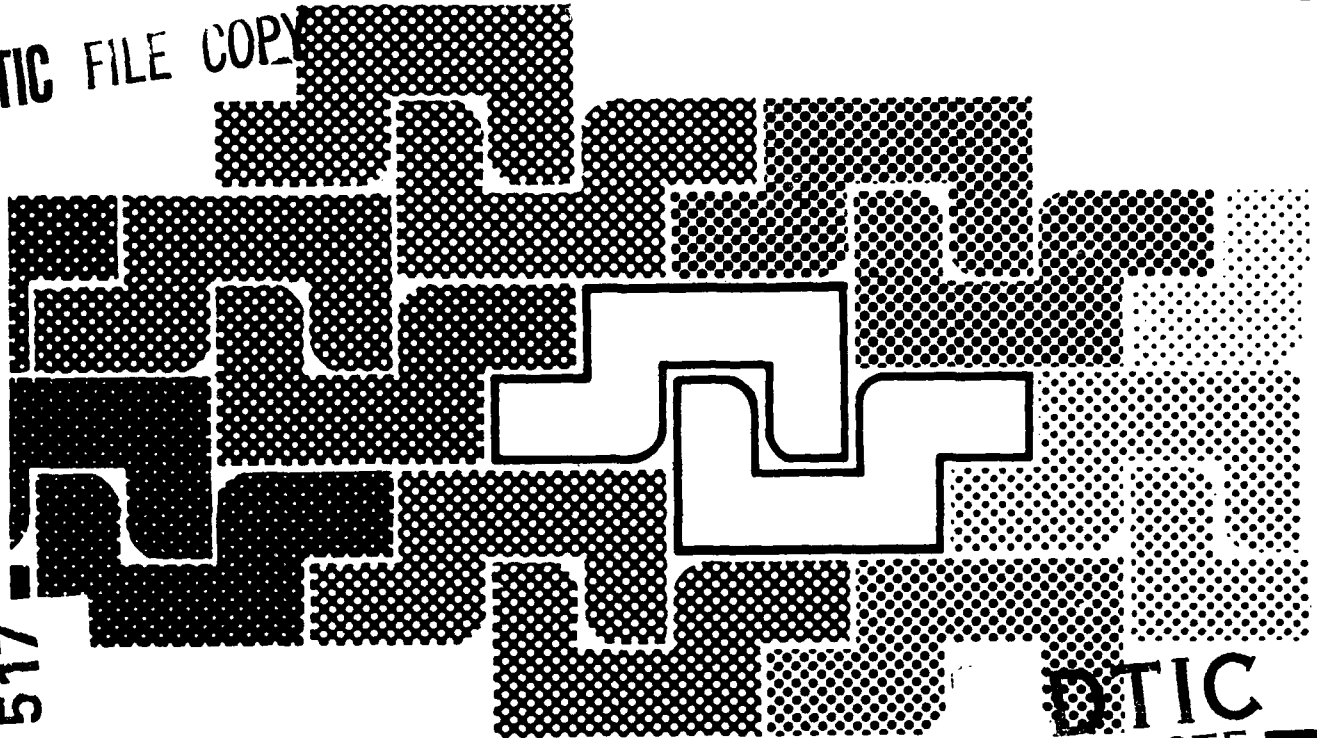


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**NATO-ADVANCED STUDY INSTITUTE
DIAMOND AND
DIAMOND-LIKE FILMS
AND COATINGS**

IL CIOCCO, CASTELVECCHIO PASCOLI, ITALY

JULY 22 - AUGUST 3, 1990

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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 considerable 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	<u>per person per day</u>
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.

Transportation:

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	Opening - Clausing	Coburn	De Vries	Catherine	McHargue	Free or Excursion to Florence
	Yoder					
0900	Coffee Break	Coffee Break	Coffee Break	Coffee Break	Oelhafen	
1000	Field	Coburn	Angus	Catherine	Coffee Break	
1100		Discussion		Discussion	Kalish	
1200		Chalker		Mackowski	Martinu	
1300	Discussion		Discussion	Wild	Discussion	
	Lunch	Discussion Lunch		Discussion Lunch	Lunch	
1700	Refreshments	Refreshments	Excursion to Pisa or Free	Refreshments	Refreshments	
1800	Sungren	Smith		Robertson	Möller	
1900					Discussion	
2000	Discussion Reception	Discussion Wine & Cheese		Discussion	Discussion	
2100	Dinner	Dinner	Dinner	Barbecue	Dinner	Dinner

