a growth or deposition process on a smooth surface subject to contaminant-free particle fluxes. It will be demonstrated how facets can develop, how the planarization of electronic structures can be simulated and how redeposition of low energy material in a higher energy sputtering process can occur, all within the framework of the non-linear wave model.

A second method of modelling macroscopic scale changes will be the Monte-Carlo cellular approach.[2] In this technique the substrate is divided into a regular cellular structure. Deposition occurs as a result of adding cells to the surface and erosion is simulated by their removal. The rules for adding or removing cells from the surface will be specified in terms of the local environment of the cell. It will be shown how this approach can yield the same solution as the non-linear wave model provided the local rules for cell updating are correctly chosen. By suitably varying the local rules for erosion or deposition, unusual structures can develop on initially flat surfaces. If the cells are regarded as atoms and the local potential environment of the surface is the determining factor for the growth process, then it will be shown how this Monte-Carlo method leads to a model for the simulation of epitaxial growth.

The second part of the paper will consider growth and erosion processes on the atomic scale. Molecular dynamics simulations will be used to describe erosion and deposition of individual atomic impacts. These simulations involve the solution of Newton's equations of motion for thousands of particles and are increasingly realistic as a result of the development of many-body interaction potentials during the 1980s for a number of different covalent materials including Si, C, and SiC. The primary focus of this work will be towards materials which have the diamond lattice structure[3] in particular natural diamond but also Si and SiC. The mechanisms by which atoms and molecules are ejected as a result of energetic particle bombardment will be described, and the angular and energy distributions of ejected material will be compared for carbon in both the diamond and graphite single crystal structures.

It will be shown how the angular distributions of ejected material can give information about the surface structure of crystalline carbon and how the yield of ejected material as the beam incidence angle varies can also be used to determine the surface structure. The simulations will show that when single crystal diamond and graphite are subjected to atomic carbon bombardment at beam energies of tens of electron volts, trapping of the implanted species occurs in the first few atomic layers and that bombardment energies of several hundred eV are required before sputtering can take place. Finally, recent results which demonstrate the power of molecular dynamics in modelling the initial stages of epitaxial growth will be described.

References

1. R. Smith, G. Carter, and M. J. Nobes, Proc. Royal Soc. **A407**, 405 (1986).

2. R. Smith, A. H. Osbaldestin, G. Carter, I. V. Katardiev, and M. J. Nobes, p. 205 in Materials Modification by High-Fluence Beams, R. Kelly and M. Fernando da Silva, eds., Kluwer Academic Publishers, 1989.

3. R. Smith, D. E. Harrison, Jr., and B. J. Garrison, Phys. Rev. B **40**, 93 (1989).

REVIEW OF DIAMOND-RELATED MATERIALS

R. C. DeVries
17 Van Vorst Drive
Burnt Hills, NY 12027 USA

The scope of this review will be principally on phases in the composition triangle C-B-N-Si; and within this, emphasis will be first on cubic BN with decreasing attention to B_xN_y, $B_xN_yC_z$, C_xN_y, and SiC. These materials will be considered in terms of synthesis, structure (crystal, micro-, macro-), and properties. Since most of the cubic BN available is from high pressure-high temperature (HPHT) process, these will be discussed in some detail both for direct and indirect (solvent) conversion of hexagonal BN. Sintering and crystal growth under these conditions will also be included. The synthesis of cubic BN under metastable conditions will be reviewed to try to evaluate the degree of success and potential of this mode of formation.

The important physical/mechanical, optical, thermal, and chemical properties of both single crystals and polycrystalline aggregates will be considered in the content of similar parameters for diamond and related III-V compounds. Some remarks on problems and on future possibilities of those diamond-related materials will conclude this presentation.

DIAMOND-LIKE HYDROCARBON AND CARBON FILMS*

J. C. Angus, R. W. Hoffman, Y. Wang, and H. Chen
Case Western Reserve University
Cleveland, OH 44106 USA

The term "diamond-like" has been applied to a wide range of carbonaceous films of greatly varying chemical composition, structure, and properties. In this paper we describe both hydrogenated and non-hydrogenated diamond-like materials. Each type shows no long-range order, is hard, and has high electrical resistance. The properties of the films and their relationship to structure and elemental composition are considered.

Preparation of Diamond-Like Hydrocarbons

Hydrogenated diamond-like films (diamond-like hydrocarbons) are typically prepared by impact of hydrocarbon ions in the energy range from several tens to 100 eV. Direct deposition from hydrocarbon ion beams and by RF self-bias are the most commonly employed methods. These methods provide significantly higher impact energies than are achieved in an inductively coupled plasma, which is used for the production of the so-called plasma polymers.

Chemical Composition

The hydrogen content is the primary independent variable which determines the structure, and hence the properties, of the diamond-like films. The atomic percent hydrogen is very low in the non-hydrogenated, diamond-like carbons, nominally less than 1 at. %. On the other hand, the hydrogen content of the hydrogenated diamond-like carbons ranges from approximately 16 to 60 at. % hydrogen. Hydrocarbon films with diamond-like properties have not been found outside of that range.

Physical Properties

The diamond-like hydrocarbons typically have mass densities ranging from 1.4 to 2.0 g/cm^3, with the least dense films found at the highest hydrogen content. These densities are much higher than those of hydrocarbons of similar elemental composition,[1,2] e.g., anthracene, 1.25 g/cm^3 and polyacetylene 1.16 g/cm^3. This alone indicates an unusual structure. The densities of the non-hydrogenated diamond-like films have been reported to be as high as 2.7 g/cm^3, which is significantly greater than that of graphite (2.26 g/cm^3), again indicating an unusual structure.

The empirical scratch hardness of the hydrogenated films is very high, in some cases greater than SiC. However, this empirical measure of hardness depends on many factors including the friction coefficient and the adhesive strength between the film and substrate. The hardness decreases as the hydrogen content increases.

This work was supported by the National Science Foundation under Materials Research Group Grant DMR 89-03527.

The hydrogenated diamond-like films are usually found in a state of high compressive stress. The stress level increases with increasing hydrogen content.[3] Addition of fluorine increases compressive stress, while nitrogen has been reported to reduce the compressive stress.

The optical transmission and band-gap of the hydrogenated films both increase with increasing hydrogen content. The band-gap increases from approximately 0.5 eV to over 2.0 eV for the highly hydrogenated films. The most transparent films are the softest.

Structural Studies of Diamond-Like Hydrocarbons

The unusual nature of the films must arise from their structure and bonding network. The films are amorphous, so little has been learned from conventional diffraction experiments. However, much attention has been paid to the relative numbers of sp^3 and sp^2 carbon sites. The sp^3/sp^2 ratio has been estimated by infrared absorption, NMR measurements, and by electron energy loss spectroscopy. It has been found that a significant fraction of the carbon atoms is present as sp^3, tetrahedrally coordinated sites. The sp^3/sp^2 ratio increases as the hydrogen content increases, i.e., the hardest, most dense films actually have the smallest fraction of tetrahedrally coordinated carbon.

Structural Models for Diamond-Like Hydrocarbons

Any model of the structure of the diamond-like hydrocarbons must be consistent with the observation that the films have high empirical hardness and can support high internal compressive stress. Furthermore, the structural model must explain the observed optical band-gap and very high electrical resistivity.

The electronic properties of the films, as indicated by the band-gap and electrical resistivity, were attributed by Bredas and Street[4] and Robertson[5,6] to the presence of small graphitic-like clusters of carbon atoms within a more highly hydrogenated matrix. Using electronic-structure calculations they showed that as the overall hydrogen content decreases, these π-bonded clusters increase in size, giving rise to increased optical absorption and decreased band-gap. The lack of conductivity is explained by the fact that the clusters are sufficiently spatially isolated so that there is no π-electron orbital overlap.

The hard, rigid mechanical nature of the films must arise from the structure of the matrix that makes up the bulk of the film. Angus and Jansen[7] modelled the diamond-like hydrocarbon films as a fully constrained, non-crystalline network using the constraint counting arguments of Phillips.[8] The predictions of sp^3/sp^2 ratio and the average coordination number are in agreement with the available experimental observations, particularly at the upper end of the hydrogen composition range. The model predicts a range of compositions, from 0.17 to 0.62 atom fraction hydrogen, over which a fully constrained network comprised of sp^3 and sp^2 coordinated carbon atoms and hydrogen atoms can exist. The predicted stability range is in good agreement with observation.

A qualitative picture of the constrained network model is instructive. Increasing the number of bonds (crosslinks) in a non-crystalline network contributes to stabilization because of the bond energy. However, increasing the number of bonds in a non-crystalline network also leads to increase of the strain energy because of bond stretching and bond angle distortion. The optimal coordination number just balances these two effects. The role of hydrogen in diamond-like hydrocarbons is easily understood in this context. Since hydrogen is univalent, it can only serve as a network terminator, thereby reducing bonding constraints. Increasing the hydrogen content therefor permits the fraction of tetrahedrally coordinated (sp^3) carbon to increase at the expense of trigonally coordinated (sp^2) carbon while still keeping the overall average coordination number constant.

Tamor has recently proposed a "defective graphite" model for the structure of the diamond-like hydrocarbons.[9] In this model an initially perfect graphite crystal is modified by removing carbon atoms and saturating the resulting dangling bonds with hydrogen. Percolation theory is used to predict the upper and lower limits of hydrogen concentration. The defective graphite model predicts an existence range of diamond-like hydrocarbons from 0.2 to 0.6 atom fraction hydrogen. It is quite remarkable that this model, which is based on different assumptions, predicts virtually the same existence range as the random network model.

Structure of Diamond-Like Carbon

Dense, hard carbon films containing little hydrogen can be prepared by sputtering, by direct ion beam deposition from carbon ion beams or by condensation of carbon plumes produced by laser vaporization. These films have received less attention than the hydrogenate films, in part because the lack of significant amounts of hydrogen makes them more difficult to study by either NMR or infrared spectroscopy. It is clear, however, that the films are an unusual form of carbon with mass densities greater than graphite, but less than diamond, and with very high hardness.[10]

The constraint counting agreements used to describe the hydrogenated films show that a non-hydrogenated random network made up solely of sp^3 and sp^2 carbon sites will be highly overconstrained. True "amorphous diamond" or even "amorphous graphite" is unlikely to exist. The bonding constraints are reduced by formation of clusters or microcrystallinity, and this may be the source of stability for these unusual materials. In fact, recent molecular dynamics studies[11] show that several types of medium range order may be present in the non-hydrogenated amorphous carbons including 5-, 6-, and 7-member rings and local clustering of sp^3 sites. Tamor has concluded on the basis of his defected graphite model that it is unlikely that more than 10% of the carbon sites in non-hydrogenated diamond-like carbons are four-fold coordinated.[9]

References

1. J. Angus, Thin Solid Films **142**, 145 (1986).

2. J. Angus and C. C. Hayman, Science **241**, 913 (1988).

3. J. Angus, C. C. Hayman, and R. W. Hoffman, in "Diamond Optics," Proceedings SPIE, **969**:2, 1988.

4. J. L. Bredas and G. B. Street, J. Phys. Chem. **18**, L651 (1985).

5. J. Robertson, Adv. Phys. **35**, 317 (1986).

6. J. Robertson and E. P. O'Reilly, Phys. Rev. B. **35**, 2946 (1987).

7. J. Angus and F. Jansen, J. Vac. Sci. Technol. **A6**, 1778 (May/June 1988).

8. J. C. Phillips, Phys. Rev. Lett. **42**, 153 (1979).

9. M. A. Tamor and C. H. Wu, J. Appl. Phys. **67**, 1007 (1990).

10. S. M. Rossnagel, M. A. Russack, and J. J. Cuomo, J. Vac. Sci. Technol. **A5**, 2150 (1987).

11. G. Galli, R. M. Martin, R. Car, and M. Parrinello, Phys. Rev. Lett. **62**, 555 (1989).

PREPARATION TECHNIQUES FOR DIAMOND-LIKE CARBON

Y. Catherine
Laboratoire des Plasmas et des Couches Minces
Institut de Physique et de Chimie des Materiaux, UMR CNRS 110
2 rue de la Houssiniere, 44072 NANTES Cedex 03, France

Plasma deposition of diamond-like carbon films is a particularly interesting field owing to the fact that these carbons are typically denser, harder, more transparent and resistant to chemical attack than any other carbonaceous films. These semi-transparent hard carbon coatings can be obtained by several techniques such as ion beams, cathodic sputtering, and plasma enhanced chemical vapor deposition. The purpose of this presentation is to describe these various techniques and to show their advantages and limitations. Because ion beam deposition is,at least conceptually, easier to understand, we will first discuss this method then the discharge techniques.

The first part will be devoted to the various ion beam techniques used for hard carbon deposition. Emphasis will be made on the relation between the nature and the energy of the ions and the deposited layers.

The second part will concern the various discharge techniques including plasma sputtering, DC and RF glow discharges, ECR discharges and plasma remote discharge deposition or downstream deposition technique. For each technique we shall describe the experimental setup and give their particularities. Also the characteristics of the carbon layers will be investigated.

However, by far the most widespread deposition process for DLC films comprises the use of a low-pressure DC or RF glow discharge in hydrocarbons or their mixture with hydrogen or inert gases. Therefore, a large part of this paper will cover the study of their electrical behavior (more particularly the low and high frequency regime) in conjunction with the deposition process, the film structure and properties.

Pertinent glow discharge plasma diagnostics such as ion flux and energy measurements, mass spectrometric and optical emission measurements, mass spectrometric and optical emission measurements, will also be described. An analysis of the results will aid in the understanding of the plasma properties and deposition process.

Also some aspects of the modeling of electron and chemical kinetics in hydrocarbon RF glow discharge deposition plasmas will be discussed.

In conclusion, a comparison of the carbon layers obtained with the various deposition processes will be made and future trends in deposition technology will be outlined.

CORRELATION BETWEEN PRECURSOR GAS AND STRUCTURE

J-M Mackowski
Institut de Physique Nucleaire
Universite Claude Bernard, Lyon I
43 Bd du 11 Novembre 1918
69622 F Villeurbanne Cedex, France

ABSTRACT NOT AVAILABLE

PROCESS CHARACTERIZATION OF a-C:H PLASMA DEPOSITION

Ch. Wild
Fraunhofer Institut für Angewandte Festkörphysik
Eckerstrasse 4, D-7800 Freiburg, FRG

A detailed study of the deposition of amorphous, hydrogenated carbon (a-C:H) films in asymmetric, capacitively coupled radiofrequency discharges is presented. Emphasis is put on the role of process gas, plasma chemistry, and plasma surface interaction.

From the mass distribution of positive ions in hydrocarbon radiofrequency discharges, a variety of plasma chemical processes can be derived, which are specific for the hydrocarbon gas used. The influence of these plasma chemical processes on the deposition and properties of a-C:H films has been investigated by depositing a-C:H films using different types of hydrocarbon process gases. It was found that for hard a-C:H films there is no dependence of film properties on the type of process gas. This independence of film properties is explained by the fragmentation of energetic hydrocarbon ions impinging on the cathode, i.e., on the surface of the growing a-C:H film, as shown by spatially resolved optical emission spectroscopy.

The fragmentation efficiency, however, depends critically on the energy of the film forming hydrocarbon ions. For low deposition energies (<50 eV) insufficient fragmentation occurs leading to hydrogen-rich, polymer-like hydrocarbon films. In contrast, at high impact energies (>100 eV) complete fragmentation of hydrocarbon ions leads to the formation of hard, strongly cross-linked a-C:H films with precursor independent properties.

Hence the energy of the film forming hydrocarbon ions is the most important process parameter. In radiofrequency discharges the energy of the ions impinging on the cathode is determined by the potential drop across the cathode sheath and by inelastic collisions occurring in the sheath. To study the direct dependence of a-C:H film properties on the deposition energy, the energies of ions impinging on the cathode were measured. It was found that the distribution of ion energies exhibits a series of pronounced peaks, which are explained by the rf modulation of the sheath potential and by the creation of thermal ions in the sheath, e.g., by charge exchange processes. From the observed structures in the ion energy distributions, information about the spatial and temporal variation of the electric field in the ion sheath is obtained.

The average ion energy $\bar{E}$ at the cathode in a benzene discharge, operated under standard conditions, was found to be $\bar{E} = 0.4 \cdot U_B$, where U_B is the bias voltage. This is in agreement with calorimetric measurements of the energy flux onto the cathode during a-C:H deposition. The observed transition from polymer-like to diamond-like a-C:H thus corresponds to average ion energies of 40-80 eV as expected by considering the bonding energies of the film forming hydrocarbon ions.

ELECTRONIC STRUCTURE AND PROPERTIES OF DIAMOND-LIKE CARBON

J. Robertson
Central Electricity Research Laboratory
National Power TEC
Leatherhead, Surrey, KT 22 7SE, UK

The structural and electronic properties of a-C:H (hydrogenated amorphous carbon or diamond-like carbon) are closely related. Their properties lie intermediate between the extremes of diamond, graphite, and hydrocarbon polymers in that they contain variable amounts of sp^3 carbon, sp^2 carbon and hydrogen. It is also useful to bear in mind the behavior of evaporated amorphous carbon and glassy carbon, two purely sp^2 forms of disordered carbon.

The key to understanding the electronic structure of all amorphous carbons is to realize that they are controlled by the π electrons of the sp^2 sites, as these states lie close to the Fermi level, E_F.[1-3] It turns out that the sp^2 sites segregate into aromatic (graphitic) clusters whose characteristic size controls the band gap of the carbon and thereby all its electronic properties. In a-C:H, the clusters are embedded in sp^3 bonded, often polymeric, material and in a-C they are separated from adjacent clusters by a perimeter of defects or sp^3 sites.

The behavior of the π electrons can be adequately understood in terms of the Huckel model which decouples them from the σ electrons whose bonds form the backbone of the network. The π electrons form a half-filled band. Their contribution to the binding energy is maximized if a gap is created in their spectrum at E_F which stabilizes the resulting structure. These structures are, of course, analogues of organic molecules. The smallest structure is the ethylenic double bond but the most stable small structure is the six-fold or benzene ring. The π electron binding energy per site is further increased if the benzene rings fuse together into aromatic sheets, and thus aromatic clusters are built up. While the binding energy of σ electrons is roughly the sum of contributions from each two-centered bond, the π electron binding energy contains multi-centered terms. It is these terms which lead to the segregation of sp^2 sites into graphitic clusters and the generation of medium-range order in amorphous carbons.

The most favored clusters are compact as these possess the fewest edge sites. The band gap of such clusters is given by the simple formula

$$E_g = \frac{2\beta}{N^{1/2}} \simeq \frac{6}{N^{1/2}} \text{ eV}$$

where N is the number of rings in the cluster and β is the nearest neighbor interaction of two π states. The optical gap of the sample is an average of these local band gaps. This allows the typical cluster size in any form of carbon to be estimated from its optical gap, an alternative to using the intensity of the Raman disorder mode at $\simeq$1350 cm^{-1}, which tends to be used for more ordered graphitic carbons.

The elctronic and structural properties of a-C:H will then be reviewed using this model as a basis. In a-C:H the clusters are surrounded by sp^3 bonded polymeric regions which have a much larger band gap. The polymeric regions act to localize the π states within their parent cluster,[3] which produces interesting effects in the luminescence and resonant Raman spectra, and which provide evidence in favor of the cluster model.[4-6]

The wide band optical spectra reveal that the π and σ excitations occur largely in separate energy ranges, which has been used to obtain estimates of the relative proportions of sp^3 and sp^2 sites.[7,8] The sp^3 to sp^2 ratio of a-C:H may also be found by NMR and infra-red spectroscopy.[9,10]

The presence of sp^2 sites is revealed in the XANES spectra of a-C:H, the excitation spectrum of the carbon 1s core level, by the $1s \rightarrow \pi^*$ transitions found at 285 eV, before the onset of the main $1s \rightarrow \sigma^*$ transitions above $\approx$ 288 eV.[7]

The photoemission spectra reveal the presence of π states in a-C:H and also the dominance of graphitic clusters in a-C.[11]

I shall also discuss recent EXAFS measuremetns by Stohr[12] showing that a-C was two-fold coordinated, which cannot be correct.

A useful property of a-C:H is that it can be doped n- or p-type from the gas phase by including diborance, phosphine or ammonia in the gas stream.[13] A true substitutional mechanism seems to be involved but the doping efficiency is low, lower even than in a-Si:H, because of the high density of gap states and because many of the dopant atoms tend to form electrically inactive trivalent sites. On the other hand, because the band gap of a-C:H is much lower than that of diamond, N now acts as a shallow donor not a deep center.

The first principles Car-Parrinello and other simulations of the local atomic and electronic structure will also be discussed.[14,15]

References

1. J. Robertson and E. P. O'Reilly, Phys. Rev. B 35, 2946 (1987).
2. J.Robertson, Adv. Phys. 35, 317 (1986).
3. J. Robertson, Phil. Mag. Lett. 57, 143 (1988).
4. J. Wagner et al., J. Appl. Phys. 59, 2044 (1986); Phys. Rev. B 40, 1817 (1989.
5. M. Yoshikawa et al., Appl. Phys. Lett. 52, 1639 (1988).
6. M. A. Tabor et al., Appl. Phys. Lett. 54, 123 (1989).
7. J. Fink et al., Solid State Commmun. 47, 887 (1983); Phys. Rev. B 30, 4713 (1984).
8. C. Gao et al., Phys. Rev. Lett. 62, 945 (1989).
9. A. Grill et al., J. Appl. Phys. 61, 2874 (1987).
10. B. Dischler, Proc. ERS (1987).
11. P. Oelhafen and D. Ugolini, in Proc. European MRS (1987).
12. G. Comelli, J. Stohr et al., Phys. Rev. B. 38, 7511 (1988).
13. D. I. Jones and A. D. Stewart, Phil. Mag. B 46, 423 (1982).
14. G. Galli, R. M. Martin, R. Car, and M. Parrinello, Phys. Rev. Lett. 62, 555 (1989).
15. J. Tersoff, Phys. Rev. Lett. 61, 2879 (1988).

MECHANICAL PROPERTY MEASUREMENTS OF THIN FILMS AND HARD MATERIALS*

C. J. McHargue, M. E. O'Hern, and D. L. Joslin**
Metals and Ceramics Division
Oak Ridge National Laboratory
P.O. Box 2008, Oak Ridge, TN 37831-6118 USA

Determination of the hardness of thin films is difficult due to the small thickness of such films relative to the penetration of the indenter used in conventional microindentation tests. In addition, the large elastic contribution to the deflection of a diamond surface under test also contributes to inaccurate measurements. The recent development of load-depth sensing or ultra-low load microindentation testing equipment (the mechanical properties microprobe or Nanoindenter) allows accurate values for the hardness and elastic modulus to be obtained for amorphous carbon films (hard carbon or diamond-like films) and diamond films of the thickness commonly prepared by the techniques discussed at this meeting.

The hardness values of the diamond-like films studied lie in the range of 7 to 15 GPa and the corresponding elastic modulus values are in the range of 100 to 125 GPa. Diamond films obtained from a number of sources exhibit hardness and modulus values similar to those of type II natural diamond, [100] orientation.

---

*Research sponsored jointly by the Division of Materials Sciences, U.S Department of Energy, and the U.S. Army Strategic Defense Command under MIPR #W31RPD-8-C4114 with the U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

**Guest, University of Tennessee.

IN SITU CHARACTERIZATION OF a-C:H FILMS AND FILM-SUBSTRATE INTERFACES BY PHOTOELECTRON SPECTROSCOPY

P. Oelhafen
Institut für Physik
Universitat Basel, Klingelbergstrasse 82
CH-4056 Basel, Switzerland

The emphasis of the present contribution is on the preparation of amorphous hydrogenated carbon based films under ultra-high vacuum conditions and their in-situ characterization by photoelectron spectroscopy (PES) measurements.

The electronic structure of the materials under investigation is of particular interest and it will be shown how the valence band structure and the core electron states are studied. The various information in terms of basic electronic structure and deduced properties (chemical bonding, atomic structure) obtained from the measurements will be discussed. The application of PES for the investigation of "bulk" properties will be illustrated through a few examples of measurements on metallic and insulating films.

The intrinsic short information depth (i.e., surface sensitivity) of PES which amounts to a few nanometers allows the investigation of surface properties and the observation of surface-substrate interactions upon film deposition. It will be shown that the interface between a-C:H films (prepared in-situ by direct ion beam deposition) and various substrates is not abrupt but exhibit generally a reacted zone extending over a thickness of a few nanometers. The observation of this reacted zone by other experimental techniques such as high resolution transmission electron microscopy (TEM), Rutherford backscattering (RBS) and channeling will be presented.

In a second part, the application of PES to more complex problems is discussed. A first example is devoted to the characterization of a-C:H films prepared under different experimental conditions and using different process gases. It will be shown how PES can directly monitor the formation of diamond-like and polymeric films. Finally, the application of PES to the study of more complex interfaces such as a-C:H on GaAs will be presented. The implications of the different observations at the film-substrate interface for the adhesion properties will be discussed.

POST-DEPOSITION TREATMENTS AND STABILITY OF DIAMOND-LIKE FILMS

R. Kalish
Solid State Institute and Physics Department
Technion-Israel Institute of Technology
Haifa 32 000, Israel

The effects that energy deposition by photons, ions, and electrons have on the structure and properties of diamond-like carbon (amorphous hydrogenated carbon) films are reviewed. In all cases the treated films turn electrically conductive and optically opaque; nevertheless it is shown that different physical processes are responsible for the observed changes for the different modes of energy deposition. Results obtained by a variety of experimental techniques which probe the structural and compositional changes are described. Models which fit the experimental data on hydrogen loss and on changes in electrical and optical properties as a result of ion irradiation are proposed.

AGING PROCESSES IN DIAMOND-LIKE CARBON AND CARBON/METAL FILMS

L. Martinu
Ecole Polytechnique
Case Polstale 6079, Succursale A
Montreal H3C 3A7, Canada

Microstructure of diamond-like carbon (DLC) films, in particular the relative proportions of sp^1, sp^2, and sp^3 hybridizations and the concentration of hydrogen, strongly depends on the deposition process conditions: "monomer" pressure and flow rate, power input, substrate temperature and as a consequence on the deposition rate and energy fluxes impinging upon the growing surface. The microstructural features are linked with such film characteristics as internal stresses, film density and "rigidity" which, in turn, control the film stability.

This contribution surveys aging phenomena in DLC films, particularly how the films' electrical, optical, and mechanical properties change as a function of time after the deposition, with post-deposition thermal treatment, and thermal cycling. Three different types of DLC films are discussed:

1. DLC coatings grown in an RF glow discharge on the biased electrode.[1,2] These are compared with coatings deposited in ion beam systems (so called i-C films).

2. DLC films deposited in a dual frequency system, where microwave and RF discharges are applied simultaneously.[3] This approach makes it possible to investigate over a wide range the effect of energy fluxes bombarding the surface. It has been found that improved film stability can be achieved this way.

3. DLC films containing metal clusters.[4-7] Metals were evaporated during film growth on the RF biased electrode. The properties of these composite layers are generally dependent upon the concentration and morphology of the metal inclusions. This type of material is particularly interesting to the present context since the aging process is very sensitively reflected by the facility with which the DLC matrix permits structural rearrangement of the metallic constituents. Both experimental and theoretical approaches (based on the effective medium theory) are used to analyze these effects. It is important to note that there exists a critical concentration of incorporated metal, beyond which the DLC matrix loses its unique properties.

Application aspects of aging phenomena in DLC and DLC/metal films will be discussed.

References

1. J. C. Angus, P. Koidl, and S. Domitz, in "Plasma Deposited Thin Films," J. Mort and F. Jansen, eds., CRC, Boca Raton, FL, 1986.

2. L. Martinu, in "High Energy Density Technologies in Materials Science," F. Garbassi and E. Occhiello, eds., Kluwer Academic Publishers, Dordrecht, 1989.

3. L. Martinu, J. E. Klemberg-Sapieha, and M. R. Wertheimer, Appl. Phys. Lett. **54**, 2645 (1989).

4. H. Biederman, Hong jon Chjok, L. Martinu, J. David, S. Kadlec, and P. Lukac, p. 499 in Proc. E-MRS Conf., Strasbourg, June 2-5, 1987, Vol. 17, Les Editions de Physique, Paris, 1987.

5. H. Biederman, I. Chudacek, D. Slavinska, L. Martinu, J. David, and S. Nespurek, Vacuum **39**, 13 (1989).

6. H. Biederman, L. Martinu, D. Slavinska, and I. Chudacek, Pure Appl.Chem. **60**, 607 (1988).

7. H. Biederman and L. Martinu, in "Plasma Deposition: The Treatment and Etching of Polymers," R. d'Agostino, ed., Academic Press, Boston, 1990.

COMPUTER MODELLING OF C:H FILM GROWTH

W. Möller and D. Boutard
Max-Planck-Institut für Plasmaphysik
EURATOM Association, D-8046 Garching, FRG

Recently, an improved understanding has been obtained on the mechanisms governing the formation of a-C:H layers by the bombardment of graphite with energetic ions. In the saturated layer, the local hydrogen concentration results from the balance of ion deposition and ion-induced depletion. The latter can be modelled as a knock-off of hydrogen atoms from their hydrogen-carbon bonds by ion-atom collisions, and a subsequent local molecule formation and fast diffusion of hydrogen molecules to the surface.

These ideas can also be applied to the formation of C:H films by plasma-enhanced chemical vapor deposition. Basically, adsorbed hydrocarbon molecules or radicals are thought to release excess hydrogen atoms under the influence of atomic collisions. The release rate and thereby the resulting hydrogen concentration will then depend on the species and the energy of the incident ions.

First calculations have been performed by means of a dynamic binary-collision Monte-Carlo code, which also treats the sputtering at the surface and the collisional mixing at the layer-substrate interface correctly. Indeed, they show correct trends, e.g., with respect to the hydrogen concentration, which varies from 25 at.% (a-C:H) to 50 at.% (polymer-like layer) for ion energies between 200 eV (from e.g., an RF plasma) and 20 eV (microwave plasma).

In addition to a detailed description of the above models and computer codes, the paper will also compare their results to recent experimental findings for ion-induced isotope exchange in a-C:H and the plasma-enhanced deposition of a-C:H films from hydrogen/methane gas mixtures using different hydrogen isotopes.

GAP STATES AND ELECTRON SPIN RESONANCE IN AMORPHOUS CARBON AND HYDROGENATED AMORPHOUS CARBON

F. Demichelis
Dipartimento di Fisica
Politecnico di Torino
Corso Duca degli Abruzzi, 24
10129 Torino, Italy

Hydrogenated amorphous carbon a-C:H has been found to be, if prepared under convenient conditions, a transparent, insulating, hard material that is diamond-like in its properties. Even amorphous carbon, however, can be obtained with some diamond-like properties.

The ability of carbon atoms to form both threefold coordinated (sp^2) sites, as in graphite, and fourfold coordinated (sp^3) sites, as in diamond, has a strong influence on the properties of amorphous carbon films.

Previous results indicate that the a-C is predominantly sp^2 bonded, while hydrogenation introduces many sp^3 sites, increasing the optical gap.

For comparison a-C and a-C:H films were prepared by sputtering of carbon in Ar and Ar + H_2 mixture. The sub-gap states and their density were determined by photo acoustic spectroscopy (PAS) and photothermal deflection spectroscopy (PDS) measurements. The number of spin states near the Fermi level were deduced by their characteristic electron spin resonance (ESR) signals.

The integrated values of the absorption coefficient in the region $\alpha < 10^3$ have been correlated with the density of spins as obtained by ESR measurements. A model fitting the experimental values of optical data and Urbach tails allows us to obtain information about the distribution of the density of states in the gap.

CHARACTERIZATION AND PROPERTIES OF DIAMOND-LIKE CARBON FILMS

Peter Koidl
Fraunhofer Institut für Angewandte Festkörperphysik
Eckerstrasse 4, D-7800 Freiburg, FRG

An overview is given on the characterization and properties of dense amorphous carbon films with diamond-like properties.

Amorphous carbon may contain appreciable concentrations of hydrogen which influences essentially the bonding and network structure of the films. As a result the properties of these amorphous hydrogenated carbon (a-C:H) films may cover a wide range which is limited by the properties of the structurally ordered solids: diamond, graphite, and hydrocarbon polymers.

Under appropriate deposition conditions, very hard and dense, chemically inert and infrared transparent films can be prepared. We will concentrate on this class of diamond-like a-C:H films. They are characterized by a high degree of three-dimensional cross-linking which results in a high atom number density of $>0.2\ N_o$ atoms/cm^3, where N_o is Avogadro's number. Hydrogen is incorporated with typical concentrations of $H/C \approx 0.5$. A major fraction of the carbon atoms are sp^3 hybridized in contrast to evaporated amorphous carbon which consists totally of sp^2 bonded carbon.

There are many deposition techniques suitable for the growth of diamond-like a-C:H films. An appropriate and common method is the condensation of energetic hydrocarbon ions either from an ion source or a glow discharge. The most important deposition parameter in determining the film properties is the deposition energy, i.e., the impact energy of the film-forming hydrocarbons.

The present contribution reviews the mechanical, optical, and electronic properties of diamond-like a-C:H films. The individual merits of the relevant characterization techniques are briefly discussed. The dependence of the film properties on the deposition parameters, their possible modifications by post-deposition treatment and the relationship to basic structural data like hydrogen content, the details of hydrogen and carbon bonding, and the medium range order of the carbon skeletal network are discussed.

Mechanical properties of a-C:H films are reported as studied by micro-mechanical indentation techniques and Brillouin scattering. The a-C:H films show a mixed elastic/plastic response to deformation. The ratio of plastic to elastic deformation may be changed by special deposition conditions or post-deposition treatment. For most applications good adhesion to the substrate is important. Chemical bonding at the interface is shown to be responsible for the excellent adhesion to carbide forming substrates.

The optical constants (refractive index and absorption coefficient) have been determined from transmission and reflection spectra. The optical properties in the infrared are characterized by residual absorption due to C-H and C-C vibrations. At shorter wavelengths the onset of electronic absorption, as described by the optical gap, is determined by excitations of π-electrons. Optical gap energies between 1 and 1.5 eV are typical for diamond-like a-C:H.

Additional optical characterization techniques like luminescence and Raman spectroscopy are shown to provide structural data on network density and medium range order, respectively.

As grown diamond-like a-C:H films exhibit a low electrical conductivity of typically 10^{-12} $\Omega^{-1}cm^{-1}$. Doping, either p- or n-type, is possible. However, the electrical activation of the group III or V dopants is much poorer than, for example, in amorphous silicon, even for strongly hydrogenated a-C:H films, the reason being the flexibility of the carbon network and the ease in forming trigonal sp^2-sites where substitutional group III or V elements are electrically inactive.

It is known that the diamond-like properties of dense a-C:H films get lost at elevated temperatures. Under annealing, the hydrogen content decreases and the films undergo a transition towards a distorted graphitic material. The temperature induced changes have been studied by thermal desorption spectroscopy and by characterizing a set of differently heat-treated films. Typical diamond-like a-C:H films are thermally stable up to about 350°C. However, the decomposition temperature depends on the network structure of the a-C:H films and hence on the preparation conditions. The thermal stability of a-C:H increases generally for a-C:H films prepared at higher deposition energies.

APPLICATIONS OF DIAMOND-LIKE (HARD CARBON) FILMS

A. H. Lettington
Royal Signals and Radar Establishment
St. Andrews Road
Malvern, Worcs. WR14 3PS, UK

This paper will discuss the known and potential uses for diamond-like carbon. It has quite remarkable physical properties in thin film form. Some of these such as its excellent abrasion resistance and chemical durability and long-wave infrared transmission are reminiscent of pure diamond. Other properties such as electrical conductivity, compatibility with tissue, and hydrophobic behavior result from the inclusion of graphite and hydrogen in the films and are strongly dependent on deposition parameters.

The paper will discuss the various conditions under which these films are deposited and the effects these have on potential applications.

One important application has been the use of diamond-like carbon as a durable anti-reflection coating on germanium in infrared optics. Germanium is the most commonly used window and lens material in the 8-13-μm waveband. It is easily scratched by sand, readily attacked by salt water and has a high refractive index. Diamond-like carbon has an ideal refractive index-match to germanium to produce a single layer AR coating of extreme durability. Various test procedures and specifications for this coating are described.

Another application of carbon coatings has been to protect front surface aluminum mirrors for use in the infrared. Conventional coating materials produce phase changes at oblique incidence between the radiation reflected at the air-coating interface, and that reflected at the coating-metal interface, resulting in severe reflection losses. These losses have been eliminated in carbon coated reflectors.

The wavelength selective properties of diamond-like carbon have been used for the photothermal conversion of solar radiation, the coating having high absorption in the visible and low emissivity at the peak of the black body curve.

These coatings have also been used to protect silica optical fibers from surface degradation and subsequent brittle fracture.

The paper will conclude with examples of other mechanical, optical, and medical applications and a review of production costs and market surveys.

TECHNIQUES FOR THE GROWTH OF DIAMOND

T. R. Anthony
General Electric Corporate Research and Development Center
River Road, Schenectady, NY 12309 USA

Diamond has been synthesized by both equilibrium and non-equilibrium methods. Diamond was first grown as an equilibrium phase at high pressures and high temperatures in 1954. A few years later in 1962 diamond was grown as a metastable phase at subatmospheric pressures and moderate temperatures.

Today, all commercial production of synthetic diamond is carried out by the equilibrium process at high temperatures and pressures. Diamond becomes the stable phase of carbon at high pressures because the density of diamond is 1.56 times greater than the density of graphite. High temperatures accelerate the conversion rate of graphite to diamond. The most widely used high-pressure high-temperature process uses a high-pressure cell containing a mixture of graphite and a liquid metal catalyst. Two opposing anvils are pressed inward by a large press into a heated diamond growth cell surrounded by a carbide belt to generate 50,000 atm of pressure. Under these conditions, diamond becomes the stable phase of the carbon phase diagram. The now metastable graphite dissolves into the liquid metal catalyst and precipitates out as diamond. The liquid metal catalyst enables one to grow diamond close to the diamond-graphite phase boundary. This quasi-reversible process can produce large diamond crystals with a high degree of perfection and purity at rates up to 10,000 microns/h.

An alternative high-pressure high-temperature process grows diamond directly from graphite without an intermediating agent. The pressures and temperatures required for direct graphite-to-diamond conversion are very high and diamond growth is rapid and irreversible. The resulting crystal quality and size is significantly diminished as a result. A number of methods have been developed to carry out this direct conversion of graphite to diamond. One uses a high-pressure high-temperature cell that is driven deep into the diamond stable region. Such operations are very hard on the equipment and are only used in selective scientific investigations. A second method uses a large underground cell of reinforced concrete in which a mixture of graphite and a high-energy explosive are buried. Ignition of the explosive produces a very high-temperature and high-pressure shock wave that directly converts the graphite to very small particles of hexagonal diamond. This process is used commercially to produce fine diamond powder that is used as a polishing agent. A third way of directly converting graphite to diamond is with a high energy laser pulse. Small particles of graphite are illuminated with a high energy laser that generates a high-temperature shock wave that directly converts the graphite to diamond. Because of the low production rate and high cost of the laser pulse process, it has not been commercialized.

In 1962, Eversole developed the first process to make diamond as a metastable phase. Eversole alternatively exposed diamond substrates to a hydrocarbon gas and then hydrogen at moderate temperatures and low pressures. Under these conditions, the hydrocarbon was pyrolysized to form diamond and graphite and then the hydrogen was used to etch the graphite away. This process did not attract much interest because it required diamond substrates and had a very low diamond growth rate. In the late 1970s, an important invention by Spitsyn and his co-workers changed this cyclic 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.

This invention was the addition of atomic hydrogen to the first reaction used by Eversole. Atomic hydrogen serves several critical roles in metastable 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 in the gas; (6) abstraction of hydrogen from hydrocarbons attached to the surface; (7) production of vacant surface sites; (8) etching of graphite; and (9) suppression of polycyclic aromatic hydrocarbons. Atomic hydrogen can be generated by various methods, each of which generally leads to a "new" chemical vapor deposition diamond (CVD) growth process. These methods include hot-filament CVD, hot-filament electron-assisted CVD, low- and high-pressure glow discharge CVD, low- and high-pressure microwave CVD, low- and high-pressure RF CVD, low- and high-pressure combustion flame CVD, photolysis CVD, radiolysis CVD, and stellar CVD. Each growth method has different nucleation rates, growth rates and carbon utilization efficiencies because of different gas concentrations, atomic hydrogen concentrations and gas temperatures. For any particular application, a "best" method may exist, but in general, there is no over-all superior process for all uses.

So far, research indicates that metastable CVD diamond is inferior in quality and more expensive than diamond made at equilibrium at high pressures. As a result, researchers have tried to develop alternative processes that use substitutes for atomic hydrogen such as the F, Cl, Br, I, N, O, OH, and combinations of these atoms to develop a better diamond CVD process. So far, such elements have only been successful as "helpers" in the basic atomic hydrogen CVD process and have not reduced the cost nor improved the crystal quality of the diamond.

Another approach to grow diamond at low pressures utilizes alternating exothermic chemical reactions that deposit a monolayer of diamond during each reaction. An example of this type of reaction is alternating exposure of a diamond substrate to CH_4 and to CF_4. The desired product of these reactions is diamond plus HF. Both reactions are exothermic because the C-H and the C-F bonding energies are both less than the H-F bonding energy.

Two other proposed processes to grow diamond at low pressures use liquid baths as a medium for diamond growth. Both methods supersaturate, respectively, a bath of molten salt and a bath of molten metal with carbon and then expose a diamond seed to this supersaturated carbon solution to grow diamond. Although both methods have been reported in the literature, neither method has yet been independently confirmed by other researchers.

DEVICE APPLICATION FOR DIAMONDS*

M. W. Geis
Lincoln Laboratory
Massachusetts Institute of Technology
224 Wood Street
Lexington, MA 02173 USA

Diamond is a high band gap (5.5 eV) semiconductor that has superior properties to many of the commonly used semiconductors. The high breakdown voltage (ten times that of Si), exceptionally high thermal conductivity (five times that of copper), and hole and electron mobilities near 2000 $cm^2\ V^{-1}\ s^{-1}$ result in projections of higher operating frequencies and significantly higher output powers than those obtainable with devices made of Si or GaAs.

Fabrication technology has been developed to etch diamond and to form both ohmic and Schottky contacts. Permeable base transistors (PBTs) and diodes have been formed which exhibit some of the highest reported operating temperatures.

This presentation will discuss techniques used to obtain semiconducting diamond films, electrical properties of diamond, device results including diodes and PBTs, and future diamond applications.

*This work was sponsored by SDIO/OST through the Office of Naval Research.

THEORY AND MODELS FOR NUCLEATION OF DIAMOND

Michael Frenklach
Departent of Materials Science and Engineering
The Pennsylvania State University
University Park, PA 16802

Research on the growth of crystalline diamond films at low pressures has been intensified in recent years. It has been demonstrated that high-quality diamond films can be produced employing different experimental techniques. A variety of hydrocarbons has been used as starting material. It becomes evident, however, that further technological advancement, particularly in such challenging areas as single-crystal growth for electronic applications and low-temperature deposition for coating of optic and plastic materials, requires detailed understanding of the fundamental phenomena responsible for diamond nucleation and growth. In this presentation, I will (1) review the concepts and ideas advanced towards understanding the mechanism of diamond formation at metastable conditions; (2) review the basic knowledge on hydrocarbon chemistry, with particular emphasis on the issues related to deposition of diamond films; and (3) summarize the results of detailed modeling of surface reactions and gas-phase processes obtained for diamond nucleation and growth.

Proposed Concept and Ideas

The Russian school of Derjagin, Fedoseev, and co-workers developed a global model for diamond nucleation and growth based on macroscopic concepts of classical nucleation theory and adsorption-desorption kinetics and equilibrium. They provided a persuasive argument that the growth of diamond is controlled by kinetics. The basic picture, advocated by the Russian group and by Angus and co-workers in the United States and accepted now by the majority of the scientific community, states that the formation of diamond competes with the formation of graphite and that hydrogen atoms suppress the formation of graphite but not that of diamond. Unfortunately, this theory identifies neither the possible growth species nor the specific reactions taking place at the surface; it is formulated in rather general terms of surface coverage, formation of surface complexes, and etching of graphtie by atomic hydrogen. Similar thermodynamic and classical nucleation approaches have been suggested by others.

Tsuda et al. searched for the lowest energy path of diamond growth using quantum chemical computations. Assuming that only C_1 radicals and ions can be the growth species in CH_4-H_2 plasma, the authors reported the following two-step reaction sequence. In the first step, the (111) plane of the diamond surface is covered by the methyl groups either via methylene insertion or hydrogen abstraction followed by methyl radical addition. Then, following the attack of a methyl cation, three neighboring methyl groups on the (111) plane are bound to form the diamond structure. In the subsequent publication, Tsuda et al. extended their analysis and concluded that the epitaxial growth of a diamond film is sustained, provided the surface maintains a positive charge and there is a supply of methyl radicals.

Frenklach and Spear proposed that the main monomer growth species is acetylene, and the reaction mechanism consists of two alternating steps: surface activation by H atom abstraction of a hydrogen atom from a surface carbon and the addition of one or two acetylene molecules. This proposal was motivated by the results of a similar reaction mechanism identified for the formation and growth of polycyclic aromatic hydrocarbons in hydrocarbon pyrolysis and combustion and the realization that acetylene shoud be the main gaseous species present in the hydrocarbon plasma. The latter prediction was recently confirmed in experimental studies by several research groups. A quantum mechanical study performed by our group indicated that the acetylene addition mechanism of diamond growth is energetically more favorable than the mechanism of Tsuda et al. driven by methyl ions and radicals.

Hydrocarbon Chemisry

A large amount of information has been accumulated on pyrolysis and oxidation of hydrocarbon fuels. Many complex systems, like laminar premixed flames, are now being described in terms of elementary chemical reactions. The formation and growth of polycyclic aromatic hydrocarbons (PAH) have also been modeled on a very fundamental basis. It has been postulated that the chemical reactions of graphite and diamond growth are very similar to those of the PAH chemistry. The most important classes of reactions appear to be abstraction of hydrogen atoms, radical-molecule addition, and radical decomposition.

Detailed Modeling of Diamond Deposition

Several research groups have begun using detailed chemical kinetic modeling to describe gas-phase reactions occurring in diamond deposition processes, including transport phenomena. The computational predictions for major gaseous species are in good agreement with the experiment. Recently, we developed a detailed kinetic model of surface processes occurring in diamond CVD. The deposition is described in terms of elementary chemical reactions for both gas-phase and surface phenomena. The model was tested by simulating diamond film deposition in a hot-filament reactor using methane-hydrogen, methane-argon, and methane-oxygen-hydrogen gas mixtures. The model reproduces correctly the dependence of the growth rate and film quality on the substrate temperature observed in various experimental studies. Also reproduced by the model is the pressure effect reported by Spitsyn and co-workers. The model successfully predicts the effect of oxygen--the addition of small amounts of O_2 does not necessarily increase the deposition rate but rather improves the film quality, particularly at low temperatures, thus allowing low-temperature deposition of diamond films.

The analysis of the computational results along with various sensitivity tests led us to the following conclusions:

1. The key role of hydrogen and oxygen in the diamond deposition process is to suppress the formation of aromatic species by H_2 and O_2 in the gas phase and thereby to prevent their condensation and subsequent growth into non-diamond, graphitic phases on the deposition surface. This conclusion can be further supported by recent observations in our laboratory on homogeneous nucleation of diamond and graphite in a microwave reactor. For example, whereas no solid-phase nucletion occurs in C_2H_2-H_2 mixtures even at acetylene concentration as high as 20%, graphitic phases readily form in very dilute C_2H_2-Ar mixtures. Replacing argon for oxygen results in formation of diamond crystallites.