Sunday July 29	Monday July 30	Tuesday July 31	Wednesday August 1	Thursday August 2	Friday August 3	Saturday August 4
Free or Excursion to Siena and San Gimignano	Koidl	Anthony	Frenklach	Bachmann	Setaka	Buses to Pisa
	Coffee Break Koidl	Coffee Break Anthony	Coffee Break Frenklach	Coffee Break Bachmann	Coffee Break Setaka	
	Discussion	Discussion	Discussion	Discussion	Discussion	
	Lettington	Geis	Lux	Spitsyn	Pinneo	
	Discussion Lunch	Discussion	Discussion Lunch	Discussion Lunch	Discussion Lunch	
	Refreshments	Picnic	Excursion to Lucca or Free	Refreshments	-----1500----- Panel Discussion	
	Poster Session I	Special Session a) High rate deposition b) In situ diagnostics [Speakers to be announced]		Poster Session II	-----1600----- Summary -----1630----- Institute Ends	
Dinner	Dinner	Dinner	Dinner	Gala Dinner	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 Sp'n Resonance 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
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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 applications 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
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University of Cambridge
Madingley Road, Cambridge CB3 0HE, 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 not 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 $5.50 \pm 0.15 \text{ Jm}^{-2}$ 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 $\langle 100 \rangle$ direction there is four-fold symmetry in the friction. The lowest friction is along the $\langle 011 \rangle$ or cube diagonal direction; the highest along the $\langle 100 \rangle$ or cube edge direction. If the cube face is polished in the $\langle 110 \rangle$ 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 $\langle 011 \rangle$ direction and low in the $\langle 100 \rangle$ direction. For diamond sliding on diamond under vacuum conditions, the friction can reach a high value ($\mu \sim 1$). The high friction is accompanied by a very high wear rate.

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

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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

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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

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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

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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 wavefront¹ 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 structure³ 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.

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REVIEW OF DIAMOND-RELATED MATERIALS

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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*

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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/cm³, 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/cm³ and polyacetylene 1.16 g/cm³. 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/cm³, which is significantly greater than that of graphite (2.26 g/cm³), 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.

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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 Street⁴ 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 Jansen⁷ 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 hydrogenated 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 studies¹¹ 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

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PREPARATION TECHNIQUES FOR DIAMOND-LIKE CARBON

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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, 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

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ABSTRACT NOT AVAILABLE

PROCESS CHARACTERIZATION OF a-C:H PLASMA DEPOSITION

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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

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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

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

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 $\approx 1350 \text{ cm}^{-1}$, which tends to be used for more ordered graphitic carbons.

The electronic 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 ≈ 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 measurements by Stohr¹² 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 diborane, 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}

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MECHANICAL PROPERTY MEASUREMENTS OF THIN
FILMS AND HARD MATERIALS*

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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.

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

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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

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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

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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.

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COMPUTER MODELLING OF C:H FILM GROWTH

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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

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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 + H₂ 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

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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 $>0.2 N_0$ atoms/cm³, where N_0 is Avogadro's number. Hydrogen is incorporated with typical concentrations of H/C $\approx$ 0.5. A major fraction of the carbon atoms are sp³ hybridized in contrast to evaporated amorphous carbon which consists totally of sp² 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 $10^{-12} \Omega^{-1}\text{cm}^{-1}$. 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

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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- μ m 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

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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 pyrolyzed 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*

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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 $2000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ 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.

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THEORY AND MODELS FOR NUCLEATION OF DIAMOND

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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 graphite 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 should 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 Chemistry

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 O₂ 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 nucleation 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

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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 defect-free Si wafer 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.

B. Lux
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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 ionically bonded carbides, seem to be detrimental not only for nucleation, but also for adherence.

CHARACTERIZATION AND PROPERTIES OF ARTIFICIALLY GROWN DIAMOND

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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 paper¹ 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 1987² 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 $\approx 1332 \text{ cm}^{-1}$. 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.

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

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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 1×10^{-3} $\mu\text{m/h}$) 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 excited 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

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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

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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 $\sim 1 \times 10^8$ dynes/cm² 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.

P O S T E R S

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

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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 $10^{15}/\text{cm}^2\text{-s}$ 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

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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

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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 (Kaptontm) 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

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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

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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 3×10^{-4} Pa residual pressure to 0.5 at. % for 6.4×10^{-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

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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 phosphine, 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)

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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) back-scattering 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

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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

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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 $[N(E_f)/\alpha]^{1/2}$. This is inconsistent with the constancy of the $\ln \sigma$ vs $(1/T)^{1/4}$ slope near room temperature which hinders the constancy of $N(E_f) \cdot \alpha^3$.

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

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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

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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

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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

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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*

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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.

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Howard K. Schmidt
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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)

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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*

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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.

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

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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

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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 $150 \times 120 \mu\text{m}^2$ 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 $150 \times 120 \mu\text{m}^2$. 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

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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 defects⁴ 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.

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

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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

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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

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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 $800^\circ C$, 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 CH₄ SOURCES

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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 H₂ (99.5%)-/CH₄ (0.5%) plasma. This deposition system was changed for the present investigation into a flow reactor, allowing a separate feeding of H₂ and CH₄. With this modification, atomic hydrogen is initially the only reactive species. In the flow reactor ·CH₃ (and other radicals) are formed outside the microwave discharge. The ·H/·CH₃ 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

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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

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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.

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

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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 H₂ at a total flow rate of 100 sccm. Additionally, films were deposited with trimethylboron added to the CO/H₂ 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.

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

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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 GHz microwave) at the deposition area. Then the high density plasma (above $1 \times 10^{11}/\text{cm}^3$) 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

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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 torch. By judicious selection of plasma reaction gases and the use of a reaction retort we have achieved growth rates in the range of 500 $\mu\text{m/h}$. 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

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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% H₂, 1% CH₄) 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

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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 $2 \cdot 10^{-3}$ 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/cm² 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

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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

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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

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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

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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*

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Diamond films have been deposited on silicon, molybdenum, aluminum and various other substrates by either a stationary¹ or a scanning² oxy-acetylene flame. The as-deposited diamond films exhibit high electrical resistivity³ 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 μ m for the flame deposited diamond films in comparison with those deposited from hydrocarbon plasmas with hydrogen dilution.

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⁴Y. 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

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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 as 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***

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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

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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

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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 $\langle 110 \rangle$ textures, and a third special material grown under conditions which produce "near $\langle 100 \rangle$ " 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 determination² and the TEM microstructural analysis¹ 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 $\langle 100 \rangle$ 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

R. E. Clausing
Page 2

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/mm² and a modulus of 1.1×10^5 kg/mm² 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- μ m thick while they were still attached to the silicon {100} substrates on which they were grown.