2. Abstraction of surface H atoms by gaseous H atoms activates the surface by creating radical sites. Counterbalancing this activation is the deactivation reaction of radical sites with H_2 molecules and recombination with H atoms, which keeps the surface carbon atoms in sp^3 state.

3. Gasification of sp^2 carbon by H atoms is very slow, except for very high temperatures, and it is much faster by OH radicals. However, the conversion of sp^2 carbon atoms to sp^3 state by H atom addition is one of the major processes at low and medium temperatures. At high temperatures, the reaction runs in reverse and is responsible for graphitization of diamond.

The presentation will expand on all of these points.

NUCLEATION AND GROWTH OF LOW-PRESSURE DIAMOND

B. Lux and R. Haubner
Institut für Chemische Technologie
Anorganischer Stoffe
Technische Universitat Wien
Getreldemarkt 9/161, A-1060 Wien, Austria

Though low-pressure diamond has been grown successfully on many non-diamond substrates, its nucleation mechanism is not yet well understood.

On a pure, highly polished detect-free Si waver surface diamond nucleates with more difficulties than after being scratched with a hard material. It was shown that the material producing the scratch influences the diamond nucleation at the groove more than the defects created at the Si-surface by the scratching. Diamond itself, used as scratcher, was particularly effective, and it is assumed that small diamond particles left on the substrate surface are acting directly as nuclei. Also other hard materials, such as cBN, SiC and metal carbides, help the diamond nucleation by leaving small particles on the surface but are less effective than diamond.

There are not enough reliable data available to classify different substrate materials according to their effectiveness in diamond nucleation, nor will possible epitaxial relationships between specific substrates and the diamond lattice be discussed here. It is clear however, that for comparable diamond growth conditions, large differences in diamond nucleation exist between substrates of different chemical nature. Some of the reasons for these differences will be discussed.

The diamond particles formed during the early growth stages can easily be observed and counted. Most likely each of them corresponds to a nucleus that survived. These crystals rapidly grow in preferred orientations and finally join to form the typical columnar growth type structure of CVD layers.

Chemical reactions occurring between gases and the substrate surface play an important role in the hetero-epitaxial diamond nucleation. Oxides, nitrides and other substrates may interact with both the carbon to form intermediate ionic carbide layers, and with the atomic hydrogen to form volatile phases before the diamond layer can cover the substrate.

Carbon diffusion is an important parameter for metallic substrates. It is easily understandable that an exceedingly rapid carbon diffusion into the substrate will not allow the C-concentration at the substrate to reach that needed to form a critical diamond nucleus. The difficulty of nucleating diamond on iron, which has a high capability to dissolve carbon at high temperatures, demonstrates this.

A number of refractory metal substrates form stable carbide layers. Diamond nucleation occurs only after the intermediate layer has reached a minimum thickness and slows down the carbon-diffusion rate from the surface sufficiently. Some of the small diamond particles formed during the early nucleation period may even redissolve due to the increased diffusion rate of the solid carbon.

Adherence of a diamond layer is another important problem to be solved for most practical uses. Mismatching of the thermal expansion coefficients creates stresses at the substrate/diamond interface which can be mastered only by chemical bonding. Reasonably good layer bonding can be achieved on certain substrate materials, as has already been proven by severe metal cutting tests. It is obvious that all chemical interactions occurring at the substrate surfaces before coverage and also at the diamond/substrate interface strongly influence the chemical bonding. Gaseous species developing during the nucleation period, as well as the formation of weak intermediate layers, such as ionicly bonded carbides, seem to be detrimental not only for nucleation, but also for adherence.

CHARACTERIZATION AND PROPERTIES OF ARTIFICIALLY GROWN DIAMOND

P. K. Bachmann and D. U. Wiechert
Philips Research Laboratories
D-5100 Aachen, FRG

A major difference between the early and the present days of CVD diamond research is the lack of the highly sophisticated and sensitive analytical methods to distinguish diamond from any other form of carbon in the 1950s and early 1960s. In their paper[1] Angus and coworkers describe in much detail the many tedious methods, including visual observations, chemical analysis, sample etching, x-ray and electron diffraction, they applied to prove without doubt that they deposited diamond on diamond seeds. On the other hand, it is necessary to decisively characterize the deposited material not only to distinguish it from other carbon modifications, but also to allow for adjustment of the preparation conditions to tailor the properties of the diamond film to suit specific applications.

The aim of this lecture is to introduce a variety of characterization methods and to evaluate their usefulness with respect to the analysis of diamond. The properties of diamond coatings determined by means of these methods will be correlated with the experimental preparation conditions and will be judged with respect to the demands of specific applications.

Characterization Methods and Film Properties

The "working definition of diamond films" proposed in 1987[2] demands a crystalline morphology of the deposit discernible by electron microscopy, a single-phase crystalline structure identified by diffraction techniques and a Raman spectrum typical for diamond, i.e., a single narrow line at $\approx$1332 cm^{-1}. The basics of SEM, TEM, x-ray, and electron diffraction and, specifically, Raman spectroscopy for diamond analysis will therefore be covered in more detail. In case of Raman spectroscopy and SEM we will also include some of our latest results on the temperature dependence of the data and on morphological changes associated with Raman measurements. These results suggest to modify the "working definition."

Rutherford backscattering (RBS), electron recoil detection (ERD), neutron activation and magnetic resonance techniques (NMR, ESR) as well as Auger spectroscopy will exemplify the analytical tools to determine non-carbon contamination of the deposited diamond material. Specific emphasis is on the determination of hydrogen incorporated in the deposit and its influence on the film properties.

The measurement of the UV-VIS-IR transparency, the thermal conductivity, the electrical and mechanical properties and the luminescence of diamond are important characterization methods directly related to diamond applications such as windows for electromagnetic radiation of any kind, heat sinks, or passive and active electronic devices (thermistors, transistors, diodes). The characterization methods will be described along with their major trouble spots.

The state-of-the-art of specific diamond properties such as transparency, electrical conductivity, thermal conductivity, chemical resistivity, and hardness will be reported and compared to the requirements for applications as well as correlated with film preparation conditions. Those methods that are covered in more detail by other contributions during the seminar, e.g., electrical properties or mechanical properties will only be briefly touched.

Part of the lecture will also be devoted to the characterization of the roughness, thickness, and thickness uniformity and homogeneity of diamond films using nondestructive, mask-free optical techniques and on some deposition parameters influencing these properties in case of microwave plasma CVD of diamond films.

References

1. J. Angus et al., J. Appl. Phys. **39**(4), 2915 (1968).

2. R. Messier et al., Thin Solid Films **153**, 1 (1987).

EMERGENCE AND DEVELOPMENT OF SCIENCE AND TECHNOLOGY OF DIAMOND FILMS IN THE U.S.S.R.

B. V. Spitsyn
Institute of Physical Chemistry
U.S.S.R. Academy of Science
Leninsky Prospect 31
Moscow 117915, U.S.S.R.

Attempts to synthesize diamond in the region of thermodynamic metastability were performed for the first time in U.S.S.R. (1956) and U.S.A. (1958) by chemical crystallization from carbon-containing gaseous phase on the surface of diamond seed crystals. These first methods were characterized by two essential limitations:

(1) A very low (about 1 x 10^{-3} μm/h) linear growing rate of diamond films; and

(2) The formation of the thermodynamically more stable graphite phase on the surface of growing metastable diamond phase. The latter nucleation and growth led to gradual blocking of the gas components transport of gas components to the diamond surface, which eventually stopped the diamond film growth. The first successful attempt to increase the diamond film growth rate was by means of a high temperature chemical transport reaction. The chemical transport reaction in the system graphite-hydrogen-diamond leads to an increase (by a factor of 10) of the diamond film growth rate, and simultaneously gives the possibility to discover the full selectivity of diamond growth.

It is emphasized that the other more recently developed methods for creation of exited hydrocarbon-carbon vapor phase (DC, RF, and microwave plasmas, laser methods and other) explored the qualitatively same crystallization medium, as in the chemical transport reaction. These all give the same principal results in CVD diamond science:

(1) Growth of dielectric epitaxial diamond film at (111) face of natural diamond (B. V. Spitsyn and A. V. Lavrentiev, 1966);

(2) Growth of p- and n-type semiconducting diamond film (B. V. Spitsyn and A. E. Alexenko, 1971);

(3) Nucleation and growth of diamond crystals and microcrystalline DF on non-diamond substrates (L. L. Bouilov et al. and V. P. Varnin et al., 1975).

The dependence of the growth and etching kinetics of diamond and diamond film on the main parameters of the synthesis is discussed. The total combination of the diamond film properties (which are like those of pure single crystalline natural diamond, and in some instances surpass them) give diamond film applicability in engineering and technology.

CRITICAL ASSESSMENT OF STATE-OF-THE ART

Nobuo Setaka
National Institute for Researches in Inorganic Materials
1-1 Namiki, Tsukuba
Ibaraki 305, Japan

The earliest substantial work to grow diamond from a vapor phase at low pressure was presented by Eversole of Union Carbide Corporation in 1962 and independently by a group of researchers headed by Derjaguin and Fedoseev. This work was confirmed by Angus later. Diamond films and particles with well-defined crystal habit were synthesized on non-diamond substrates by the Russian team with a chemical transport process in a closed system.

On the other hand, Aisenberge prepared diamond-like carbon films by an ion beam deposition technique in 1973. This work was confirmed by Spencer in 1976. A single crystal diamond film was formed on a diamond substrate by Freeman using an ion beam deposition with magnetic ion separation, also a diamond-like carbon film containing hydrogen, i-carbon film, was produced by an ion plating method.

Independently, we have shown that diamond deposition is feasible by using hot filament-assisted CVD. This diamond synthesis technique has been extended to a microwave plasma-assisted CVD. Recently, diamond synthesis has been performed by using various other techniques.

It is very important that good quality diamond films have been produced by the modified CVD processes because the CVD technique has excellent capabilities as a ceramic fabrication process, such as for protective coating, powder coating, epitaxial and whisker growth, vapor forming, etc. Diamond has several unique properties that cannot be replaced by other materials, therefore, diamond CVD techniques have the possibility to develop as a valuable tool to open new areas for diamond technology.

Assessment of Diamond Growth Process

The synthesis of diamond film has been performed by various techniques using a gas mixture of methane diluted with hydrogen gas. Recently, it has been reported that oxygen-containing organic molecules have been used instead of methane. The Russian group and other researchers have pointed out that the atomic hydrogen produced from hydrogen molecules plays a significant role in diamond film growth.

There are some reports of particular interest concerning diamond synthesis from vapor phase. Before the diamond synthesis from the vapor phase had been well established, Wilson proposed a new idea in 1973 suggesting that the synthesis requires a source of individual carbon atoms in excited states; that is, having reaction energy which is required to produce the chemical bond of diamond, and furthermore that the lifetime of excited states must be increased or the chemical reaction rate of individual carbon atoms must be increased. The difficulty in growing diamond from vapor phase is due to the extremely short lifetime of the excited states. Therefore, in order to grow diamond, we have to devise some method for prolonging the lifetime of excited states. The new idea does not require high pressure as a

necessary and essential condition for diamond growth. High pressure may be required for certain aspects of the problems, but it is not a basic requirement for diamond growth. Wilson's idea, the early experimental results of the Russian group, plus CVD method, have given us the fundamental insights as to the mechanism of diamond deposition from vapor phase.

On the other hand, the problems actually encountered in diamond vapor deposition are: how to accelerate thermal decomposition of carbonaceous compounds at relatively low temperatures and how to suppress the deposition of non-diamond carbon. Also an upper limit to the temperature of a substrate is fixed in order to protect a diamond nucleus from graphitization.

The other complicated problem seems to be the fact that there exist three allotropic forms of carbon: diamond having sp^3-bonding, graphite-sp^2, and carbyne-sp^1, which is identified as third allotropic modification of carbon. Diamond synthesis is carried out in the graphite stable region. When a carbon solid phase deposits from an activated gaseous medium, the materials will consist of diamond and fragments of structure having sp^3, sp^2, sp^1 hybrid configuration. For this reason the structural identification of the deposited materials and diamond synthesis from vapor phase is very complicated.

Diamond synthesis from the vapor phase has been performed by various techniques. When reviewed, the techniques of diamond CVD have been proceeding using Wilson's idea, the early experimental work of the Russian group, and basic CVD processes. On the basis of these ideas, it could be considered that atomic hydrogen plays a role similar to extending the lifetime of the excited carbon atom. The fundamental requirement for the problem for diamond CVD may be to produce a lot of atomic hydrogen in a non-equilibrium condition at a reaction zone. In some cases it may be oxygen.

We should also remember that diamond was grown with the vapor liquid solid (VLS) mechanism by the Russian group. The VLS mechanism that was proposed by Wagner and Ellis in 1965 is a version of the VLS. The experimental facts suggest that diamond growth is feasible from molten liquid phase at a low pressure.

Assessment of Semiconducting Diamond

There exists considerable interest in diamond as an electronic material because of its wide band gap. It may be possible to develop diamond as a high temperature electronic device and light-emitting diode. However, these materials respectively have large barriers which have to be overcome in order to develop advanced devices. The p-type semiconducting diamond with low resistance has been produced by doping with boron, but the n-type with low resistance has not been achieved either by vapor deposition or the high pressure techniques. On the other hand, it is feasible to produce cBN p-type and n-type semiconductors with relatively low resistance by doping with Be or Si. The p-n junction of semiconducting cBN shows a characteristic of light emission in the range from blue to ultraviolet in the forward bias

condition and rectifying action in the temperature range from room temperature to 500°C. Much interest is being shown in cBN as a wide band gap semiconducting material, however, cBN films have a handicap in that they are difficult to produce from gaseous medium.

A common problem for diamond and cBN is how to grow large crystals using an epitaxial substrate. Relatively large crystals of diamond have been grown under high pressure conditions using the solvent/catalyst method, however the growth of large crystals of cBN is difficult. At present, cBN crystals of 2-3 mm in size have been grown under high pressure using a solvent, but to grow large crystals it is necessary to develop a new solvent for boron nitride.

We have to solve one of the following three problems to develop these materials as advanced electronic devices: (1) how to produce the n-type semiconducting diamond having low resistance; (2) how to prepare cBN films by a vapor deposition process; and (3) how to grow large single crystals of cBN under high pressure conditions. The last problem is moving toward a solution by a special technique using high pressure conditions.

In this lecture, the problems actually encountered for diamond synthesis from the vapor phase and its growth process are discussed on the basis of our experimental results, the idea proposed by Wilson, and the review of relevant literature.

APPLICATIONS OF DIAMOND FILMS

J. Michael Pinneo
Crystallume
125 Constitution Drive
Menlo Park, CA 94025 USA

Rapid laboratory development of CVD diamond materials has already brought the material to military and commercial application in selected areas, and a wider variety of products based on diamond films is about to be introduced across a broad spectrum of technologies. Successful diamond film applications development requires resolution of significant technical and economic challenges not present in fundamental research on the material. We will examine the development of a diamond film product now in OEM sales, and of several products about to be introduced. Technology development details will occupy most of the discussion, but the impacts of financing and market development, and the importance of close collaboration with application end users will be examined as well.

Diamond Film X-Ray Windows

X-ray EDS systems, common accessories on scanning electron microscopes, often employ beryllium detector windows to provide vacuum isolation and x-ray transmission. A diamond window is now available to replace beryllium windows and provides significantly enhanced x-ray energy detection range. The structure and development of this window will be described.

Process technology developed to support this application includes control over nucleation density, crystallite size, large-area compositional and growth rate uniformity, and film gas permeability. Control over these material properties was achieved by appropriate choice of process parameters,including: plasma excitation means; plasma power density; substrate temperature; time variation of carbon concentration; reactor gas dynamics; reactor materials; and careful attention to the role of introduced and in situ process impurities.

Production technology was developed in parallel with process technology in a highly interactive manner. Methods of window fabrication, assembly, testing, and quality control were established and will be discussed. Production technology development improved yields by over three orders of magnitude from program beginning to current production levels.

X-Ray Lithography Mask Membranes

One critical missing link in bringing x-ray lithography processes into commercial use is the development of a suitable membrane for mask fabrication. Materials used to date include silicon, boron nitride, and others. Diamond's high modulus, stability under radiation, thermal conductivity, and x-ray transparency suggest its utility as an x-ray lithography membrane material, but significant technical uncertainties remain.

One of the most important of these, the requirement that a diamond membrane be under residual tensile stress, was predicted to be difficult

to achieve. Simple modeling of residual stress states of diamond films deposited on non-diamond materials predicted residual compressive stress states due to diamond's low thermal expansion coefficient compared with most other materials. Experimental investigations initially supported these predictions. However, process parameters have been recently identified in which diamond films deposited at high temperatures on silicon substrates are found to be in residual tensile stress of ~1X 10^8 dynes/cm^2 after chemical removal of the silicon substrate. These films are flat and appear to be suitable for subsequent metallization form mask use.

While an understanding of the mechanisms underlying this effect is not yet in hand, the research questions which must be posed and answered are fairly clear. These will be discussed, along with data from experiments completed as of the conference date.

CVD Diamond Electronic Packaging Applications

CVD diamond's demonstrated high thermal conductivity (>15 W/cm/°C), coupled with its high electrical resistivity (>10^{14} Ω-cm), indicate its advantageous use in electronic packaging applications, particularly those involving high power density devices. Process development issues for these applications include tradeoffs between deposition parameters which yield high growth rate and those which provide best thermal conductivity, surface roughness, expansion coefficient mismatch, dielectric constant and loss factor, and other material properties. Product development challenges include material deposition cost reduction, selection of fabrication and handling means, and development of adequate testing methods. Specific data from electronic packaging products now in development will be presented.

Diamond Film Friction and Wear Coatings

Many potential applications for CVD diamond films lie in applying the material to cutting tools, bearings, and other components whose performance is largely determined by resistance to wear. Enough is now known about the friction and wear behavior of CVD diamond to validate belief in the utility of this material in selected applications. Data will be presented which show dynamic friction coefficient variations in CVD diamond films as functions of surface morphology, sp^3/sp^2 Raman ratio, and opposing material composition (i.e., sapphire vs diamond film and single-crystal diamond vs diamond film). Two applications research efforts will be described, one aimed at applying CVD diamond film to carbide tools used for machining a specific aluminum alloy, and another undertaken to apply diamond coatings to selected turbine engine parts.

POSTERS

CHARACTERIZATION OF DIAMOND-LIKE FILMS PREPARED BY LASER ABLATION OF GRAPHITE

E.B.D. Bourdon, W. W.Duley, A. P. Jones, and R. H. Prince
Department of Physics, York University
Toronto, Canada M3J 1P3

Films have been produced by graphite ablation using 20 mJ/pulse, 308 nm excimer radiation. Diamond-like films were produced by controlling the background gas mixture. Background gas mixtures consisted of pure helium (amorphous C films, a-C), variable ratios of helium to hydrogen, and pure hydrogen (hydrogenated amorphous C films, a-C:H). Typical background pressures of 5, 20, and 100 Torr were used. This method offers the capability of independently and continuously controlling the total deposition pressure as well as the helium/hydrogen partial pressures. This in turn, allows film properties to be varied according to the chemistry between hydrogen and carbon vapor as well as the translational cooling of the gaseous species. Localized heating of the graphite sample allowed a relatively low temperature vapor deposition environment. This decreases contamination during film formation and is appropriate for a wide range of substrates. Typical deposition rates were about 2 nm/s.

Film characterization techniques included VUV-VIS, FTIR, and SEM. VUV-VIS measurements gave optical band gaps ranging from 0.5 eV for a-C to 1.5 eV for a-C:H produced at 5 and 20 Torr total pressures. Films formed at 100 Torr showed a band gap as large as 3 eV. The films with large band gaps also exhibited photo-induced luminescence and photo-darkening effects. SEM revealed a rough surface as a clustering of globular material, in contrast to the smooth surfaces of vacuum-deposited films.

Films were also deposited on gold-plated quartz crystals in a quartz crystal microbalance. In situ deposition rates and film etching rates for atomic oxygen were determined. A neutral atomic oxygen beam was produced in a microwave plasma of oxygen in helium ("Surfatron" source) and subsequent supersonic expansion. Fluxes of $10^{15}/cm^2$-s with 2.5 eV kinetic energy were typically used. Reaction probability ranged from about 0.2 for a-C and to 0.4 for a-C:H.

IN SITU PLASMA AND SURFACE DIAGNOSTICS OF C:H DEPOSITION FROM ECR PLASMAS

A. Koch, W. Möller, R. Wilhelm
Max-Planck-Institut für Plasmaphysik
Boltzmannstrasse 2, D-8046 Garching bei Munchen, FRG

During the deposition of polymer-like C:H films from electron cyclotron resonance (ECR) heated plasmas, both film surface and bulk plasma are monitored with optical diagnostic techniques.

Two reactors having different dimensions and magnetic field configurations were used. One reactor is a H_{10} mode waveguide with magnetic field coils coaxially arranged to satisfy the resonance condition (B = 87.5 mT). The interior of the waveguide is coated by moving the magnetic coils along the waveguide axis. The other plasma chamber has a cylindrical shape with a diameter of approximately 26 cm. Here, the magnetic field configuration may be varied to adjust the position of the plasma and the particle fluxes.

Detailed investigations of the mechanisms of C:H film deposition require non-intrusive on-line diagnostics. Film thicknesses and refractive indices are monitored by a two-beam laser interferometer. In the case of the waveguide reactor, deposition rates of about 1.6 nm/s are found.

Optical emission spectroscopy and laser-induced fluorescence serve as species-selective plasma probes. Furthermore, process modeling is supported by line integral measurements of the electron density using microwave interferometry.

CHARACTERIZATION OF VARIOUS ION-CLUSTER SOURCES AND THEIR APPLICATION IN THE HYDROCARBON-FILM DEPOSITION

Hans-Gerd Busmann, Harald Gaber, Thomas Müller, Georg Ulmer
and Ingolf Volker Hertel
Fakultat für Physik and F.M.F.
Albert-Ludwigs-Universitat
D-7800 Freiburg, F.R.G.

Various methods for the production of pulsed ionic cluster-beams (ICB) of hydrocarbons will be discussed. Energy distributions and mass spectra of the clusters will be shown and analyzed. Deposition experiments with beams of different mass distribution and different energy will be presented and their properties will be related to the impinging beam.

The various ion cluster beam sources are: (1) a pulsed valve with ionization of the blast by an electron-beam directed directly into the high pressure region of the expansion zone; (2) a hollow cathode discharge device driven in two different modes: (a) the anode-cathode voltage is below the ignition voltage and the expanding blast is ignited by an extra electrode; and (b) the blast expands into a cw-discharge; (3) a pulsed high current arc between two face-to-face graphite electrodes in a blast of carrier gas; and (4) excimer photo-ablation of polyimide (Kapton^{tm}) and graphite. All designs, except the photo-ablation, have been driven by a pulsed valve with methane, ethylene and acetylene at pressures up to 8 bar.

The following remarks on our first deposition experiments can be made: Device(1) yields clusters with up to 100 carbon atoms and allows the cluster size to be varied by simple e-beam manipulation. However, the ion current obtained from this source is too low to obtain practical growth rates. The other devices give much higher ion currents and films up to 1 μm have been grown within 1 h. It should be noted, that due to the medium-sized vacuum pumping system, a maximum rate of 10 pulses per second is the limiting factor for the growing rates obtained.

INITIAL GROWTH OF a-C:H FILMS

V. v. Bonin and K. G. Tschersich
IGV der KFA Jülich, Postfach 1913
D-5170 Jülich, FRG

The fraction of carbon atoms being deposited in growing a-C:H films during deposition from hydrocarbon sources is known to be well below unity. Therefore model experiments have been carried out in order to quantify the different particle fluxes during the beginning of a-C:H film growth. Films of a-C:H are deposited in a combined SIMS/SNMS apparatus onto silicon (direct ion beam deposition) by a low-energy (0.9 - 2.5 keV) benzene ion beam. Neutral particles sputtered by the ion beam are ionized by an electron beam and mass-analyzed (SNMS) so that fluxes emitted back from the sample can be quantified. While the sputtering yield of the substrate is proportional to its concentration at the surface, the sputtering yield of carbon shows a more complicated behavior. By varying parameters such as energy and angle of incidence of the primary ion beam and the temperature of the substrate, different stages of a-C:H film growth can be identified. The results help to gain an understanding of the processes involved during the deposition. Different aspects of a-C:H film growth can be quantified in terms of a simple model.

FROM AMORPHOUS CARBON TO AMORPHOUS DIAMOND-LIKE CARBON

B. André, L. Lombard, and J-Ph. Nabot
CEA-CEREM-DEM-SGS
CENG 85X, 38041 Grenoble, Cedex, France

Unhydrogenated amorphous carbon films were deposited by DC magnetron, ion beam-assisted magnetron (IBAM) and dual ion beam system (DIBS) on glass, steel and silicon substrates.

Although these techniques are well known, their complementary use in this study allowed us to select the main working parameters that have a strong influence on film properties: pressure and ion beam characteristics. They were varied in order to define more carefully the limits of the domain for producing diamond-like carbon films.

Various materials were obtained: ranging from soft columnar but unstressed coatings to hard and dense diamond-like carbon.

Reducing the pressure from 1 to 10^{-2} Pa increased the hardness from 4 and 20 GPa, but reduced the greatest adherent thickness on steel from 1 to 0.2 μm.

Ion beam bombardment of the growing films was performed under various conditions to favor the diamond-like character.

Rutherford-backscattering measurements showed a linear increase of the density (from 1.6 to 2.7 g/cm^3) with the ion current, while an optimum was pointed out, both with the energy of the ion beam and the atomic mass of the bombarding inert gas. This behavior seemed to be related to the efficiency of the cascade collision with regard to the vacancy creation.

The ion beam-produced modifications to optical properties (slight increase of real and absorption indexes in the 400-700 nm range), hardness (leveling off at 40 GPa for optimized conditions), and contaminant concentrations.

The hydrogen content as determined from the ERDA spectra varied from 1 at. % for 3 x 10^{-4} Pa residual pressure to 0.5 at. % for 6.4 x 10^{-5} Pa.

This work showed the ability to prepare diamond-like coatings by low pressure sputtering, although they were of a lesser quality than ion beam-assisted deposited films. Nevertheless, for some applications (e.g. mechanical) requiring high deposition rate as well as thick adherent films, this process could offer technically convenient and economic preparation conditions.

PREPARATION AND CHARACTERIZATION OF DOPED a-C:H FILMS

K. Rohwer, P. Hammer, A. Helmbold, D. Bahnemann, and D. Meissner
Institut für Solarenergieforschung (ISFH)
Sokelantstrasse 5, D-3000 Hannover, FRG

A rf plasma-enhanced chemical vapor deposition apparatus for the preparation of amorphous hydrogenated carbon thin films will be described. It allows the production of layers with a wide range of properties which can be influenced by the monomers used, process pressure, electrode distance, flow rate, self-bias voltage, and different doping agents and concentrations. Doping with metals is done either by sputtering from a corresponding cathode, or by adding metal-organic compounds via the gas phase during film growth. On the other hand, "classical" doping of the films can be achieved using phosphane, diborane, or arsane. Thus the electrical conductivity can be varied over several orders of magnitude.

During deposition, plasma-diagnostic techniques can be applied, i.e. electrical probes, optical emission spectroscopy, and glow discharge mass spectrometry. In order to investigate the processes at the surface of the growing film, samples are taken through an aperture in the substrate-carrying electrode.

The films are characterized over a wide range of temperatures by conductivity and Hall effect measurements, UV/VIS, FTIR, and luminescence spectroscopy. Additionally, samples are investigated by scanning tunneling microscopy and electrochemical methods. The main aim of this study is to understand the charge transport mechanisms in the bulk and at interfaces with metals and electrolytes, and between hydrocarbon layers with different types of doping.

Material properties are investigated and optimized with respect to applications such as solar cell materials, protective coatings for solar cells, or selective layers for solar absorbers.

CHARACTERIZATION OF COMPOSITION, ELECTRONIC, AND MECHANICAL PROPERTIES OF DLF OBTAINED BY ION IMPLANTATION (AND COMPARISON TO ION BEAM DEPOSITION, PVD FILMS)

J. C. Pivin
C.S.N.S.M. Bat 108 Campus d'Orsay
91405 Orsay, France

Diamond-like films were grown by C+ ion beam implantation at very low energies (0.100 to 2 keV) on various substrates (Si, SiC, metals) and their properties were compared to those of films prepared either by double sputtering of a C target and of the substrate, or vapor deposition, or laser ablation. First, composition and depth profiles of C, O, H, and of substrate elements in the film and at the interface were quantitatively characterized by Rutherford (and non-Rutherford) backscattering spectrometry, nuclear reactions and secondary ion mass spectrometry. Then the nature of chemical bonds and the structure of outer electronic layers were investigated by electron-induced x-ray emission, UV and x-ray induced photoemission, spectroscopic ellipsometry in the IR to UV range and Raman spectroscopy. Finally, the hardness and elastic modulus were measured by nanometric indentation tests, and friction was studied as a function of loading conditions and atmosphere. The films grown by ion implantation exhibited only a partial diamond character, depending on the energy, but were more pure, homogeneous and also more adherent to substrates than the others.

RADIO FREQUENCY PLASMA DEPOSITION OF a-C:H FILMS: PLASMA DIAGNOSTIC AND MATERIAL PROPERTIES

V. Barbarossa, O. Martini, S. Mercuri, and F. Galuzzi
Eniricerche SPA
00015 Monterotondo, Rome, Italy

The low-temperature deposition of amorphous carbon films from hydrocarbon plasma has been the subject of several works but the relationship between plasma processes, film growth, and material properties is still not completely understood. As a contribution to this topic, we present an investigation on a-C:H films grown by CH_4/H_2 plasma, aiming to correlate plasma features and carbon deposit properties. The glow discharge reactor is a stainless steel vacuum chamber containing a small area RF powered plate, surrounded by a large area grounded electrode. The electrode asymmetry ratio is about 0.09 and the maximum self-bias voltage at the powered electrode is about -500 V. The RF plasma of CH_4/H_2 mixtures is characterized by double electrical probes and optical emission spectroscopy. In particular, electron mean energy, electron density, plasma potential, distribution of H atoms and CH species are evaluated as functions of RF power, total pressure and gas feed composition. These experimental data are compared with the numerical results of a comprehensive kinetic model, taking into account electron-impact, ion-molecule, neutral-neutral reactions and impact-induced fragmentation of high-mass species. Both cathodic and anodic carbon films are characterized by vibrational IR and Raman spectroscopy. In particular, IR spectra between 2500 and 3000 cm^{-1} allow an evaluation of carbon-bonded hydrogen atoms, while Raman line shapes between 1000 and 1600 cm^{-1} give information on diamond-like and graphite-like structures.

The characterization of the deposited films is completed by optical gap measurements in the visible region and by hardness and adhesion tests on different substrates.

CONDUCTIVITY IN AMORPHOUS HYDROGENATED CARBON FILMS

A. Tagliaferro and D.Das Gupta
Dipartimento di Fisica
Politecnico di Torino
Corso Duca degli Abruzzi, 24
10129 Torino, Italy

The data ($\ln\sigma$ vs $1/T$) obtained from conductivity measurements carried out on amorphous hydrogenated carbon films in the temperature range 300-550 K show two thermally activated conduction regimes. Near room temperature the conductivity is commonly attributed to variable range hopping, while at higher temperatures it is attributed to hopping in band tails.

The observed large change (several orders of magnitude) in the pre-exponential factor as a function of deposition temperature, T_d, indicates a correspondingly large change in the factor $[N(Ef)/\alpha)^{1/2}]$. This is inconsistent with the constancy of the $\ln\sigma$ vs $(1/T)^{1/4}$ slope near room temperature which hinders the constancy of $N(Ef)*\alpha^3$.

Since a-C:H is composed of sp^2-bonded islands in an sp^3 matrix, we propose a model involving tunneling between neighboring islands with an activation energy independent of island size to explain the conductivity near room temperature. It is found that tripling of the separation distance between the islands is sufficient to explain a change of seven orders of magnitude in the conductivity prefactor. The energy level corresponding to the observed activation energy of 0.2 and 0.3 eV is presumably due to seven-fold rings in the islands.

The conductivity at higher temperatures is consistent with a decrease in E_a with T_d, and the activation energy is thought to arise from six-fold rings.

NEUTRON AND X-RAY SCATTERING STUDY OF a-C:H

P.J.R. Honeybone, R. J. Newport, J. Franks
Ion Tech Ltd.
2 Park Street, Teddington, TW11 OLT, UK

W. S. Howells
Rutherford Appleton Laboratory
Didcot, Oxon, OX11 OQX, UK
and
R. J. Cernik
Daresbury Laboratory
Warrington, WA4 4AD, UK

The intriguing mechanical attributes of amorphous hydrogenated carbon are assumed to derive from a large number of tetrahedral, "diamond-like" bonds in the intrinsic material; this would suggest structural similarities with a-Si:H. Data from NMR, IR, and other studies indicate however that the proportion of sp^2(graphitic-π) bonds may still be as high as approximately 40%. While the short-range order in a-C:H is of crucial importance in explaining its mechanical properties, it is suggested that the order at intermediate distances is likely to account more fully for the electronic and optical properties. The role of hydrogen would appear to be significant in promoting sp^3 bonding - but no direct structural study of H sites has been made. The central objective of our experimental program, the results of which we present here, is the elucidation of the structure-property relationship using neutron and x-ray scattering techniques. Diffraction methods are of obvious importance given the likely importance of intermediate-range order as well as short-range order: the results of neutron diffraction measurements carried out at the ISIS pulsed neutron source, and of x-ray experiments using a diffractometer at the synchrotron x-ray source, SRS (both in the United Kingdom) are presented and discussed. The x-ray diffraction studies were carried out in conventional $\theta,2\theta$ "powder" geometry and using a novel technique for as-deposited films in which the angle of incidence is fixed at, or near, the critical angle. Complementary data gained from incoherent inelastic neutron spectroscopy is also presented.

THE EFFECT OF DEPOSITION BIAS ON THE TRIBOLOGICAL PROPERTIES OF HEAT TREATED DLC

A.Grill, B. Meyerson, and V. Patel
IBM Research Division
T. J. Watson Research Center
Yorktown Heights, NY 10598 USA

Diamond-like carbon (DLC) films have been prepared by the rf plasma decomposition of acetylene. The deposition was performed at substrate temperatures up to 250°C, with the substrate at negative bias between 80 and 200 V DC. The DLC films have been heat treated in vacuum at temperatures up to 600°C and their properties characterized by a variety of methods. The wear resistance of the thin DLC films has been characterized by a specially designed tribotester.

The paper will present the effect of the deposition temperature and bias on the thermal stability of the DLC films and their resistance to sliding wear, which was found to be strongly affected by the deposition bias.

ION ENERGY DISTRIBUTION AT THE SUBSTRATE IN AN ECR REACTOR

P. Reinke, W. Jacob, and W. Möller
Max-Planck-Institut für Plasmaphysik
Boltzmannstrasse 2, D-8046 Garching bei Munchen, FRG

The impact energy of particles (especially ions originating in the plasma) on the substrate surface is known to have a decisive effect on the microstructure and the macroscopic properties of C:H films. Electron cyclotron resonance (ECR) was chosen because of the high degree of ionization of the plasma and thus high achievable growth rates of deposited films. A magnetic field is used to satisfy the ECR condition (87.5 mT at 2.45 GHz microwave frequency) and for confinement of the plasma. Three sets of moveable coils surrounding the reactor enable us to vary the magnetic field configuration as well as to shift the resonance zone with respect to the substrate.

An acceleration of ions in an inhomogeneous magnetic field may be achieved by the electrostatic drag exerted by the electron drift. For ion energy analysis a retarding field analyzer is used which can be rotated through the two spherical angles. A Langmuir probe for determination of plasma parameters and a quadrupole mass spectrometer for residual gas analysis are also installed.

First measurements with argon as a sample gas were performed. Increasing the gas pressure causes a shift of the mean ion energy to lower values, but no significant broadening of the ion energy distribution (IED). Increasing the magnetic field divergence leads to a shift of the mean energy to lower energies. This can also be observed when the field becomes nearly homogeneous. Investigations of the influence of other parameters like gas flow or substrate bias on the IED and the properties of C:H films deposited from methane will be discussed.

HYDROGEN DISSOCIATION AT HOT FILAMENTS: DETERMINATION OF ABSOLUTE ATOMIC HYDROGEN CONCENTRATIONS

L. Schäfer, U Bringmann, C.-P. Klages
Philips GmbH Forschungslaboratorium Hamburg
Vogt-Kölln-Strasse 30, D-2000 Hamburg, FRG
and
U. Meier, K. Kohse-Höinghaus
DLR-Institut für Physikalische Chemie der Verbrennung
Pfaffenwaldring 38-40, D-7000 Stuttgart, FRG

Absolute values for the concentration of atomic hydrogen were measured by two-photon laser-induced fluorescence (LIF) at distances between 0.4 to 28 mm from the surfaces of heated metal wires. The spatial resolution of the measurements is determined by the spot size of the exciting laser beam, which is about 1 mm in diameter. The detected fluorescence signals were calibrated by comparison with a known H atom concentration prepared in a microwave discharge flow reactor, taking into account the different temperatures in the two systems.

Using tantalum filaments, atomic hydrogen concentrations were obtained for pressures ranging from 1.5 to 50 mbar, temperatures between 2400 and 2600 K and wire diameters from 0.3 to 2 mm. The influence of addition of various amounts of methane on the concentrations was examined. Beside the experiments with tantalum filaments, measurements were performed with tungsten and iridium.

The experimentally determined concentrations of atomic hydrogen are considerably smaller than expected for thermodynamic equilibrium. These results indicate a kinetic control of the hydrogen dissociation under the experimental conditions used. The consequences of the experimental data for filament-assisted CVD of diamond are discussed.

A NEW PROBE FOR IN SITU CHARACTERIZATION OF DIAMOND SURFACES DURING LOW PRESSURE CHEMICAL VAPOR DEPOSITION*

Howard K. Schmidt
Schmidt Instruments, Inc.
2476 Bolsover, Suite 234
Houston, TX 77005 USA

Single crystal diamond has extremely high thermal conductivity, a large bandgap, high carrier mobilities, and low neutron and ionizing radiation dislocation cross sections. These physical properties make it an ideal material in which to fabricate electronic devices for high temperature, high frequency and/or high radiation service. Despite the significant body of work to date on low pressure chemical vapor deposition (LPCVD) diamond, no methods now exist for manufacturing the large single crystal diamond substrates required to realize these potentials. It has recently become clear that the fundamental mechanisms of diamond's nucleation and growth must be determined before we can significantly improve its process technology. Prior research, focussing on the gas phase chemistry in diamond LPCVD systems, has provided some valuable clues to possible mechanisms. However, chemical transport through the boundary layer to the substrate is still rather mysterious, and any conclusions about the environment at the growing surface based upon gas phase data are speculative at best. Our contribution to the field is the first direct probe for diamond surface chemistry under LPCVD process conditions: in-situ direct recoil spectroscopy (DRS). In conjunction with the earlier gas phase results, this new tool will give us the first comprehensive description of diamond LPCVD, enabling relatively straight-forward determinations of both chemical mechanisms and improved process conditions for diamond growth.

DRS is a relatively new surface probe with sub-monolayer sensitivity. It utilizes a pulsed energetic ion beam to simultaneously detect and resolve light elements (H through F) and their isotopes rapidly and quantitatively by time-of-flight (TOF) analysis. Like the more common electron-based surface spectroscopies (e.g. XPS, AES, UPS, EELS), DRS has previously been used only under ultra high vacuum (UHV) conditions. Unlike electrons, however, energetic ions and atoms are not readily scattered or attenuated by gas molecules. Using the literature on gas phase ion scattering cross sections, we estimated that the 3-10 keV Na+ ion probes typically used in DRS would have a mean free path of at least 1 cm through 1 Torr of hydrogen, and subsequently proposed that in-situ analysis of growth surfaces under LPCVD conditions would be practical with DRS. The modest risk thus expected in extending DRS to operate in the LPCVD environment appeared small indeed in comparison to the potential value of the information it could produce. We have successfully obtained DRS spectra from diamond surfaces under actual growth conditions. This unique accomplishment is the first demonstration that the operating environment of a proven UHV surface technique can be extended into the Torr regime - a pressure some billion-fold higher than typically used in surface science.

*Supported by SDIO-IST contract N00014-89-C-0152, managed by the Office of Naval Research.

These new capabilities will be extended to determine specific step-wise reaction mechanisms for nucleation and growth of diamond in both homo- and hetero-epitaxial LPCVD systems. When the basic synthetic routes to diamond are established, we will draw upon the vast bodies of organic and surface chemical literature to develop new and improved deposition processes. Two goals of this effort are development of: (1) a controlled method of nucleating the first few layers of diamond on hetero-substrates, e.g. Ni(100), for subsequent growth into large single crystals for electronic device manufacture; and (2) a low temperature process for depositing diamond on heat sensitive materials for optical, tribological and thermal applications.

IN-SITU SURFACE ANALYSIS OF DIAMOND NUCLEATION AND GROWTH ON Si(100)

B. E. Williams, D. A. Asbury, B. R. Stoner, and J. T. Glass
Department of Materials Science and Engineering
North Carolina State University
Raleigh, NC 27695-7907

Microwave plasma chemical vapor deposition of diamond on Si(100) has been studied using x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The samples were transferred under vacuum from the growth chamber to a multi-technique surface analytical chamber. Prior to growth, XPS and AES showed a layer of SiO_2 and a small amount of carbon on the substrate surface. Films were subsequently deposited in an immersed plasma configuration. Growth times of between 15 min and 5 h were examined using a mixture of 1% CH_4 in H_2 at 25 Torr. The substrate temperature was maintained at approximately 800°C. After only 15 min exposure to the CH_4/H_2 plasma, a distinct SiC component was observed. Diamond is detectable after 30 min growth, and as the diamond growth continues, the SiC component decreases in proportion to the amount of diamond film coverage. The oxygen signal decreases steadily as the growth time increases, but only carbon (diamond) is detected once the film coverage is complete.

THERMAL WAVE AND RAMAN MEASUREMENT OF POLYCRYSTALLINE DIAMOND FILM QUALITY*

R. W. Pryor, L. Wei, P. K. Kuo, and R. L. Thomas
Institute for Manufacturing Research and Department of Physics
Wayne State University, Detroit, MI 48202 USA

The thermal wave technique and microfocus Raman spectroscopy are utilized to measure the relative quality of thin polycrystalline diamond films deposited on various substrates. The thermal wave technique uses two laser beams, one at normal and one at grazing (or slightly intersecting) incidence to the diamond film surface, to measure thermal diffusivity of the diamond films. The first laser beam is a modulated heating beam, normal to the diamond film surface, to initiate a thermal wave which propagates into the film, the substrate, and also into the overlying gas envelope. The resulting modulation of the overlying gas density is then interrogated by the second (probe) laser beam. The probe beam is deflected by the corresponding periodic changes in the gradient of the refractive index of the gas. The probe beam deflection versus offset position is measured and then fitted, using a theoretical solution of the three-dimensional thermal diffusion equation for the gas/film/substrate system.

Microfocus Raman spectroscopy is used to determine the relative peak heights of the narrow diamond peak (1331 cm^{-1}) and the broad "graphitic" peak (approx 1550 cm^{-1}). The "graphitic" peak height is adjusted for the difference in the Raman scattering factor in the "graphitic" material (approx 50) and an estimated percentage is derived. To estimate the overall quality of that polycrystalline film, the thermal diffusivity measured for each polycrystalline diamond film is combined with the estimated percentage of "graphitic" material, determined by Raman spectroscopy. For high quality polycrystalline diamond films, the "graphitic" percentage is estimated to be approximately 5% or less. We have measured a range of values for the thermal diffusivity of polycrystalline diamond films. When those diffusivities are converted to thermal conductivities, the conductivity values range from 12 W/cm-K, for high quality films, to that of graphite.

We have also made measurements on the thermal diffusivity of natural and synthetic type IIA diamonds, using the thermal wave technique, and have obtained thermal conductivities of 21.9 and 22.3 W/cm-K, respectively, in excellent agreement with measured values for natural diamonds found in the literature.

---

*Supported by the Institute for Manufacturing Research, Wayne State University, Ford Motor Company, and by the Army Research Office under contract No DAAL03-88-K-0089. The authors would like to thank Dr. T. R. Anthony of General Electric Research and Development Laboratory, Dr. R. S. Post of Astex, and Dr. R. Messier of Penn State University for supplying some of the samples used in this work.

EFFECT OF TEXTURING AND ION-IMPLANTATION OF Si AND SiC/Si BUFFER LAYER ON THE NUCLEATION OF DIAMOND FILMS FORMED BY MICROWAVE-CVD

Joseph Baglio, Barry Farnsworth, Sandra Hankin, and Marvin Tabasky
GTE Laboratories, Inc.
40 Sylvan Road
Waltham, MA 02254

The formation of appropriate nucleation sites is critical for the growth of diamond films on non-diamond substrates. The nucleation density of diamond films on polished silicon substrates is low. High nucleation density is usually achieved by abrading the silicon wafer with diamond, C-BN, TaC, and SiC powders. These abrasion techniques are, however, difficult to control and are not amenable to other processing sequences.

The objective of this study is to find, for microwave plasma-enhanced CVD, the conditions for obtaining a high density of diamond nucleation sites on silicon substrates.

Results will be presented on the nucleation of diamond on polished silicon and on silicon carbide/silicon buffer-layer substrates which have been modified by texturing and/or ion-implantation techniques. The samples were examined prior to and following diamond growth by Auger, x-ray, scanning-electron microscopic, and Raman spectroscopic techniques.

LOCAL HETEROEPITAXY DIAMOND ON (001) SILICON

David G.K. Jeng
Department of Electrical Engineering
State University of New York
Stony Brook, NY 11794 USA

The experiment of a proposed two-step process for growing hetero-epitaxy diamond has resulted in the formation of local heteroepitaxy diamond pyramids with sizes up to 150 x 120 μm^2 on silicon {001} by using the microwave plasma-assisted chemical vapor deposition (MPACVD) method. Clumps of small cubic nucleations in the same orientation with the nearby diamond pyramids were also observed. Both the large pyramids and the small cubic nucleations are characterized by being fully transparent, low reflective, and are 45° off the silicon {001} direction around z-axis. Characterizations were made by scanning electron microscopy (SEM), x-ray diffraction (XRD), and micro-Raman spectroscopy. The SEM micrographs show neighboring co-oriented pyramids each about 150 x 120 μm^2. The sharp micro-Raman spectrum with a single peak at 1332 cm^{-1} denotes the high quality of the diamond film which is very close to that of true diamond. Besides the SEM and the micro-Raman data, preferential growth of {001} diamond was confirmed by the XRD spectrum which shows an emerging {400} peak in contrast to the conventional polycrystalline diamond film.

PHYSICO-CHEMICAL STUDY OF SURFACE PRETREATMENT FOR DIAMOND NUCLEATION ENHANCEMENT

J. J. Dubray, C. G. Pantano
Ceramic Science and Engineering Department
The Pennsylvania State University
201 Steidle Building
University Park, PA 16802 USA
and
W.A. Yarbrough
Materials Research Laboratory
The Pennsylvania State University
University Park, PA 16801 USA

Achieving heteroepitaxy or selective growth of diamond films on various substrates begins by understanding the early stages of diamond nucleation. It is well known that the density of nucleation sites can vary by several orders of magnitude when the substrate is roughened by micron or submicron diamond particles[1,2] and that the crystals are aligned preferentially along the scratches.[3] We investigated several surface pretreatments for crystalline silicon, silicon carbide and amorphous silica substrates by means of AES, XPS, scanning Auger and scanning electron microscopies. We completed these experiments by comparing the effects of surface roughening with those surface indentations. We varied the load, the loading time, and the orientation of the Vickers diamond indenter with respect to the crystal orientation of the silicon and silicon carbide substrates.

Diamond particles were not detected by AES on Si (100) surfaces, though the C KLL lineshape changed with the type of surface treatment. In the case of light polishing, it turns to a graphite-like lineshape while the overall concentration of carbon diminishes. After heavy polishing, the surface color becomes a brownish hue and both C KLL and Si LVV lineshapes correspond to a silicon oxycarbide with a high concentration of oxygen and carbon. According to our first findings, the nucleation enhancement can therefore be attributed to the presence of either defects[4] that are not detected by conventional Auger analysis, or graphite, or a binary or ternary compound involving carbon, silicon, and oxygen that permits diamond nucleation. This latter assumption can be related to the presence of a silicon carbide layer in the early stages of diamond growth.[5] Experiments are now underway to confirm these assumptions.

---

1. W. A. Yarbrough and R. Messier, Science **247**, 688-695 (1990).
2. K. Hirabayashi, Y. Taniguchi, O. Takamatsu, T. Ikeda, K. Ikoma, N. Iwasaki-Kurihara, Appl. Phys. Lett. **53**, 1815 (1988).
3. A. M. Bonnot, Thin Solid Films **185**, 111-121 (1990).
4. A. Taloni and W. J. Rogers, Surface Science **19**, 371-379 (1970).
5. D. N. Belton, S. J. Harris, S. J. Schmieg, A. M. Weiner, and T. A. Perry, Appl. Phys. Lett. **54**, 416 (1989).

EMISSION SPECTROSCOPY OF THE MICROWAVE PLASMA USED FOR DIAMOND DEPOSITION; IMPORTANCE OF THE C_3 RADICAL

A. Campargue, M. Chenevier, and F. Stoeckel
Laboratoire de Spectrométrie Physique,
Université Joseph Fourier de Grenoble (UA 08), B.P. 87
38402 Saint-Martin-d'Heres, Cedex, France

B. Marcuse, M. Mermout, and F. Vinet
ENSEEG S2MC (UA143), B.P. 75, Domaine Universitaire
38402 Saint-Martin-d'Heres, Cedex, France

S. Ljungström
Department of Physics
Chalmers University of Technology
S-41296 Göteborg, Sweden

Diamond deposition on a silicon substrate has been obtained by the decomposition of a gas mixture of 1% methane in hydrogen dissociated by a microwave discharge. The typical experimental conditions were: pressure = 30 Torr, microwave power = 100 W, gas flow = 100 scc/min. The emission spectra of the plasma have been recorded using a monochromator with a resolution of about 0.1 nm. In addition to the Balmer series of atomic hydrogen and molecular hydrogen emission (mostly the $^3\Pi_u$ - $^3\Sigma^+_g$ transition near 600 nm) the CH transitions $A^2\Delta$-$X^2\Pi$ and $B^2\Sigma$-$X^2\Pi$ have been observed at 431 and 389 nm, respectively.

The C_3 radical emission $^1\Pi_u$-$^1\Sigma^+_g$ is also observed near 400 nm while the C_2 Swan system, frequently reported, is not present in our spectra. We have studied the variations in the plasma emission spectrum according to the methane molecular fraction and the total pressure. The CH radical emission increases continuously with the methane concentration and the pressure while the C_3 emission clearly shows a maximum between 0.5 and 1% volume of methane, i.e., a partial pressure of some tenths of a Torr. These conditions correspond to the "standard" conditions of diamond deposition and we conclude that the C_3 radical most probably is a key intermediate species in the mechanism of diamond deposition.

THE INFLUENCE OF GAS-PHASE COMPOSITION ON CARBON BONDING ENVIRONMENTS IN CVD DIAMOND FILMS INVESTIGATED VIA SOLID-STATE NMR

Karen Mary McNamara
Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139 USA
and
Mike W. Geis
Lincoln Laboratories
Massachusetts Institute of Technology
Lexington, MA 02173 USA

Chemical vapor deposition diamond films have been studied by solid-state nuclear magnetic resonance (NMR) spectroscopy to provide a quantitative and nondestructive means of determining the sp^2/sp^3 carbon ratio. Films with a natural abundance of ^{13}C and also isotopically enriched films have been investigated. Films with higher ^{13}C concentrations were deposited from acetone, isotopically enriched at either the methyl or the carbonyl carbon. The degree of enrichment was determined from the broadening of the ^{13}C NMR static lineshape associated with increased homonuclear dipolar interactions and compared to values calculated from Raman shifts. Magic-angle spinning was also employed to reduce homonuclear dipolar broadening, as well as broadening due to chemical shift anisotropy, and aided in the resolution of sp^2 versus sp^3 in enriched diamond films. The isotopically enriched films were grown in a hot-filament reactor, and the concentration of carbon in the reactant stream was varied to produce a series of films with widely varying sp^2/sp^3 ratios. Monitoring the transition from sp^3 to sp^2 bonding provided insight into the chemistry of diamond formation. The degree to which carbon is preferentially incorporated into sp^2 and sp^3 bonding environments from the methyl and carbonyl acetone sites was also explored.

A MODEL STUDY OF THE COVERAGE OF A DIAMOND (111) SURFACE IN AN H_2/CH_4 PLASMA

Steven M. Valone
Materials Science and Technology Division
Los Alamos National Laboratory
Los Alamos, NM 87545 USA

A model of plasma CVD diamond deposition primarily examines atomic level issues using semi-empirical molecular orbital calculations for the enthalpy of formation of various diamond-like clusters. Semi-empirical methods have been found to be quite useful for the study of hydrocarbon and related oxygenated systems.

The intent of this work is to examine proposed mechanisms for the nucleation and growth of diamond films by plasma CVD. There are two main schools of thought on the growth mechanism. One is that methyl groups displace a hydrogen overlayer on the surface and then these methyl groups are attached to one another by a cation-catalyzed mechanism which contains the rate limiting step. The other school is that, at least at higher temperatures, above 800°C, attack of hydrogen atoms from the plasma creates defects in the hydrogen overlayer. Acetylene addition then advances the film growth. In this scenario, growth is assumed to occur on a stepped surface.

The present study attempts to appraise the assumptions behind these mechanisms. An appraisal is possible from the answer to four questions.

(1) Can plasma-phase methyl groups spontaneously displace surface H atoms?
(2) Which species, CH_3 or C_2H groups, requires lesser energy to displace surface H atoms?
(3) What is the overlayer concentration of H atoms on a diamond (111) surface in a plasma environment containing H atoms?
(4) What is the relative efficiency of etching by various radicals likely to be found in commonly used plasmas?

Both CH_3 groups and C_2H groups require substantial energy to reach high coverages. At low coverages, it is easier to increase the CH_3 concentration, while at higher coverages, increases in C_2H concentration becomes more facile, due to smaller steric interferences.

According to the present calculations, H atoms from the plasma phase will always etch surface H, regardless of concentration of surface H. On the other hand, in a thermal system, formation of the H overlayer is always favored. In real plasma system, there will be some steady-state value of [H] depending on the ratio of $[H]/[H_2]$ in the plasma. In energetic terms, abstracting surface H is most facile for C_2H and least facile for CH_3 and C_2H_5.

MECHANISMS OF LOW PRESSURE DIAMOND FILM GROWTH: DEPOSITION MEASUREMENTS FROM SEPARATED ATOMIC HYDROGEN AND CH_4 SOURCES

Pierre Joeris and Carsten Benndorf
Department of Physical Chemistry
University of Hamburg, Bundesstrasse 45
D-2000 Hamburg 13, FRG

Diamond deposition techniques from low pressure hydrogen/hydrocarbon microwave plasma on different substrates are well established. Recently, we reported on the development of a small inexpensive laboratory deposition system using a tunable microwave cavity resonator powered with a commercial magnetron (2.45 GHz, 750 W). In the center of this reactor, diamond films were produced on Si and Mo substrates (700-1000°C) from a H_2 (99.5%)-/CH_4 (0.5%) plasma. This deposition system was changed for the present investigation into a flow reactor, allowing a separate feeding of H_2 and CH_4. With this modification, atomic hydrogen is initially the only reactive species. In the flow reactor $\cdot CH_3$ (and other radicals) are formed outside the microwave discharge. The $\cdot H/\cdot CH_3$ ratio at the surface of the externally heated substrate depends on the distance from the source entrances (and other parameters as well). These investigations contribute to the understanding of the mechanisms of low pressure diamond synthesis and the identification of the reactive hydrocarbon species.

INVESTIGATION OF GROWTH MECHANISMS OF DIAMOND THIN FILMS

A. M. Bonnot,* E. Caignol, E. Gheerarert, J. Mercier, T. Lopez-Rios, and R. Centi
Laboratoire d'Etudes des Propriétés Electroniques des Solides
LEPES-CNRS, B.P. 166X 38042 Grenoble, Cedex, France

*Université Aix Marseille II, Faculté des Sciences de Luminy
case 901, 13288 Marseille, Cedex, France

Diamond thin films have been synthesized by a hot-filament-assisted chemical vapor deposition technique. Dependence of the film properties on experimental conditions during deposition has been studied by scanning electron microscopy, Raman microspectroscopy, Auger electron spectroscopy, reflection high energy electron losses spectroscopy and differential reflectivity measurements. Correlation between the film morphology and Raman results has been interpreted in terms of tensile stress in the film and of microcrystallization of diamond. Optical and electron spectroscopy measurements has given insight into the nucleation and growth processes of low pressure diamond.

TEM, SEM, AND XRD INVESTIGATION OF THE NUCLEATION AND GROWTH OF DIAMOND FILMS SYNTHESIZED BY A FLAME CVD PROCESS

P. S. Nielsen, P. Balslev
NKT A/S, Corporate R&D
Sognevej 13, DK 2605 Broendby, Denmark
and
P. J. Hansen and K. Madson
Laboratory of Applied Physics
The Technical University of Denmark
Building 307, DK-2800 Lyngby, Denmark

Diamond films have been grown on a Si (111) substrate by means of an oxygen-acetylene flame. The substrate has been pretreated with 1 μm diamond particles in order to enhance the nucleation density.[1] In a number of experiments only the time of deposition has been gradually increased. The diamond films were investigated in detail by a number of techniques.

The investigations show wide variations in the morphology of the synthesized films from the center to the edge of the deposition zone. The variations are due to the non-uniform plasma chemistry and to the deposition temperature in the oxygen-acetylene flame. An interface layer has been observed between the substrate and the film. The effect of this layer on the nucleation of diamond will be discussed.

---

[1]K. Hirabayashi and Y. Taniguchi, Appl. Phys. Lett. 53, 1805 (1988).

RADIO FREQUENCY PLASMA ASSISTED CHEMICAL VAPOR DEPOSITION OF POLYCRYSTALLINE DIAMOND FILMS*

R. O. Dillon, T. B. Kustka, D. E. Meyer
Department of Electrical Engineering, 209N WSEC
University of Nebraska, Lincoln,NE 68588-0511 USA
and
T. Furtak
Department of Physics, Colorado School of Mines
Golden, CO 80401-1887

Radio frequency (RF) plasma-assisted chemical vapor deposition (RFPACVD) has been used to produce thin polycrystalline films of diamond. The inductively coupled rf plasma method offers potential advantages over other methods of deposition in terms of scale-up and cost. The relatively few papers appearing in the literature describing this method for diamond deposition indicates that there are only a few groups investigating this approach.

Plasmas were generated using a 13.56 MHz RF generator capable of producing 3 KW of output power. The RF power was inductively coupled to a tubular deposition chamber in a horizontal configuration. The system included automatic matching and power level components. Gases were introduced into the system through mass flow controllers. Deposition parameters were typically 850 to 950 W input power, 20 Torr deposition pressure, and 2.5% CO in H_2 at a total flow rate of 100 sccm. Additionally, films were deposited with trimethylboron added to the CO/H_2 mixture to introduce boron into the growing diamond films.

Polycrystalline films were typically deposited on high purity quartz substrates. The surfaces of these substrates were polished, rough cut, or modified by the application of a diamond paste. Polycrystalline films were also deposited on steel alloy tool bits using isobutane as a carbon source. The films were characterized using optical and electron microscopies, Raman spectroscopy, and electrical resistance.

---

*Research supported by the Center for Microelectronic and Optoelectronic Materials Research at the University of Nebraska and by the U.S. Air Force Ballistic Systems Division under contract No. F04704-89-C-0059.

LOW PRESSURE AND LOW TEMPERATURE GROWTH OF WIDE AREA DIAMOND FILMS USING MAGNETO-PLASMA CVD

Akio Hiraki
Faculty of Engineering
Osaka University
Suita, Osaka 565, Japan

Chemical vapor deposition (CVD) is a main technique used to fabricate diamond films. Usually the technique uses a high-pressure plasma formed above 20-30 Torr. This plasma produces diamond at a reasonably high rate. However, control of the plasma at that high pressure is limited to a small area. Moreover, compared with a low-pressure plasma, the properties of the plasma itself has not been clarified because of too many collisions in the plasma -- this fact prevents the study of the plasma for the growth mechanism of diamond.

In order to attain a breakthrough from this conventional high-pressure CVD, we have applied a magneto-active plasma at a much lower pressure (down to 10^{-2}) for the deposition of diamond. The important point of the system is to set the electron cyclotron resonance (ECR) condition (875 G in the case of a 2.45 GH_z microwave) at the deposition area. Then the high density plasma (above $1 \times 10^{11}/cm^3$) necessary for diamond formation has been obtained through the enhancement of microwave absorption by employing a higher magnetic field than the ECR condition, i.e., the so-called off-resonance mode. The plasma is quite uniform at the discharge area (160 mm in diameter) and uniform diamond films with high quality have been obtained. In addition, it has been found that our low pressure CVD decreases the formation temperature down to 500°C.

The activities for the application of our diamond films, especially its prospects for semiconductor and optical (electroluminescent) devices will be explained.

PREPARATION OF DIAMOND FILMS FOR ABRASION RESISTANCE USING THERMAL PLASMAS

F. J. Worzala and C. W. Florey
Department of Materials Science and Engineering
University of Wisconsin
Madison, WI 53706 USA

The use of natural and synthetic diamond for cutting tool inserts and other abrasive applications is growing significantly. The combination of high hardness, good corrosion, and wear resistance and high thermal conductivity make diamond the ultimate material for such applications. The possibility of coating tool inserts with diamond could open up vast commercial markets, if a relatively inexpensive process can be developed.

A variety of methods are currently being used to apply diamond coatings. However, most have limitations which preclude the attainment of useful inexpensive coatings. The need for extensive vacuum systems and the slow growth rates achieved are specific limitations of note. We have developed a technique wherein rapid growth rates can be achieved in air, using a commercially available DC plasma touch. By judicious selection of plasma reaction gases and the use of a reaction retort we have achieved growth rates in the range of 500 μm/h. The experimental details of the process and the characteristics of the diamond coatings obtained will be presented.

DIAMOND CRYSTAL GROWTH BY HOT FILAMENT CVD AND ITS CHARACTERIZATION

P. Ascarelli, S. Fontana (Eniricerche Fellowship)
Consiglio Nazionale delle Ricerche
Istituto Metodologie Avanzate Inorganiche
Casella Postale 10, 00016 Monterotondo Scalo, Roma, Italy

E. Molinari, R. Polini, M. L. Terranova
II Universita degli Studi di Roma, "Tor Vergata,"
Dipartimento di Scienze c-Tecnologie Chimiche
via O. Raimondo, 00173 Roma, Italy
and
E. Cappelli
Eniricerche
Gruppo di Scienza delle Superfici
via Ramarini, 00016 Monterotondo, Roma, Italy

It has recently been demonstrated that thin diamond films can be deposited at low pressure and temperature (100 torr, 950°C) in a phase space region where graphite is the stable carbon phase.

The unique combination of physical, optical, thermal and electric properties has made this research area very attractive with an expectation for a wide range of applications from hard protective films to optical and semiconductor devices.

Many chemical and physical vapor deposition techniques have allowed the deposition of diamond films and diamond-like coatings, yet the basic understanding and control of the film nucleation and growth is still in its infancy.

As these topics are fundamental to the subsequent tailoring of diamond films for specific applications, we arranged an experimental system to this aim.

We set up a hot filament CVD apparatus with the idea that this method is more easily amenable to elucidate the molecular mechanism of the diamond deposition and growth processes. This comes from the observation that the hot filament temperature (2100°C) and gas molecular interaction on its surface are such to generate molecular science and excitation but negligible ionization. Thus, the plasma generated by the hot filament activation of a gas mixture (99% H_2, 1% CH_4) near the diamond growth surface, should be of simpler composition than plasmas activated by other CVD techniques. where large quantities of ionized species are present.

Our equipment is a typical HFCVD; but the basic apparatus contains two in situ diagnostic tools: a laser interferometer for film thickness evaluation and a mass spectrometer for the detection of gaseous species, near the diamond growth surface.

Thin diamond films have been deposited on silicon (111) substrates previously activated by scratching with diamond paste of 0.25 to 1 microns, in agreement with previous published works.

Rapid growth of diamond crystals is observed on scratched samples as opposed to the unscratched ones in various atmospheres.

Raman spectroscopy, electron microscopy, and surface techniques (XPS, EELS) have been used to characterize samples.

SOME PROPERTIES OF CVD-DIAMOND SEMICONDUCTING STRUCTURES

A.E. Alexenko and B. V. Spitsyn
Institute of Physical Chemistry
USSR Academy of Sciences
Leninsky Prospekt 31
Moscow 117915 USSR

Semiconducting multilayer diamond structures -prototypes of solid state electronic devices - were made using chemical crystallization of diamond layers from the gaseous phase. Boron and phosphorus doping during growth resulted in the formation of epitaxial diamond layers with p- and n-types of conductivity. The simplest device of this type was a thermistor designed for measuring real temperature of the face of a diamond crystal grown by the method of the high-temperature high-gradient chemical transport reaction. The thermistor represented a 0.1-μm thick boron-doped diamond layer with a resistance of hundreds of ohm in the region of working temperatures. To protect it from the etching effect of atomic hydrogen, a layer of dielectric diamond was grown on it. Using this thermistor the kinetics of diamond crystallization by the above method was studied in the range 600 to 1100°C.

The metal-dielectric-semiconductor (MDS) structure, made on the basis of the layers of dielectric diamond and p-type diamond, had asymmetric current-voltage characteristics; the asymmetry sign depended on the thickness of the dielectric layer. This structure possessed photoconductivity. The photocurrent increased by approximately the same value regardless of the polarity of external voltage. The maximum integral sensitivity was about 1 mA/lm. Photoconductivity was observed over the whole visible region and beyond it, with a maximum at approximately 560 nm.

The p-n transition between the boron and phosphorus-doped diamond layers had low characteristics: the current density achieved $2\text{-}10^{-3}$ A at a direct voltage of a few volts and the asymmetry coefficient was about 10, which may be attributed to its shunting and to the absence of a good ohmic contact with n-diamond. The hetero-transition between the single crystal of p-diamond and the n-type hexagonal SiC substrate had increased conductivity in the direction of the current from diamond to SiC (asymmetry coefficient about 10) and allowed a rather high current density - up to 100 A/cm^2 at a direct voltage of up to 20 v. At a reverse voltage of about 30 v blue electroluminescence was observed.

RADIATION RESPONSE OF DIAMOND FILMS

N. K. Annamalai and Reginald F. Blanchard
Rome Air Development Center
Solid State Sciences Directorate
Hanscom AFB, MA 01731

Highly resistive diamond films 0.5 and 2.0 μm in thickness were grown on 3-in. p-type silicon. Titanium dots 50 nm thick and 1.6 mm in diameter were deposited on the top diamond surface to serve as ohmic contacts. Aluminum was deposited on the titanium dots to decrease the resistance of the contacts. The entire bottom surface of the silicon substrate was covered with evaporated aluminum.

On applying a voltage ramp, the leakage current (I) through the diamond film is given by

$$I = gV + C(dV/dt)$$

where g = diamond conductance, C = static capacitance (diamond and silicon), and dV/dt = ramp rate (V/s).

The leakage current, measured 30-60 s after applying a step voltage, is the conductive component, I_g. Therefore, the static capacitance is obtained from

$$C = (I - I_g)/(dV/dt).$$

The conductivity of the diamond film can be obtained, knowing the diamond thickness (d) and the area of the contact (A), from

$$\sigma = (I_g//v) \times (d/A).$$

High frequency (1 MHz) capacitance of this structure was also measured.

Conductivity, static capacitance and high frequency capacitance as a function of total gamma dose will be presented. The results will be compared with those for silicon-silicon dioxide structures.

ELECTRICAL PROPERTIES OF HOMOEPITAXIAL DIAMOND FILMS

S. A. Grot, G.Sh. Gildenblat, C. W. Hatfield, C. R. Wronski,
A. R. Badzian, T. Badzian, and R. Messier
The Penn State University
University Park, PA 16802 USA

Homoepitaxial diamond films were grown using a microwave plasma-assisted chemical vapor deposition process. Single crystal diamond (100) oriented substrates were obtained by cutting natural industrial type diamond. Both boron-doped and undoped diamond films were investigated. The doping was achieved by placing boron powder on the substrate holder prior to insertion into the deposition chamber. The diamond nature of the films was confirmed using Raman spectroscopy, x-ray diffraction, and other methods.

After film growth, surface treatments can induce drastic changes in the metal/CVD diamond contact characteristics. In particular, exposure of the (100) diamond surface to hydrogen plasma results in the ohmic behavior of evaporated gold contacts, whereas certain wet chemical cleaning will result in the formation of Schottky-type contacts when metal is evaporated to the film surface. Both of these surface treatments are reversible.

Electrical measurements were performed to determine the sheet resistance of the diamond film and the properties of metal contacts to the homoepitaxial diamond films. Contacts were formed by thermally evaporating metal at 10^{-7} Torr. The sheet resistance of the boron-doped films was thermally activated, with an activation energy of 0.15 eV. Ohmic contacts were formed by depositing 700 Å of gold over 100 Å of titanium and annealing the structure at 580°C for 5 min. Schottky diodes, formed by evaporating gold, operated at temperatures in excess of 500°C. A rudimentary MESFET was fabricated by photolithographically patterning the Schottky and ohmic contacts.

METAL POINT CONTACTS TO BORON-DOPED DIAMOND FILMS

K. Miyata, Y. Matsui, K. Kumagai, S. Miyauchi, K. Kobashi, and A. Nakaue
Electronics Research Laboratory
Kobe Steel, Ltd., 1-5-5 Takatsukadai
Nishi-ku, Kobe 673-02, Japan

Current-voltage characteristics of metal point contacts to boron-doped diamond films were measured. Boron-doped diamond films were prepared on p-type Si substrates with a resistivity of 1-10 ohm·cm by microwave plasma CVD using CH_4, H_2, and B_2H_6 for the source gas. Here, the CH_4 concentration with respect to H_2 was 0.5% and the B/C ratio in the reaction gas was 0, 2, 4, 20, or 40 ppm. For metal electrodes, Al, W, Ti, Au, and Pt wires were used.

For diamond films synthesized using the B/C ratio <20 ppm, Al, W, Ti, and Au contacts exhibited good Schottky characteristics with rectifying ratios $>10^2$ whereas the values became smaller for B/C > 20 ppm. The barrier heights estimated from the observed I-V characteristics were between 0.7 and 1 eV. However, the Pt point contact showed an ohmic characteristic for all diamond films. Such a dependence of the I-V characteristics and the barrier heights on metals seems to arise from different work functions of the contact metals. During the I-V measurements, a weak, blue emission of light was observed for Al, Ti, and Pt when the reverse electric field was 10^6 V/cm.

ELECTRICAL PROPERTIES OF DIAMOND FILMS

G. A. Sokolina, A. A. Botev, L. L. Bouilov,
S. V. Bantsekov, and O. I. Lazareva
Institute of Physical Chemistry of the Academy of Science
Union of Soviet Socialist Republics
Moscow, USSR

Diamond polycrystalline films with the thickness of a few tens of microns have been obtained by chemical crystallization from an electrically activated gaseous phase on tungsten substrates. The films consist of crystallites having a laminated structure. These films have been characterized by the grain size and the regions of coherent scattering (RCS).

The temperature dependence of static [$\sigma_{dc}(T)$] and dynamic [$\sigma_{ac}(T)$] electrical conductivity measured at the frequencies 10^2-10^4 Hz has been studied in the temperature range 150-800 K. It has been shown that $\sigma(T)$ has an activation character. The energy band structure of diamond polycrystal, where the bending of the zones at the interfaces of crystallites and RCS determines the height of the energy barriers for the transfer of current carriers through the film is considered.

There are three temperature regions, where the activation energy of conductivity is determined by the sum of the activation energies of impurities and by the barrier height either at the interfaces of RCS or at the interfaces of crystallites.

An assumption has been made about a considerable crystallization temperature effect on the height of intercrystalline energy barriers.

Dielectric polycrystalline diamond films have been shown to possess high thermal stability.

ELECTRICAL AND OPTICAL PROPERTIES OF DIAMOND THIN FILMS DEPOSITED FROM AN OXY-ACETYLENE FLAME*

Y. Tzeng, R. Phillips, C. C. Tin
Department of Electrical Engineering
Auburn University, Auburn, AL 36849 USA
J. Goela
CVD, Inc
185 New Boston Street, Woburn, MA 01801 USA
and
B. H. Loo
Department of Chemistry
University of Alabama at Huntsville
Huntsville, AL 35899 USA

Diamond films have been deposited on silicon, molybdenum, aluminum and various other substrates by either a stationary[1] or a scanning[2] oxy-acetylene flame. The as-deposited diamond films exhibit high electrical resistivity[3] exceeding 10^{14} Ω-cm as well as excellent optical transparency in a wide range of wavelength including the visible light.

Current-voltage measurements made on both free-standing diamond films and diamond thin films on silicon show trap-dominated current conduction characteristics. The resistivity of the as-grown diamond film is more than seven orders of magnitude higher than that deposited from hydrocarbon plasmas with hydrogen dilution.[4] The current conduction phenomena and proposed mechanism for the electrically highly resistive diamond film will be presented in conjunction with its correlation with the flame chemistry and the related optical emission spectroscopy data.

The excellent optical properties of the diamond films are promising for applications to free-standing diamond optical windows and for protective coating of infra-red windows such as ZnSe and ZnS.

We will present the results of optical transparency for wavelengths up to 20 μm for the flame deposited diamond films in comparison with those deposited from hydrocarbon plasmas with hydrogen dilution.

---

[1]T. Tzeng, C. Cutshaw, R. Phillips, T. Srivinyunon, A. Ibrahim, and B. H. Loo, "Growth of Diamond Films on Silicon From and Oxygen-Acetylene Flame," Appl. Phys. Lett. **56**(2), 134 (1990).

[2]Y. Tzeng, R. Phillips, C. C.Tin, Y. Chen, T. Srivinyunon, and C. Cutshaw, "Deposition of Diamond Films by Scanning Oxy-Acetylene Flame," Proc. Symposium on Diamond, Boron, Nitride, Silicon Carbide and Related Wide Bandgap Semiconductors, Materials Research Society, Boston, 1989.

[3]Y. Tzeng, C. C. Tin, R. Phillips, T. Srivinyunon, and Y. Chen, "Electrically-Insulating Diamond Films Deposited from an Oxy-Acetylene Flame," submitted to Appl. Phys. Lett. 1990.

[4]Y. Tzeng, P. J. Kung, R. Zee, K. Legg, H. S. Legg, D. Burns, and B. H. Loo, Appl. Phys. Lett. 53, 2326 (1988).

*This work is partially supported by SDIO/TNI-NSWC.

OHMIC CONTACTS TO SEMICONDUCTING DIAMOND VIA SOLID STATE REACTION PROCESSES

James Zeidler
Code 7601, Naval Ocean Systems Center
San Diego, CA 92152-5000 USA

The goal of this study is to develop strongly adherent, ohmic contacts to semiconducting diamond which have minimal contact resistance over precisely defined contact dimensions. To produce such contacts, a controlled chemical reaction between the contact metallization and the diamond surface is required. Although surprisingly diverse methods have been shown to provide ohmic contacts to semiconducting diamond, many of these methods are inadequate for the development of a durable ohmic contact technology for diamond devices intended for high temperature or other adverse operating conditions. In this paper, vapor deposition and annealing of appropriate metals is shown to provide strongly adherent wire-bonded contacts over precise contact dimensions as defined by a photolithographic process which is compatible with the high temperatures encountered in the vapor deposition process.

It will be shown that vapor deposition and annealing of carbide-forming metals such a Mo, Ta, and Ti provide ohmic contacts to diamond via a solid-state reaction process. A dramatic change (typically ten orders of magnitude) in the electrical resistance is shown to occur when the deposited metals are annealed. Characterization of the interface of the metal contacts using AES, SIMS, RBS, XRD, SEM, and metallography clearly indicates that metal-carbide precipitates nucleate and grow at the diamond-metal interface during annealing. These data indicate that the size and areal density of these precipitates at the interface are the principal factors which control the adhesion and the contact resistance. It is shown that the time and temperature of the annealing process affects the contact resistance. A minimum contact resistance is shown to occur prior to the formation of a monolithic carbide phase at the interface.

MECHANICAL PROPERTIES TESTING OF DIAMOND AND DIAMOND-LIKE FILMS BY ULTRA-LOW LOAD INDENTATION*

Michael E. O'Hern** and Carl J. McHargue
Metals and Ceramics Division
Oak Ridge National Laboratory
P.O. Box 2008, Oak Ridge, TN 37831-6118 USA

The mechanical properties of diamond-like carbon and diamond films have been studied using an ultra-low load indentation technique. The elastic/plastic properties of the films can be evaluated from the continuous load and displacement data acquired with a mechanical properties microprobe. Values for hardness and elastic modulus are given for both types of films relative to natural diamond and single-crystal sapphire. Determination of hardness and modulus of elasticity in thin films (particularly those with high values such as diamond) requires more information than can be obtained from conventional (e.g., Knoop or Vicker's) microhardness testing. The use of the mechanical properties microprobe to characterize these properties is addressed.

---

*Research sponsored by the Division of Materials Sciences, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

**Guest from University of Tennessee, Knoxville.

TURNING OF ALUMINUM ALLOY USING AN INSERT WITH A BRAZED DIAMOND FILM

Masao Murakawa and Sadao Takeuchi
Nippon Institute of Technology
4-1 Gakuendai, Miyashiro-town
Saitama 345, Japan

Recently, the CVD process has made it possible to form a thin diamond coating on different materials permitting its applications to various fields. One of the expected applications of diamond films is in wear. Research effort is being focused on the development of diamond-coated tools such as cutting inserts. At present, the biggest problem with diamond films, as applied to tools, is their poor adhesion strength to the substrate.

In an effort to solve this problem we propose a WC-Co alloy insert with a brazed diamond film made by the hot filament-type CVD equipment using ethanol as a diamond source.

This paper will describe the results of the performance test of an insert with a brazed diamond film, wherein turning of Al-18% Si alloy was conducted. This application was very successful with little abrasion and no adhesion of aluminum on the tool tip compared with a cemented carbide tool; the diamond film also had adequate adhesion strength.

GROWTH MECHANISMS, FILM MORPHOLOGY, TEXTURE, AND STRESSES FOR HOT FILAMENT ASSISTED CVD DIAMOND FILM GROWTH

R. E. Clausing, L. Heatherly, E. D. Specht, K. L. More, and G. M. Begun
Oak Ridge National Laboratory
P.O. Box 2008, Oak Ridge, TN 37831-6093

The structure and properties of diamond films grown by activated chemical vapor deposition vary greatly depending on the growth conditions. Both the nucleation and the growth processes can be major factors in determining the structure and thereby the properties of the films. The development of two commonly observed polycrystalline morphologies, the so-called "{111}" material and a microcrystalline material both of which give rise to <110> textures, and a third special material grown under conditions which produce "near <100>" textured films have been studied.[1]

We are investigating how nucleation and growth processes operate to determine the structure of these diamond films. The films are characterized with scanning electron micrography (SEM) and transmission electron microscopy (TEM) (microstructure, growth rates, grain size, and morphology); x-ray diffraction (texture and internal stresses), and Raman spectroscopy (bond character and internal and applied stresses). The x-ray diffraction texture determination[2] and the TEM microstructural analysis[1] together with a structure analysis based on scanning electron micrographs of the growth surface topography provide evidence to support the hypothesis that twinning plays an important role in the nucleation and growth of the "{111}" and microcrystalline films. Crystallites in these films contain numerous stacking faults and twins which appear to be instrumental in the film growth and texture development as has been proposed to explain a similar texture seen in silicon film growth.[3]

The growth surface of the third type of film exhibits {100} facets perpendicular to the growth direction (and therefore nearly parallel to the substrate) and a columnar grain structure free of intracrystalline stacking faults and twins. Good quality homoepitaxial {100} single crystal films with no stacking faults or twins have also been grown using the same basic technique, which does not make use of boron or oxygen additions to the growth environment. A 50-μm thick {100} single crystal film was grown with a surface that remained smooth and apparently free of microscopic growth steps except near the edges of the deposit.

The <100> texture develops under conditions where this is the direction of fastest growth. Examination with SEM revealed that the films nucleate as randomly oriented cubo-octahedra with many single and multiply twinned nuclei. Crystals nucleated with their fastest growth directions oriented normal to the substrate are able to out-grow and over-grow the less favorably oriented crystals leading to texture development.

Growth on {100} facets does not appear to require special nucleation sites such as steps or ledges and would not permit twins or stacking faults to nucleate. Single carbon additions to double bonded sites are possible on the flat {100} faces, but only to the correct position to propagate a proper continuation of the existing crystal. No

twins are seen inside these crystallites, but the grain interfaces often contain a very high density of stacking faults and twins.

The x-ray diffraction measurements for all three polycrystalline films give average lattice constants consistent with that of pure diamond, therefore we conclude that the peak widths are due to stress rather than an inhomogeneous distribution of hydrogen or other impurities which would expand or contract the lattice. The symmetric diffraction intensity distribution about zero strain suggests that stress is created internally, perhaps between the diamond grains. Stresses due to interactions with the substrate would likely produce a tensile or compressive bias.

The measured strains are much larger than the thermal expansion mismatch of 5×10^{-4} for silicon and diamond between room temperature and the growth temperatures. The strain in the microcrystalline sample approaches that of a diamond at the point of fracture. Based on a fracture stress of 1050 to 1800 kg/mm^2 and a modulus of 1.1×10^5 kg/mm^2 the strain at fracture would be 1.0×10^{-2} to 1.7×10^{-2}. We measure strains of 5.2×10^{-3} in the microcrystalline material and 2.4×10^{-3} in both the "(111)" and "near (100)" materials. These strain data were obtained on films approximately 100-μm thick while they were still attached to the silicon (100) substrates on which they were grown.

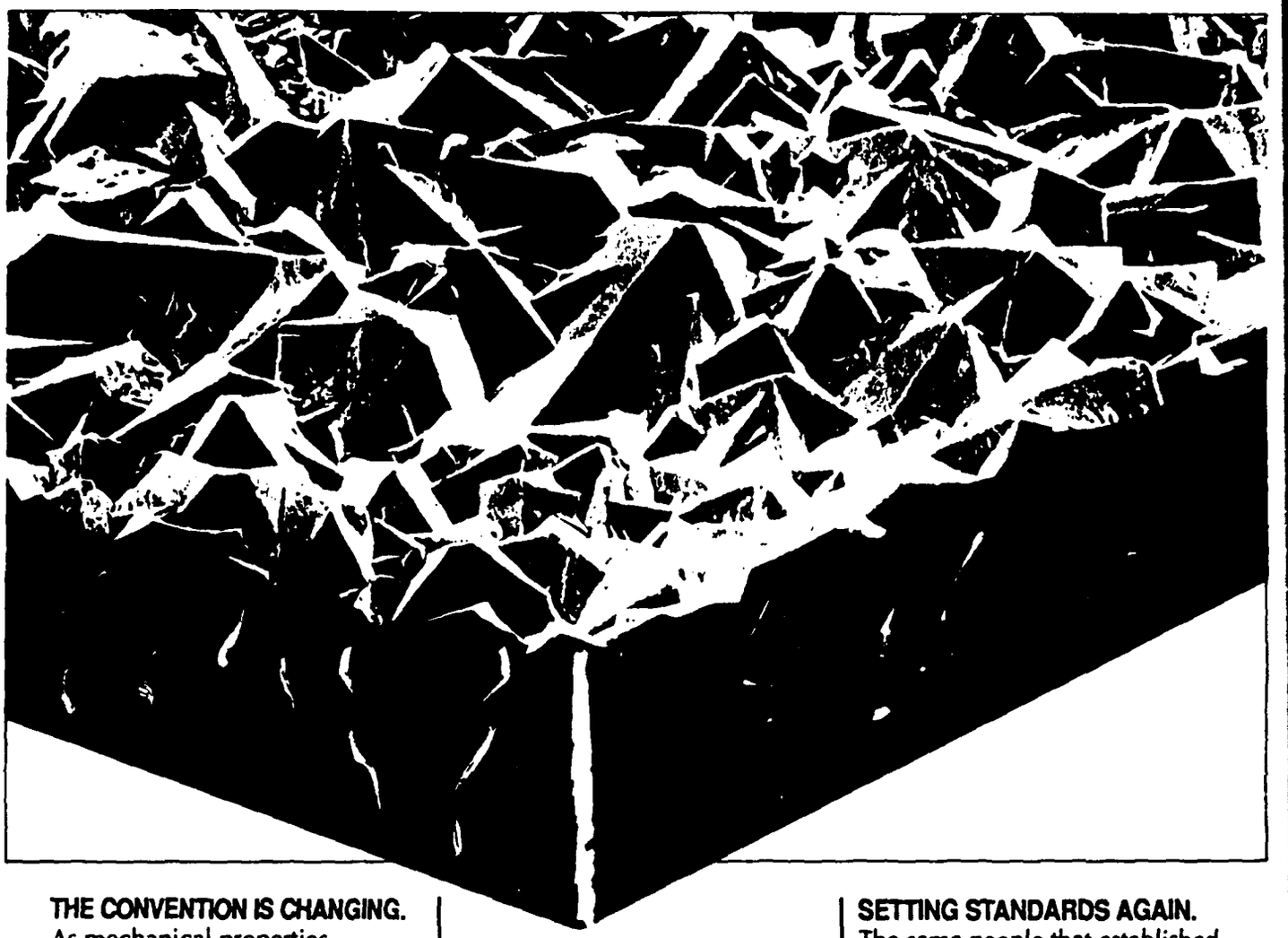
Acknowledgement

This research was jointly sponsored by: (1) the Exploratory Studies Program of Oak Ridge National Laboratory; (2) the U.S. Department of Energy, Division of Materials Sciences, Office of Basic Energy Sciences; and (3) U.S. Department of Energy, Assistant Secretary for Conservation and Renewable Energy, Office of Transportation Systems, as part of the High Temperature Materials Laboratory Program. The research sponsored by the U.S. Department of Energy was under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

References:

1. R. E. Clausing, L. Heatherly, Jr., K. L. More, and G. M. Begun, Surface and Coatings Technology **39/40**, 199-210 (1989).
2. E. D. Specht, R. E. Clausing, and L. Heatherly, Measurement of Crystalline Strain and Orientation in Diamond Films Grown by Chemical Vapor Deposition, submitted for publication in Journal of Materials Research.
3. D. Meakin, J. Stoemenos, D. Miglierate, and N. A. Economan, J. Appl. Phys. **61**, 5031 (1987).

On the Cutting Edge.



THE CONVENTION IS CHANGING.
As mechanical properties determination on the submicron scale becomes increasingly critical in the research and development of diamond and diamond-like films, the discerning research scientist is being forced from optically imaged indentation testing into systems yielding real-time, load-displacement data.

THE STANDARD WAS SET.
In 1984, Nano Instruments set the standard for the mechanical properties measurement industry. The **NANO INDENTER** provided unprecedented sensing resolution, spatial resolution, automation, state-of-the-art technology and software flexibility.

The Nano Indenter was the first instrument to make substrate-free mechanical properties determinations on DLC films and it remains the only one shown to evaluate indentation properties of diamond films.

SETTING STANDARDS AGAIN.
The same people that established the industry's standard have reestablished the limits to nano-mechanical properties determination. The **NANO INDENTER II** has reset the boundaries of system stiffness, load and displacement resolution and indentation placement.

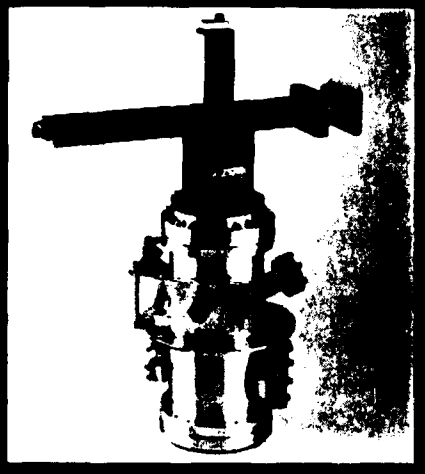
Your research requires dependable, reproducible results. Our instrument can provide those results thanks to the highest machine stiffness in the industry and the most flexible operating system available.

WE'RE "ON THE CUTTING EDGE".

NANO

Nano Instruments, Inc.
P.O. Box 14211 Knoxville, TN 37914
Phone: 615-927-1461
Fax: 615-927-3110

SERIOUS DIAMOND DEPOSITION.



Our diamond deposition systems allow you to grow polycrystalline films of diamond and related materials on substrates up to four inches in diameter. ASTeX microwave plasma sources help achieve high growth rates with excellent mechanical, optical, thermal, and electrical properties. We offer basic systems for research, as well as turnkey systems for advanced development. This is serious diamond film capability. Call for our catalog.

ASTeX®

BY APPLIED SCIENCE AND TECHNOLOGY, INC.
35 Cabot Road, Woburn, MA 01801
Telephone (617) 933-5560

6[illegible] - MS-C2

PUBLICITY

1. Direct mailing of 1000 first announcement folders (attached). The mailing list was developed from the attendance list of the MRS-Europe Conference on Amorphous Hydrogenated Carbon Films-1987; the MRS Symposium on Diamond Films-1989; the USA Defense Department mailing list for Diamond Research; and lists assembled by members of the Organizing Committee in France, Federal Republic of Germany, Italy, and Britain, and by Dr. Rui Vilar in Portugal.

2. Five copies were mailed to each national representative of the NATO Scientific Committee.

3. An announcement was sent to the following journals:

   Bulletin of the Materials Research Society (copy of published announcement attached)
   Physics Today
   Materials Engineering
   Research and Development
   Ceramic Industry
   ASM International News (copy attached)
   Advanced Materials and Processes
   Bulletin of the American Ceramic Society
   Materials and Processing Report (Newsletter)

4. Publicity material was supplied to the database "Conferences in Energy, Physics, and Mathematics," Fachinformationszentrum Karlsruhe, FRG.

5. A second notice and formal application were mailed to approximately 200 who returned the card from the first announcement.

CONFERENCE ANNOUNCEMENT

A NATO Advanced Study Institute on "Diamond and Diamond-Like Films" will be held at the Il Ciocco International Conference Center, Castelvecchio Pascoli, Italy (Near Pisa) during the period July 22 to August 3, 1990. Subjects to be covered include: plasma chemistry and physics, nucleation and growth models, preparation techniques, structure and property characterization and relationships, and applications. The Institute will be limited to 90 participants and some financial support will be available for students. Deadline for submission of abstracts and applications is February 15, 1990. For information contact Dr. Carl J. McHargue, Metals and Ceramics Division, Oak Ridge National Laboratory, P. O. Box 2008, Oak Ridge, TN 37831-6118, Phone: 615-574-4344, Fax: 615-574-7659; or Prof. P. Koidl, Fraunhofer Institut fur Angewandte Festkorperphysik, Eckerstrasse 4, D-7800 Freiburg, FRG, Phone: 0761-5159-280, Fax: 0761-5159-200.

M Calls for Papers

PICAL CONFERENCES

ress, 20-24 August 1990.

Electronic Materials & ... in the following areas ... ably: TAB Technology ... ing, Interface Reaction ... Film Diffusion, Bar ... & Encapsulation, Thin ... Interconnect, Microelectr... Interconnection, Sur... sign, Materials & Pro... SMT, Coating of SMT ... & Printed Wiring Board ... Substrates, PWB Card ... Frame & Microelectronic ... ies, Materials, Processes ... Interconnection, Micro... e Housing, Workshop or... on, Corrosion & Preven... nd Prevention, Reliabili... ges, Workshop on Micro... re Analysis of Packages ... Interconnection - Design ... nd Microelectronic Inter... of SMT Solder Joints ...

...d before 1 March 1990 to ... at Materials Park. Most ... listed may be purchased ... their respective publishers ... that appear in boldface may ... owed by members through ... interlibrary loan program. ... books are noncirculating. ... available for reference use ... erials Park. For more infor... contact Eleanor Baldwin, ... ry supervisor, (216) 338-... 450.

... Annual Technical Conference ... NY, May/June 1990, Society of Plastics ... Inc., Brookfield CT.

... and Adhesives, 20th Annual Confer... ... Proceedings, Leeds, UK ... Event, Leeds, UK.

... Coatings Materials, Vol. 4, Pro... ... Metallurgical Society of the ... of Mining and Met... Lakeside Conference Center, Fort W... Texas, Nov. 1990, Pergamon Press, New York, NY.

... Code, American Welding Soc... Miami, FL, Dec. 1988.

... Conference, Houston, TX, May ... Society, Inc., Houston, TX.

... Proceedings, Vol. 1, Proceedings ... Society, Anaheim, CA, ... Society, Los ... IL.

... Proceedings, Vol. 2, Proceedings ... Society, Anaheim, CA, ... Society, Los ... IL.

... Diamond and Diamond-Like Films, ... September 1990, The Minerals ... and Materials Society, Warrendale, PA.

... Theory and Practice, Pro... ... 7th European Conference on ... Vol. 1 and 2, Budapest, Hungary, ... 1989, Engineering Materials Ad... Services Ltd., Surrey, UK.

Technical presentations are solicited on the subject of fabrication processes of metal matrix composites reinforced by particulates, as well as on the elaboration by the casting powder metallurgy or P/M processes.

Papers are requested on the following topics: fundamentals influencing fabrication: wetting, diffusion, metallurgical reactions, kinetics, solidification; fabrication processes: infiltration, squeeze casting, gravity casting, compocasting, rheocasting; relationship between fabrication methods and obtained final properties: microstructure, mechanical behaviour, wear and corrosion resistance; forming of composites: forging, extrusion, machining, drawing, near net shape forming; techniques to control the process and to characterize the final properties: metallography, microscopy, fractography, mechanical testing, interface characterization.

Submit abstract (up to 300 words) by 16 March 1990 to Francois G. Hamel or Jacques Masounave, Industrial Materials Research Institute, 75 de Montagne Blvd., Boucherville, Quebec, Canada, J4B 6Y4, Tel: (514) 641-2280. Papers accepted by reviewers will be published in a book of proceedings.

6th Annual ASM ESD Advanced Composites Conference/Exposition, 8-11 October 1990, Detroit, Michigan

Sponsored by ASM INTERNATIONAL and the Engineering Society of Detroit (ESD). Papers are solicited in the area of design, manufacturing, materials science, and processing, and a variety of related topics. Original papers dealing with topics in these areas

Brazil, November 1988, ILAFA (Latin American Iron And Steel Institute), Santiago, Chile.

Copper: Technology & Competitiveness, Office Of Technology Assessment, Washington DC, 1988.

Corrosion-Resistant Coatings Technology, I. Suzuki, Marcel Dekker, Inc., New York, 1988.

Degradation and Stabilization of Vinylchloride Based Polymers, K.S. Minsker, Pergamon UK, Oxford, 1987.

Design in Composite Materials Conference, London, UK, March 1989, Institution Of Mechanical Engineers, London, UK.

Diffusion in Solids, 2nd Edition, P. Shewmon, The Minerals, Metals & Materials Society, Warrendale, PA, 1989.

Ductile Fracture Handbook, Vol. 1, A. Zahoor, Novatech Corporation, Gaithersburg, MD, 1989.

Effects of Welding on Health VI, American Welding Society, Miami, FL, EWH-6, 1988.

Electronic Structure and Lattice Defects in Alloys, United States Japan Seminar, Honolulu, HI, May 1987, Trans Tech Publications, Brookfield, VT.

Gases in Plastics, Information and Education, National Physical Laboratory, Teddington, Middlesex, UK.

Fracture 89, International Conference, IUMRS - Advances in Fracture Research, Vol. 1, 2, 3, 4, 5, 6, Honolulu, HI, March 1989, Pergamon Press, Oxford.

Fracture Technology, Proceedings of the ASME Symposium on Fracture Technology, Vols. 1 and 2, Proceedings, Hilton Head, SC, September 1988, The American Society of Mechanical Engineers, Elsevier Science Publishers, New York.

High Power Lasers, V. Velikhov, Pergamon, Oxford, 1987.

High Temperature Materials in Engineering, Metal Ceramics, Plastics, 2nd European Conference, London, UK, April 1989, IBC Technical Services, London, UK.

Industrial Applications of Lasers, Chicago, IL, April 1988, Society of Manufacturing Engineers, Dearborn, MI.

Iron Ore, Proceedings of the Iron Ore Symposium, Vol. 15, 28th Annual Conference of Metallurgists of CIM, Montreal, Quebec, Canada, August 1989, Pergamon Press, New York.

Joining of Materials, JOM-4, Proceedings of the International Conference on the Joining of Materials, Helsingor, Denmark, May 1989, Ingeniorhojskolen, Helsingor, Denmark.

Lasers in Manufacturing, Proceedings of the 8th International Conference, Chicago, IL, November/December 1988, American Society for Mechanical Engineers, New York, NY, 1988.

Materials and Engineering Design: 1990s/1999, The Next Decade, B.F. Dyson, Institute of Metals, London, UK, 1988.

Primary and Secondary Lead Processing, Proceedings of the International Symposium, Vol. 15, 28th Annual Conference of Metallurgists of CIM, Halifax, Canada, August 1989, Pergamon Press, New York.

Proceedings of IPENZ Annual Conference 1989, Engineering Our Natural Resources, Vols. 1 and 2, February 1989, Dunedin, Institution of Professional Engineers, New Zealand, Wellington, Australia.

Proceedings of the 1989 SEM Spring Conference on Experimental Mechanics, Cambridge, MA, May/June 1989, Society for Experimental Mechanics, Bethel, CT.

Proceedings of the International Conference on the Joining of Materials, JOM-4, Denmark, March 1989, Ingeniorhojskolen, Helsingor Teknikum, Helsingor, Denmark.

Process Gas Handling and Cleaning, Proceedings of the International Symposium, Vol. 13, 28th Annual Conference of Metallurgists of CIM, C. Taylgge-Mooney, Halifax, Canada, August 1989, Pergamon Press, New York.

Processing of Ceramics and Metal Matrix Composites, Proceedings of the International Symposium, 20th Annual Conference of Metallurgists of CIM, Vol. 17, Halifax, Canada, August 1989, Pergamon Press, New York.

Processing of Copper-Zinc, Proceedings of the International Symposium, Vol. 12, 28th Annual Conference of Metallurgists of CIM, Halifax, Canada, August 1989, Pergamon Press, New York, Oxford.

Sampling in the Non-Ferrous Metals Industry, Concentrates and Recycled Commodities, International Symposium, Hamburg, FRG, May 1989, Gesellschaft Deutscher Metallhutten- Und Bergleute, Clausthal-Zeller, FRG.

Semiconductor and Metal Binary Systems, Phase Equilibria and Chemical Thermodynamics, V.M. Glazov, Consultants Bureau, New York.

Calendar of Events

ASM EVENTS

NORTH AMERICAN

1990

13-15 Mar., Indianapolis, IN - 12th Heat Treating Equipment Exposition, ASM Heat Treating Society.

26-29 Mar., Los Angeles, CA - WESTEC '90, Western Manufacturing Technology Exposition, SME and AMTDA.

26-29 Mar., Myrtle Beach, SC - Failure Analysis Applications of Metallurgy, ASM.

15-19 April, Phoenix, AZ - 5th Automotive and Engine Technology International Congress & Exposition, SAE.

1-3 May, Oak Ridge, TN - Tribology of Composite Materials, ASM Specialty Materials Division.

21-24 May, Long Beach, CA - 2nd National Thermal Spray Conference Exposition, ASM Thermal Spray Division.

21-24 May, Long Beach, CA - AERO MAT, Advanced Aerospace Materials, Processes Conference Exposition, ASM.

21-24 May, Long Beach, CA - Lasers in Materials Processing, ASM W. Coast Exposition Liaison Committee.

11-14 June, Glasgow, Scotland - 10th International Conference on NDE in the Nuclear & Pressure Vessel Industry, ASM Materials Testing & Quality Control Division and British Institute of Nondestructive Testing.

12-15 June, Detroit, MI - 2nd Annual ASM ESD VERANTEC, ASM and Engineering Society of Detroit.

1990

2-6 April, San Diego, CA - 8th International Conference on Thin Films (ICTF-8) and 17th International Conference on Metallurgical Coatings (ICMC-17). For more information contact: Dr. W.D. Sproul, Bas. Ind. Res. Lab., Northwestern University, 1801 Maple Ave., Evanston, IL 60201-3135.

15-17 May, Oak Ridge, TN - 4th Annual Conference on Fossil Energy Materials. For more information contact: D.N. Braski, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6084, (615) 574-5992.

20-24 May, Cleveland, OH - Workshop on the Science and Technology of Diamond Thin Films, sponsored by Case Western Reserve University. For more information contact: Joan C. Angus, Chemical Engineering Department, Case Western Reserve University, Cleveland, Ohio 44106.

20-23 Aug., Wrightsville Beach, NC - 45th Sea Horse Institute Meeting. For more information contact: E. Eubanks, Laser Center for Corrosion Technology, Inc., P.O. Box 456, Wrightsville Beach, NC 28480, (919) 256-2351.

SEPT/OCT., Detroit, MI - TMS Fall Meeting, sponsored by The Minerals, Metals & Materials Society, 420 Commonwealth Drive, Warrendale, PA 15086.

INTERNATIONAL

1990

11-15 June, Beijing, China - 10th International Conference on Vacuum Metallurgy featuring Special Melting and Metallurgical Coatings. For more information contact: Prof. T. Shaojie, 10th ICVM, The Chinese Society of Metals, 46 Dongsi Xi Dajie, Beijing 100711, China.

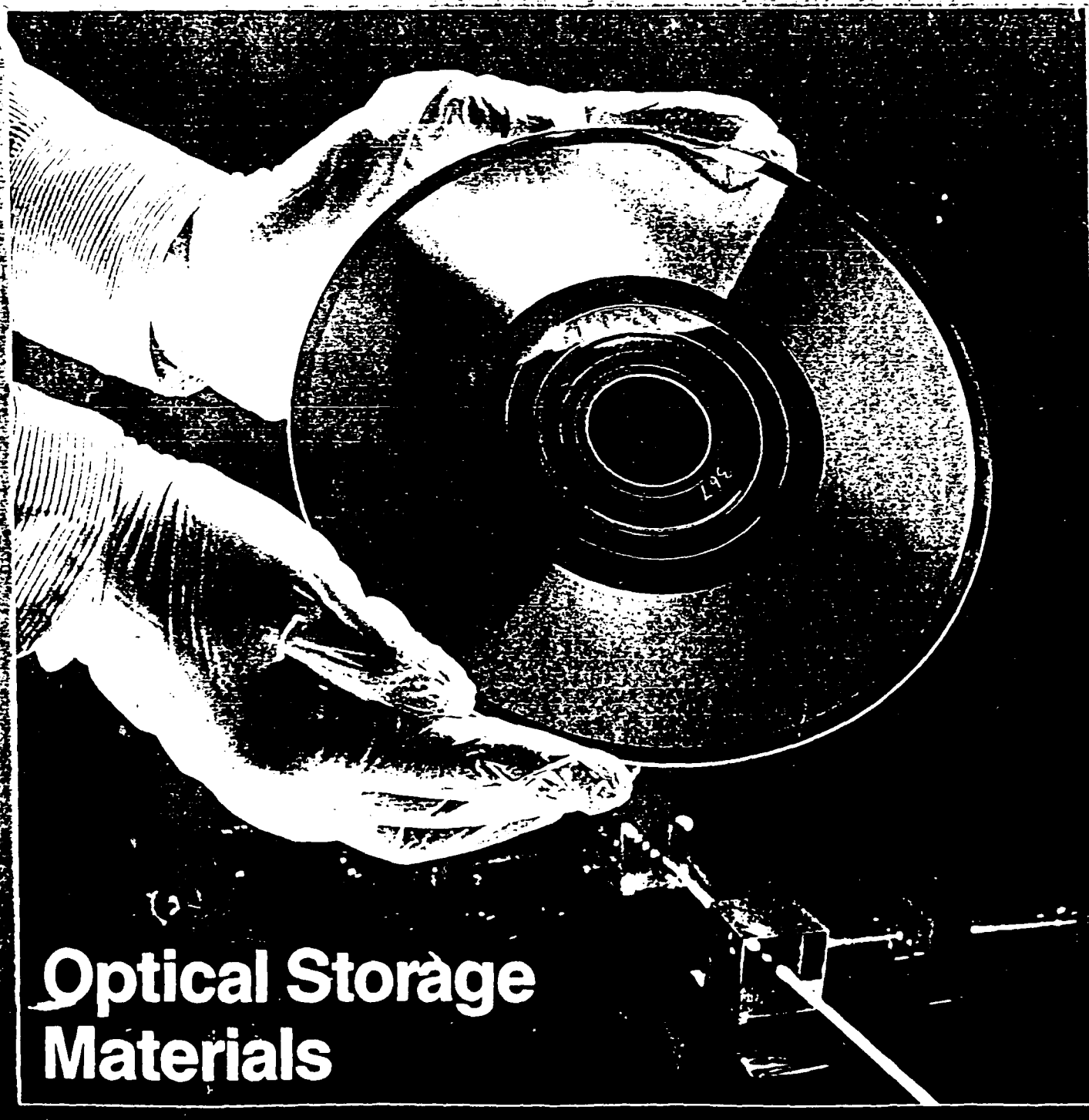
22 July - 2 August, Castelvecchio Pascoli, near Pisa, Italy - NATO Advanced Study Institute - Diamond and Diamond-Like Films. For more information contact: Dr. Carl J. McHargue, Metals and Ceramics Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6118.

MRS BULLETIN

April 1990

Volume XV, Number 4

Serving the International Materials Research Community



Optical Storage Materials

11-14
11th Biennial Conference on National Materials Policy
Williamsburg, VA
B. Houston, Federation of Materials Societies, 1727 L St., NW, Suite 333, Washington, DC 20036, (202) 296-9282

11-15
Basic Course: SEM and X-Ray Microanalysis
Bethlehem, PA
J.I. Goldstein, Dept. of Materials Science and Engineering, Bldg. 5, Lehigh University, Bethlehem, PA 18015, (215) 758-5133

11-15
Gordon Research Conference on Condensed Matter Physics
Wolfeboro, NH
A.M. Chaikin, Gordon Research Center, Univ. of Rhode Island, Kingston, RI 02881-0801, (401) 783-4011, fax (401) 783-7644

11-15
10th International Conference on Vacuum Metallurgy
Beijing, China
T. Shabbe, Chinese Society of Metals, 46 Dongsix, Dajie, Beijing 100711, China, fax 512 4122

12-14
4th International Electronic Materials and Processes Conference
Albuquerque, NM
SAMPE, P.O. Box 2459, Covina, CA 91722, (818) 331-0616, fax (818) 332-8929

13-15
Atomic Layer Epitaxy
Helsinki, Finland
L. Niinistö, Dept. of Chemical Engrg., Helsinki Univ. of Tech., Kemistintie 1, SF-02150 Espoo, Finland, 358-0-4512600, fax 3580-462373

18-21
Advanced Topics: SEM and X-Ray Microanalysis
Bethlehem, PA
J.I. Goldstein, Dept. of Materials Science and Engineering, Bldg. 5, Lehigh University, Bethlehem, PA 18015, (215) 758-5133

18-21
Analytical Electron Microscopy
Bethlehem, PA
J.I. Goldstein, Dept. of Materials Science and Engineering, Bldg. 5, Lehigh University, Bethlehem, PA 18015, (215) 758-5133

18-21
5th International Conference on Metallurgical Vapor Phase Epitaxy
Aachen, Germany
H. Henke, Institute für Halbleitertechnik, RWTH Aachen, Templergraben 55, D-5100 Aachen, W. Germany, (241) 80 77 50, fax (241) 80 77 51

18-22
C-MRS International '90
Beijing, China
Hengde Dai, Dept. of Materials Science & Engineering, Tsinghua Univ., Beijing 100084, China, 655646, fax CP 22-8583 (See related ad herein, MRS Bull., Vol. 9)

18-June 29
Mini-workshop on Strongly Correlated Electron Systems
Trieste, Italy
Condensed Matter Group Secretary, International Center for Theoretical Physics, P.O. Box 586, I-34100 Trieste, Italy, (040) 224241, fax 224531

21-22
Thin Specimen Preparation
Bethlehem, PA
J.I. Goldstein, Dept. of Materials Science and Engineering, Bldg. 5, Lehigh University, Bethlehem, PA 18015, (215) 758-5133

21-22
Workshop on MOMBE, CBE, GSMBE, and Related Techniques
Aachen, Germany
H. Henke, Institut für Halbleitertechnik, RWTH Aachen, W. Germany, Templergraben 55, D-5700 Aachen, (241) 80 77 50, fax (241) 80 77 51

24-30
7th CIMTEC—World Ceramics Congress
Florence, Italy
Seventh CIMTEC, P.O. Box 174, 48018 Faenza, Italy, 545-664143; fax 545-664138

25-29
Gordon Conference on Defects in Glass
Tilton, NH
R.J. Eagan, Sandia National Labs., Organization 1800, P.O. Box 5800, Albuquerque, NM 87185-5800, (505) 844-9274

26-28
Computer-Aided Assessment and Control of Localized Damage
Ashurst, Southampton, United Kingdom
J. Putters, Computational Mechanics Institute, Ashurst Lodge, Ashurst, Southampton, SO4 2AA, United Kingdom, (042129) 3223, (042129) 2853

27-29
Electronic Materials Conference
Santa Barbara, CA
V.G. Keramidas, Bellcore, 331 Newman Springs Rd., Red Bank, NJ 07701-7040, (201) 758-3359, fax (201) 758-4606

JULY 1990

2-5
7th CIMTEC-Defects in Semiconductors
4th High Tc Superconductors
(See June 24-30 CIMTEC listing)
Trieste, Italy
7th CIMTEC, Defects in Semiconductors
4, P.O. Box 474, 48018
Faenza, Italy, 545-664143
fax 545-664138

6-13
International Symposium on Optical and Optoelectronic Applied Science and Engineering
San Diego, CA
SPIE, P.O. Box 10, Bellingham, WA 98227-0010, (206) 676-3290, fax (206) 647-1445

9-12
Conference on Nondestructive Evaluation of Modern Ceramics
Columbus, OH
American Ceramic Society, 757 Brooksedge Plaza Drive, Westerville, OH 43081, (614) 890-4700, fax (614) 899-6109

11-13
Optoelectronics Conference
Chiba, Japan
K. Ito, OEC '90 c/o Business Center for Academic Societies Japan, Conference Dept., Crocevia Hongo 2F, 3-23-1 Hongo, Bunkyo-ku, Tokyo 113, Japan, 81-3-817-5831, fax 81-3-817-5836

15-20
8th American Conference on Crystal Growth
Vail, CO
B.L. Sopori, Solar Energy Research Institute, 1617 Cole Blvd., Golden, CO 80401-3393; (303) 231-1383

17-19
Low Temperature Engineering and Cryogenics Conference, LTEC 90
Southampton, England
Cryogenics Conference Office, Institute of Cryogenics, University of Southampton, SO9 5NU, United Kingdom, 0703-595000, ext. 2059 or 2662, fax 0703-593939

22-27
13th International Liquid Crystal Conference
Vancouver, Canada
B. Bergersen, Dept. of Physics, Univ. of British Columbia, Vancouver, V6T 2A6 Canada, (604) 228-2603

22-3
NATO Advanced Study Institute on Diamond and Diamond-Like Films
Castelvecchio Pascoli, Italy
C.J. Mchargue, Metals and Ceramics Div., Oak Ridge National Lab., P.O. Box 2008, Oak Ridge, TN 37831-6118, (615) 574-4344, fax (615) 574-7659

23-26
Conference on Advances in Cementitious Materials
Gaithersburg, MD
American Ceramic Society, 757 Brooksedge Plaza Drive, Westerville, OH 43081, (614) 890-4700, fax (614) 899-6109

23-27
5th International Conference on Scanning Tunneling Microscopy/Spectroscopy and 1st International Conference on Nanometer Scale Science & Technology
Baltimore, MD
J.S. Murday, Code 6100, Naval Research Lab., Washington, DC 20375-5000, (202) 767-3026, fax (202) 404-7139

24-26
Conference on Polymer Blends
Cambridge, United Kingdom
D.C. Varley, Conf. Mgr., PRI, 11 Hobart Place, London SW1W 0HL

29-3
37th International Field Emission Symposium
Albuquerque, NM
G.L. Kellogg, Div. 1114, Sandia National Laboratories, Albuquerque, NM 87185

30-1
Powder Metallurgy: Key to Advanced Materials Technology
Vancouver, Canada
Member/Customer Service Center, ASM International, Metals Park, OH 44073, (216) 338-5151; fax (216) 338-4634

30-2
8th International Conference on Ion Implantation Technology
University of Surrey, United Kingdom
P.L.F. Hemment, Dept of Electronic & Electrical Engineering, Univ. of Surrey, Guildford, Surrey GU2 5XH, (0483) 571281; fax (0483) 300803

30-3
POLYSE '90: Polycrystalline Semiconductors
Schwäbisch Hall, W. Germany
H.P. Strunk, Max-Planck Institute FKF, Heisenbergstr. 1, D-7000 Stuttgart 80, FRG, (711) 6860-645, fax (711) 6874 371 or J.H. Werner, Max-Planck-Institute, Heisenbergstr. 1, 7000 Stuttgart 80, W. Germany, (49) 711/6860-645

30-3
5th International Conference on the Physics of Electro-Optic Microstructures and Microdevices
Heraklion, Crete, Greece
A. Christou, Code 6830, Naval Research Laboratory, 4555 Overlook Ave., S.W., Washington, DC 20375-5000, fax (202) 767-0546

30-3
Particulate Ceramics Processing: The Future for Manufacturing
Cambridge, MA
Director of the Summer Session, M.I.T., Rm. E19-356, Cambridge, MA 02139, (617) 253-2101

31-2
4th International Conference on Shallow Impurities in Semiconductors
London, United Kingdom
G. Davies, Physics Department, Kings College London, The Strand, London WC2R 2LS, United Kingdom

AUGUST 1990

6-10
20th International Conference on the Physics of Semiconductors
Thessaloniki, Greece
N.A. Economou, P.O. Box 19615, 54006 Thessaloniki, Greece, (30) 31-991439, fax (30) 31-214276

8-10
Specialty Polymers '90
Baltimore, MD
W. Harvey, SP '90, Butterworth Scientific Ltd., P.O. Box 63, Westbury House, Bury St., Guildford, Surrey, GU2 5BH, United Kingdom, 0483 300966, fax 0483 301563

12-18
12th International Congress for Electron Microscopy
Seattle, WA
R.M. Fisher, Univ. of Washington, 5001 25th Ave. NE, GH-22, Seattle, WA 98195, fax (206) 545-9359

13-15
LT-19 Satellite Conference on High Temperature Superconductivity
Cambridge, United Kingdom
K.S. Dilley, IRC in Superconductivity, Madingley Rd., Cambridge CB3 0HE, UK, (0223) 337472, fax (0223) 337074

30-3
5th International Conference on the Physics of Electro-Optic Microstructures and Microdevices
Heraklion, Crete, Greece
A. Christou, Code 6830, Naval Research Laboratory, 4555 Overlook Ave., S.W., Washington, DC 20375-5000, fax (202) 767-0546

30-3
Particulate Ceramics Processing: The Future for Manufacturing
Cambridge, MA
Director of the Summer Session, M.I.T., Rm. E19-356, Cambridge, MA 02139, (617) 253-2101

31-2
4th International Conference on Shallow Impurities in Semiconductors
London, United Kingdom
G. Davies, Physics Department, Kings College London, The Strand, London WC2R 2LS, United Kingdom

6375-MS-02

FINAL SCIENTIFIC PROGRAM
DIAMOND AND DIAMOND-LIKE FILMS AND COATINGS

July 22-August 3, 1990

OPENING OF INSTITUTE

Opening Remarks
R. E. Clausing (Oak Ridge National Laboratory, USA)
Introduction/Overview (Diamond: Potential and Status) (1 hr)
M. Yoder (Office of Naval Research, USA)

PART 1. FUNDAMENTAL CONCEPTS

Lectures:

Natural Diamond (The Standard) (2 hr)
J. E. Field, (Cambridge University, UK)

Physics of Plasmas and Plasma/Surface Interactions (2 hr)
J-E. Sundgren (Linköping University, Sweden)

Reactive Gas Glow Discharges (2 hr)
J. W. Coburn (International Business Machines, USA)

Modelling and Simulation of Particle-Surface Interactions (2 hr)
R. Smith (Loughborough, UK)

Oral Presentations

Overview of the Characterization of Diamond and Diamond-Like Carbon Films (1 hr)
P. R. Chalker (Harwell Laboratory, UK)

Review of Diamond-Related Materials (BN, SiC,...) (1 hr)
R. C. DeVries (USA)

PART 2. DIAMOND-LIKE FILMS

Lectures:

Diamond-Like Hydrocarbon and Carbon Films (2 hr)
J. C. Angus (Case Western University, USA)

Preparation Techniques for Diamond-Like Carbon (2 hr)
Y. Catherine (University Nantes, France)

Electronic Structure and Properties of Diamond-Like Carbon (2 hr)
J. Robertson (National Power TEC, UK)

Characterization and Properties of Diamond-Like Carbon Films (2 hr)
P. Koidl (Fraunhofer Institut, FRG)

Applications of Diamond-Like Films (1 hr)
A. H. Lettington (R.S.R.E., UK)

Oral Presentations

Correlation Between Precursor Gas and Structure (1/2 hr)
J. M. Mackowski (IPN, France)

The Hardness and Elastic Modulus of Diamond and Diamond-Like Films (½ hr)
C. J. McHargue (Oak Ridge National Laboratory, USA)

Process Characterization of a-C:H Plasma Deposition (½ hr)
Ch. Wild (Fraunhofer Institut, FRG)

In Situ Characterization of a-C:H Films and Film Structure Interfaces by Photoelectron Spectroscopy (1½ hr)
P. Oelhafen (Universitat Basel, Switzerland)

Post-Deposition Treatments and Stability of Diamond-Like Films (1 hr)
R. Kalish (Technion, Israel)

Aging Processes in Diamond-Like Carbon and Carbon/Metal Films (½ hr)
L. Martinu (University Montreal, Canada)

Computer Modelling of C:H Film Growth (1 hr)
W. Möller (Max-Planck Institut, FRG)

Gap States and Electron Spin Resonance in Amorphous Carbon and Hydrogenated Amorphous Carbon (1/2 hr)
F. Demichelis (Corso Duca degli Abruzzi, Italy)

PART 3. DIAMOND FILMS

Lectures:

Techniques for the Growth of Diamond (2 hr)
T. R. Anthony (General Electric, USA)

Theory and Models for Nucleation of Diamond (2 hr)
M. Frenklach (Pennsylvania State University, USA)

Characterization and Properties of Artificially Grown Diamond (2 hr)
P. K. Bachmann (Philips Research Laboratories, FRG)

Critical Assessment of State-of-the-Art (2 hr)
N. Setaka (National Institute for Researches, Japan)

Oral Presentations

Device Application for Diamonds (1 hr)
M. W. Geis (Massachusetts Institute of Technology, USA)

Nucleation and Growth of Low-Pressure Diamond (1 hr)
B. Lux (Technische Universitat Wien, Austria)

Emergence and Development of Science and Technology of Diamond Films in the U.S.S.R. (1 hr)
B. V. Spitsyn, Academy of Science, U.S.S.R.

Applications of Diamond Films (1 hr)
J. M. Pinneo (Crystallume, USA)

A special session on (a) High Deposition Rate Processes and (b) In Situ Diagnostics will be organized for the second Thursday evening session. The major lecturers will lead the discussion.

PART 4. SUMMARY

Panel Discussion: Where are we? Where do we go?

Summary: Opportunities and Needs
R.E. Clausing, J. C. Angus, and P. Koidl

NOTE:

(a) Two poster sessions are scheduled for contributed papers.

(b) A discussion period of 30 minutes has been scheduled after each lecture and 15 minutes after the other oral presentations. The discussion leaders have been chosen from the Directors and Organizing Committee and have been instructed to ensure that these periods provide a useful extension of the information presented during the lectures.

6/21/90
6375-MS-02

DIAMOND AND DIAMOND-LIKE FILMS AND COATINGS
NATO ADVANCED STUDY INSTITUTE, IL CIOCCO HOTEL
CASTELVECCHIO PASCOLI, ITALY
July 22 - August 3, 1990

PARTICIPANTS

Dr. Alexander E. Alexenko
Institute of Physical Chemistry
U.S.S.R. Academy of Science
Leninsky Prospect 31
Moscow 117915, U.S.S.R.
Phone: 234-00-14, Ext. 427 FAX: 7-095-2302332

Mr. David B. Allen
Carnegie Mellon University
900 S. Negley Avenue
Apt. 19
Pittsburgh, PA 15232
Phone: 412-441-9198 FAX:

Ms. Marylu Allouard
C.S.N.S. M.
Bat 108 Campus D'Orsay
91405 Orsay, France
Phone: 33-69415212 FAX: 33-169415268

Dr. Marianna Ambrico
Instituto di Chimica
Universitat Della Basilicata
85100 Potenza, Italy
Phone: 39-971-55743/55748 FAX: 39-334223

Dr. Bernard Andre
Centre d'Etudes Nucleaires de Grenoble
Department d'Etudes des Materiaux
Section de Genie des Surfaces
BP-85X
38041 Grenoble, Cedex, France
Phone: 33-76-884034 FAX: 33-76-885130

Prof. John C. Angus
Department of Chemical Engineering
Case Western Reserve University
Cleveland, OH 44106
Phone: 216-368-4133 FAX: 216-368-3016

Dr. Nagappan K. Annamalai
U.S. Air Force - RADC/ESR
Hanscom Air Force Base, MA 01731
Phone: 617-377-3047 FAX: 617-377-5041

Dr. Thomas R. Anthony
General Electric Company
GE Research Laboratories
P.O. Box 8, K15B39
Schenectady, NY 12301
Phone: 518-387-6160 FAX: 518-387-5592

Dr. Peter K. Bachmann
Philips Research Laboratories
P.O. Box 1980
Aachen D-5100, FRG
Phone: 49-241-600-3314 FAX: 49-241-600-3465

Dr. Joseph A. Baglio
GTE Laboratories, Inc.
40 Sylvan Road
Waltham, MA 02254
Phone: 617-890-4224 FAX: 617-890-9320

Dr. William F. Banholzer
Manager, Advanced Inorganic
Materials Labortory
GE Corporate Research & Development
Building K-1; Room 5A59
P.O. Box 8
Schenectady, NY 12301
Phone: 518-387-5951 FAX: 518-387-7563

Dr. Vincenzo Barbarossa
Eniricerche SPA
Via E. Ramarini 32
00015 Monterotondo (Rome), Italy
Phone: 39-690021279 FAX: 39-690021243

Dr. Alessandro Bellone
Olivetti Office
Via Jervis 20
10015 Ivres (Turin), Italy
Phone:
FAX: 39-125528116

Mr. Antonio Sao Miguel Bento
Physics Department
University of Coimbra
P-3000 Coimbra, Portugal
Phone: FAX: 351-39-29158

Dr. J. Y. Bhardwaj
Surface Technology Systems, Ltd.
Prince of Vales Industrial Estate
Abbrcarn, Gwent. NP1 6AR
United Kingdom
Phone: 44-495-244459 FAX: 44-495-249476

Mr. Bart Blanpain
c/o Prof. J. R. Roos
Katholicke Universiteit Leuven
Department Metallkunde en
Toegepaste Materiaalkunde
de Croylaan 2
B-3030 Heverlee, Belgie
Phone: 32-16220931 FAX: 32-16207995

Mr. Pierre Bou
C.N.R.S.
Centre de Recherches sur la Chimie
de la Combustion et des Hautes Temperatures
1C Av. de la Recherche Scientifique
45071 Orleans Cedex 2, France
Phone: 33-38515489 FAX: 33-38642670

Dr. Elisa Bourdon
Department of Physics
York University
4700 Keele Street
North York, Ontario, Canada M3J IP3
Phone: 416-736-2100 FAX: 416-736-5516

Dr. Pascal Bradu
DRET/SDR/G34
25/6 Boulevard Victor
75996 Paris-Armees, France
Phone: 33-45524737 FAX: 33-145524681

Dr. Hans-Gerd Busmann
Fakultat fur Physik und F-M-F
Albert-Ludwig-Universitat
Hermann-Herder Strasse 3
D-7800 Freiburg, FRG
Phone: 49-761-2033432 FAX: 49-761-2034527

Dr. A. Campargue
Laboratoire de Spectrometrie Physique
BP-87
38402 St. Martin d'Heres, France
Phone: 33-76514319 FAX: 33-76514544

Dr. Yves Catherine
Laboratoire des Plasmas et des Couches Minces
institut de Physique et Chimie des Materiaux
UMR C.N.R.S. 110
2 rue dela Houssiniere
44072 Nantes Cedex 03, France
Phone: 33-40373965 FAX: 33-40373991

Dr. P. R. Chalker
Materials Development Division
Harwell Labortory
Oxfordshire OX11 ORA, United Kingdom
Phone: 44-235-821111 FAX: 44-235-432916

Dr. Robert E. Clausing
Metals and Ceramics Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6093
Phone: 615-574-4084 FAX: 615-574-7659

Dr. John W. Coburn
Department K33/801
IBM Almaden Research Center
650 Harry Road
San Jose, CA 95120
Phone: 408-927-2414 FAX: 408-927-2100

Dr. G. Cocito
Head, Optical Technologies Department
CSELT
Via G. Reiss Romoli, 274
10148, Torino, Italy
Phone: 39-11-2169256 FAX: 39-11-2169520

Dr. Olinda Conde
Physics Department
University Lisbon
Lisbon, Portugal
Phone: 351-39-28725 FAX: 351-39-29158

Dr. Joseph B. Darby, Jr.
Division of Materials Sciences
Office of Basic Energy Sciences
Department of Energy
G-226, ER-13
Washington, D.C. 20585
Phone: 301-353-3884 FAX: 301-353-6594

Prof. F. Demichelis
Dipartimento di Fisica
Politecnico di Torino
Corso Duca degli Abruzzi, 24
10129 Torino, Italy
Phone: 39-11-5567321 FAX: 39-11-5567399

Dr. Paolo DeTassis
R&D Manager
Clevite Italy
Via B. Todesca 12
38100 Trento, Italy
Phone: 39-461-990321 FAX: 39-461-991860

Dr. Robert C. DeVries
17 Van Vorst Drive
Burnt Hills, NY 12027
Phone: 518-399-5225 FAX: 614-438-2235

Prof. Rodney Dillon
Department of Electrical Engineering
209N WSEC
University of Nebraska
Lincoln, NE 68588-0511
Phone: 402-472-5891 FAX: 402-472-4732

Ms. Concetta deMartino
Department of Nuclear Engineering
c/o Prof. F. Demichelis
Dipartimento di Fisica
Politecnico di Torino
Corso Duca degli Abruzzi, 24
10129 Torino, Italy
Phone: 39-11-3358240 FAX: 39-11-5567399

Ms. Filomena Pinto DosSantos
Physics Department
University of Coimbra
P-3000 Coimbra, Portugal
Phone: FAX: 351-39-29158

Dr. Jean-Jacques Dubray
Ceramic Science & Engineering Department
217, Steidle Building
University Park, PA 16802
Phone: 814-865-7131 FAX: 814-865-2917

Dr. Rainer Dohl-Oelze
VDI Technologiezentrum
Graf-Recke Strasse 84
4000 Dusseldorf 1, FRG
Phone: 49-211-6214567 FAX: 49-211-6214575

Prof. Helmut Ehrhardt
Fachbereich Physik
Universitat Kaiserslauten
Erwin-Schrodinger Strasse 46
6750 Kaiserslauten, FRG
Phone: 49-631-2052382 FAX: 49-631-2053300

Dr. Svend Stensig Eskildsen
Danish Technological Institute
Aarhus Tribology Centre
Teknologiparken
DK-8000 Aarhus C, Denmark
Phone: 45-86-142400 FAX: 45-86-147722

Dr. Hermann Ferber
Daimler Benz
Department FVG/CH
Postfach 600202
7000 Stuttgart, FRG
Phone: 49-711-1722211 FAX: 49-711-1753267

Dr. John E. Field
Cavendish Laboratory
University of Cambridge
Madingley Road
Cambridge CB3 OHE, United Kingdom
Phone: 44-223-337318 FAX: 44-223-63263

Dr. Stefano Fontana
Gruppo di Scienza della Superfici
Eniricerche
00016 Via Ramarini
Monterotondo (Rome), Italy
Phone: 39-690021263 FAX: 39-690021243

Dr. Michael Frenklach
Materials Science and Engineering
Pennsylvania State University
University Park, PA 16802
Phone: 814-865-4392 FAX: 814-865-3075

Dr. Michael Geis
Microelectronics
Lincoln Laboratory
Massachusetts Institute of Technology
224 Wood Street
Lexington, MA 02173
Phone: 617-981-7810 FAX: 617-981-4983

Prof. Alfred Grill
Ben Gurion University
Beer-sheva, Israel
Phone: 617-945-1492 FAX: 914-945-2141

IBM Research Division
T.J. Watson Research Center
23-227, P.O. Box 218
Yorktown Heights, NY 10598

Mr. Steve Grot
Department of Electrical Engineering
Center for Electronic Materials Programs
130 Hammond Building
Pennsylvania State University
University Park, PA 16802
Phone: 814-865-9432 FAX:

Mr. Lee Heatherly, Jr.
Metals and Ceramics Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6093
Phone: 615-574-5088 FAX: 615-574-7659

Prof. Reinhard Helbig
Lehrstuhl fur Angewandte Physik
Universitat Erlangen-Nurnberg
Gluckstrasse 9
D-8520 Erlangen, FRG
Phone: 49-9131-858425 FAX: 49-9131-858423

Dr. Hans-Jurgen Hinneberg
ISI-2, KFA Julich
Postfach 1913
D-5170 Julich, FRG
Phone: 49-2461-613149 FAX: 49-2461-614673

Mr. John Richard Honeybone
Physics Laboratory
University of Kent
Canterbury, kent CT27NR, United Kingdom
Phone: 44-227-764000 FAX: 44-227-762616

Dr. Linda L. Horton
Metals and Ceramics Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6118
Phone: 615-574-5081 FAX: 615-574-7659

Mr. David G.K. Jeng
Department of Electrical Engineering
State University of New York
Stony Brook, NY 11794
Phone: 516-567-0520 FAX: 516-567-0684

Mr. Piere Joeris
c/o Dr. Carsten Benndorf
Universitat Hamburg
Institut fur Physikalische Chemie
Bundesstrasse 45
2000 Hamburg 13, FRG
Phone: 49-40-41233455 FAX: 49-40-41232449

Prof. Rafael Kalish
Director, Solid State Institute
Israel Institute of Technology
Technion City
Haifa, 32 000, Israel
Phone: 972-4293906 FAX: 972-4221581

Dr. Alexander W. Koch
Max-Planck-Institut fur Plasmaphysik
Boltzmannstrasse 2
D-8046 Garching bei Munchen, FRG
Phone: 49-89-3299601 FAX: 49-89-32999200

Prof. Peter Koidl
Fraunhofer Institut fur
Angewandte Festkorperphysik
Eckerstrasse 4
D-7800 Freiburg, FRG
Phone: 49-761-5159280 FAX: 49-761-515920

Dr. Ritalba Lamendola
Centro di Studio Chimica de Plasmi
Dipartiment di Chimica
Universita degli studi Bari
Via Amendola 173
Bari, Italy
Phone: 39-80-242009 FAX: 39-80-242129

Prof. Mauro Lenzi
Institute Metodologie Avanzate Inorganiche
C.N.R.
Area della Ricerca di Roma
Via Salaria Km 29 300, Carella Pottale 10
00016 Monterotondo Salo (Roma), Italy
Phone: 39-6-80020218 FAX: 39-6-9005849

Dr. A. H. Lettington
Royal Signals and Radar Establishment
St. Andrews Road
Great Malvern, Worcs.
WR14 3PS, United Kingdom
Phone: 44-684-894658 FAX: 44-684-894540

Mr. Roland Locher
Fraunhofer Institut fur
Angewandte Festkorperphysik
Eckerstrasse 4
7800 Freiburg, FRG
Phone: 49-761-5159282 FAX: 49-761-5159200

Dr. Benno Lux
Institut fur Chemische Technologie
Anorganischer Stoffe
Technische Universitat Wien
Getreldemarkt 9/161
A-1060 Wien, Austria
Phone: 43-222-58801 FAX: 43-22-5874835

Dr. Ida Veronica Marotta
V. Adriatico No. 9
8500 Potenza, Italy
Phone: 39-971-45678 FAX: 39-971-474223

Dr. Ludvik Martinu
Department of Engineering Physics
Ecole Polytechnique
Case Postale 6079, Succursale A
Montreal, Canada H3C 3A7
Phone: 514-340-4099 FAX: 514-340-4440

Dr. Alan Matthews
Department of Engineering
Design and Manufacture
The University of Hull
Cottingham Road
North Humberside, HU6 7RX, United Kingdom
Phone: 44-482-465073 FAX: 44-482-466205

Dr. Carl J. McHargue
Metals and Ceramics Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6118
Phone: 615-574-4344 FAX: 615-574-7659

Ms. Karen McNamara
Department of Chemical Engineering
66-421
Massachusetts Institute of Technology
Cambridge, MA 02139
Phone: 617-253-6480 FAX:

Dr. Ida Veronica Marotta
Via Adriatico No. 9
85100 Potenza
Italy
Phone: 39-971-45678 FAX: 39-971-474223

Mr. Jean Mercier
IEPES
BP 166
38092 Grenoble Cedex, France
Phone: 33-76-881183 FAX: 33-76-887988

Dr. Koichi Miyata
Kobe Steel Research Laboratory USA
79 TW Alexander Drive
Bldg. 4401, Suite 101
Box 13608
Research Triangle Park, NC 27709
Phone: 919-549-9823 FAX: 919-549-9106

Prof. Wolfhard Möller
Max Planck Institut ur Plasmaphysik
Boltzmannstrasse 2
D-8046 Garching, FRG
Phone: 49-89-3299312 FAX: 49-89-32999591

Dr. Renato Mondini
Via delle Volta, 94
I-25129 Bresua, Italy
Phone: 39-30-347491 FAX: 39-30-342906

Prof. Masao Murakawa
Nippon Institute of Technology
4-1 Gakuendai
Miyashiro-town
Saitama 345, Japan
Phone: 81-480-344111 FAX: 81-480-342941

Dr. Peter S. Nielsen
NKT Corporate Research & Development
Building 61, Sognevj 13
DK-2605 Broendby, Denmark
Phone: 45-43432010 FAX: 45-42630099

Dr. Peter Oelhafen
Institut fur Physik
Universitat Basel
klingelbergstrasse 82
CH-4056 Basel, Switzerland
Phone: 41-61-3212244 FAX: 41-61-3211440

Mr. Michael E. O'Hern
Department of Materials Science
and Engineering
Dougherty Engineering Hall
University of Tennessee
Knoxville, TN 37996
Phone: 615-574-4344 FAX: 615-574-7659

Dr. Ahmet Oztarhan
Dokuz Ezlul Universitesi
Mukendislik Mimarlik Fakultesi
Mikina Muhendisligi Bolumu
35100 Bornova, Izmir, Turkey
Phone: 90-51-183138 FAX: 90-51-216148

Prof. Paolo Paroli
Dipartimento di Ingegneria Meccanica
II Universita dgli Studi di Roma
Via Orazio Raimondo
I-00173 Roma, Italy
Phone: 39-624990664 FAX: 39-624990662

Ms. Deborah T. Peeler
353 Charlotte Avenue
Lebanon, OH 45036
Phone: 513-932-0784 FAX:

Dr. J. M. Pinneo
Crystallume, Inc.
125 Constitution Drive
Menlo Park, CA 94025
Phone: 415-324-9681 FAX: 415-324-2958

Dr. Jean Claude Pivin
C.S.N.S. M.
Bat 108 Campus D'Orsay
91405 Orsay, France
Phone: 33-69415212 FAX: 33-69415268

Prof. Nicolaos S. Platakis
School of Chemical Engineering
Aristotelian University of Thessaloniki
Faculty of Technology
Thessaloniki 54006, Greece
Phone: 31-991547 FAX: 31-206138

Dr. Roger W. Pryor
Institute for Manufacturing Research
Wayne State University
666 West Hancock Street
Detroit, MI 48202
Phone: 313-577-0846 FAX: 313-577-7743

Ms. Lou Pyatt
Institute Secretary
Metals and Ceramics Division
Oak Ridge National Laboratory
P.O. Box 2008
Oak Ridge, TN 37831-6118
Phone: 615-574-4344 FAX: 615-574-7659

Ms. Petra Reinke
max-Planck-Institut fur Plasmaphysik
Boltzmannstrasse 2
D-8046 Garching bei Munchen, FRG
Phone: 49-89-32991757 FAX: 49-89-32992591

Dr. John Robertson
Central Electricity Research Laboratory
GB-Leatherhead KT22-7SE, UK
Phone: 44-372-374488, Ext. 2209 FAX: 44-372-374488-2515

Dr. Klaus C. Rohwer
Institut fur Solarenergieforschung
Sokelantstrasse 5
D-3000 Hannover 2, FRG
Phone: 49-511-35850, Ext. 44 FAX: 49-511-35850-10

Mr. Louis St.Onge
Physics Department
University of Montreal
P.O. Box 6128
Montreal, Canada H3C 3J7
Phone: 514-343-6671 FAX: 514-343-2071

Dr. Nobuo Setaka
Director General
National Institute for Research
in Inorganic Materials
1-1 Namiki, Tsukuba
Ibaraki, 305 Japan
Phone: 81-298-513351 FAX: 81-298-527449

Dr. Lothar Schäfer
Philips GmbH
Forschungslaboratorium
Vogt-Kolln Strasse 30
D-2000 Hamburg 54, FRG
Phone: 49-40-5493-560 FAX: 49-40-5493-210

Dr. Howard K. Schmidt
Schmidt Instruments,Inc.
2476 Bolsover No. 234
Houston, TX 77005
Phone: 713-529-9040 FAX: 713-529-8411

Dr. Jose F. Azevedo Silva
Departamento de Fisica
Faculdade de Ciencias
Campo Grande, Ed. Cl, Piso 4
1700 Lisboa, Portugal
Phone: 351-1-7583141 FAX: 351-1-7597716

Dr. Piran Sioshansi
Vice President
Ion Implantation
SPIRE Corporation
Patriots park
Bedford, MA 01730
Phone: 617-275-6000, Ext. 271 FAX: 617-275-7470

Dr. Roger Smith
Department of Mathematical Sciences
University of Technology
Loughboroughm Leicestershire LE11 3TU, United Kingdom
Phone: 44-509-263171 FAX:
BITNET: MULTICS.LUT.AC.UK

Dr. Galina A. Sokolina
Institute of Physical Chemistry
U.S.S.R. Academy of Sciences
Leninsky Prospect 31
Moscow 1117 915, U.S.S.R.
Phone: 7-95-2340014, Ext. 427 FAX: 7-95-2302332

Dr. Boris V. Spitsyn
Institute of Physical Chemistry
U.S.S.R. Academy of Sciences
Leninsky Prospect 31
Moscow 1117 915, U.S.S.R.
Phone: 7-95-2340014, Ext. 427 FAX: 7-95-2302332

Prof. F. Stoeckel
c/o Dr. A. Campargue
Laboratoire de Spectrometrie Physique
BP-87
38402 St. Martin d'Heres, France
Phone: 33-76514600 FAX: 33-76514544

Dr. J-E. Sundgren
Department of Physics
Linköping University
Linköping S-581 83, Sweden
Phone: 46-131281000 FAX: 46-13137568

Dr. Alberto Tagliaferro
Dipartimento di Fisica
Politecnico di Torino
Corso Duca degli Abruzzi, 24
10129 Torino, Italy
Phone: 39-11-5567329 FAX: 39-11-55677399

Dr. F. Teyssandier
IMP-CNRS
Universite
66025 Perpignan Cedex, France
Phone: FAX: 33-68668499

Prof. D. E. Tsatis
University of Patras
Physics Department
Patra 2610, Greece
Phone: 61-993133 FAX: 61-991980

Dr. Yonhua Tzeng
Department of Electrical Engineering
200 Broun Hall
Auburn University
Auburn, AL 36849-5201
Phone: 205-844-1869 FAX: 205-844-2432

Dr. Steven M. Valone
Materials Science and Technology Division
Los Alamos National Laboratory
Los Alamos, NM 87545
Phone: 505-667-2067 FAX: 505-665-2104

Prof. Rui Vilar
Department of Engineering Materials
Instituto Superior Technico
Av. Rovisco Pais
1096 Lisboa, Codex, Portugal
Phone: 351-1-802045 FAX: 351-1-899242

Mr. Victor vonBonin
IGV, KFA Julich
Postfach 1913
D-5170 Julich, FRG
Phone: 49-2461-615925 FAX: 49-2461-613907

Prof. M. R. Wertheimer
Department of Engineering Physics
Ecole Polytechnique
Case Postale 6079, Succursale A
Montreal, Canada H3C 3A7
Phone: 514-340-4749 FAX: 514-340-4440

Dr. Ch. Wild
Fraunhofer Institut fur
Angwandte Festkorperphysik
Eckerstrasse 4
D-7800 Freiburg, FRG
Phone: 49-761-5159280 FAX: 49-761-515920

Mr. Brad Williams
Department of Materials Science & Engineering
North Carolina State University
Box 7907
Raleigh, NC 27695-2031
Phone: 919-737-2031 FAX:

Prof. Frank J. Worzala
Department of Materials Science & Engineering
University of Wisconsin-Madison
1509 University Avenue
Madison, WI 53706
Phone: 608-262-0389 FAX: 608-262-6707

Dr. Max Yoder
Office of Naval Research
800 N. Quincy Street
Arlington, VA 22217-5000
Phone: 202-696-4218 FAX: 202-696-3945

Mr. Mark Zaleski
Department of Materials Science
Bard Hall
Cornell University
Ithaca,NY 14853
Phone: 607-255-4648 FAX:

Dr. James R. Zeidler
Code 7601
Naval Ocean Systems Center
San Diego, CA 92152-5000
Phone: 619-553-1581 FAX: 619-553-6003