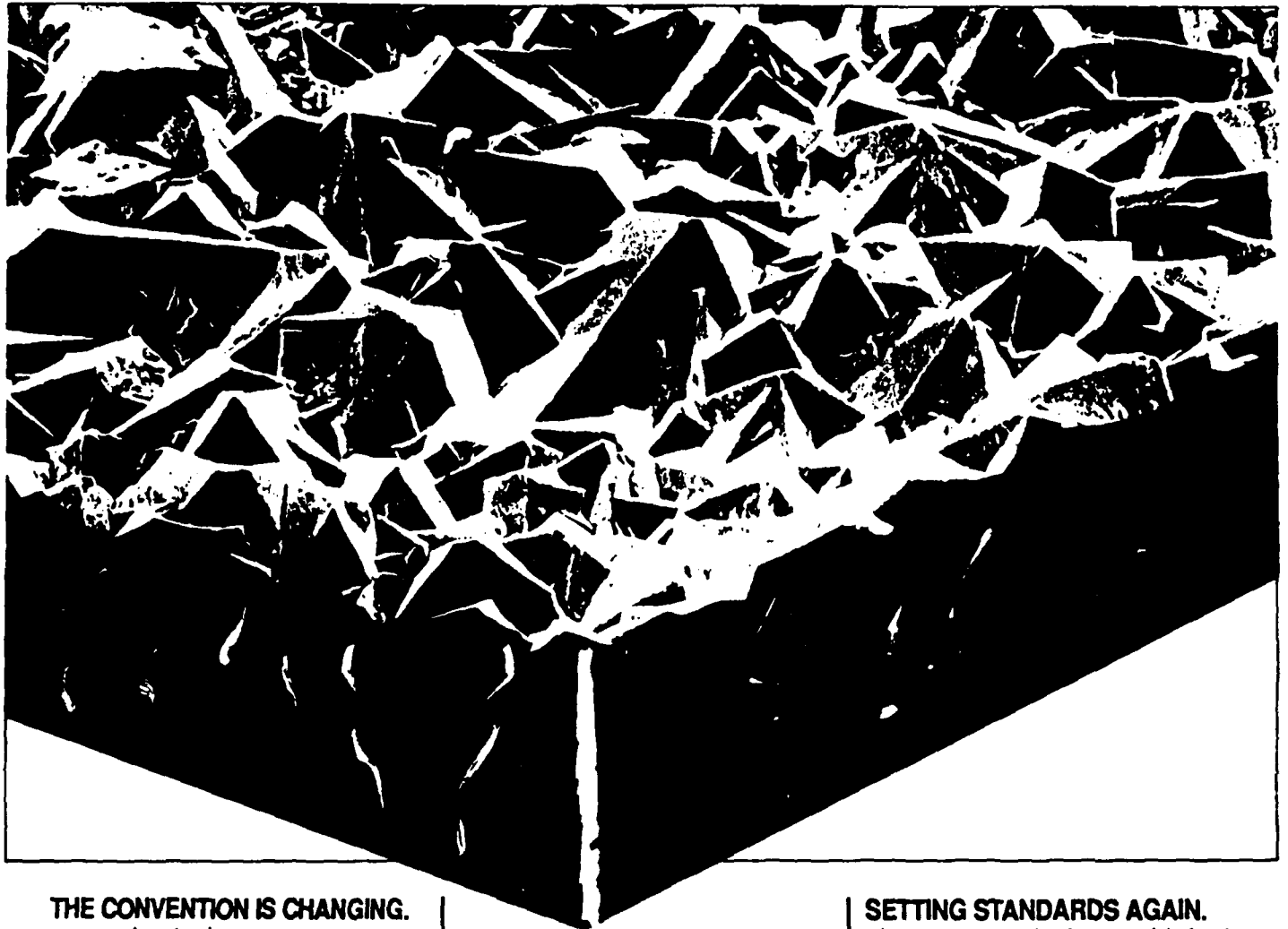
Acknowledgement

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.

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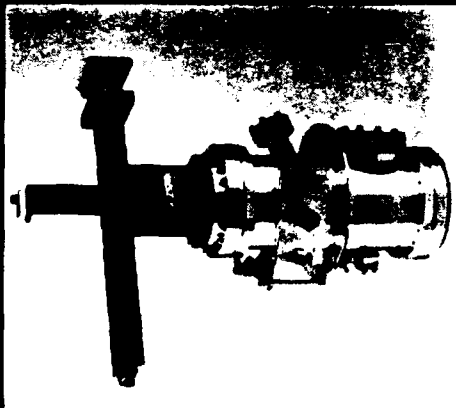
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1. Direct mailing of 1000 first announcement folders (attached). The mailing list was developed from the attendance list of the MRS-Europe Conference on Amorphous Hydrogenated Carbon Films-1987; the MRS Symposium on Diamond Films-1989; the USA Defense 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)
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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, Castelvechio 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.

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Metals, Vol. 75, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 76, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 77, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 78, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 79, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 80, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 81, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 82, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 83, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 84, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 85, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 86, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 87, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 88, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 89, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 90, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 91, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 92, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 93, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 94, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 95, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 96, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 97, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 98, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 99, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.
Metals, Vol. 100, Proceedings of the Metallurgical Society of the Institute of Materials, London, UK, 1989, Pergamon Press, New York, NY.

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 metal 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. Zaher, Novotek Corporation, Gaithersburg, MD, 1988.
Effects of Welding on Health VI, American Welding Society, Miami, FL, EWHV, 1988.
Electronics Structure and Lattice Defects in Alloys, United States Japan Seminar, Hiroshima, HI, May, 1987, Trans Tech Publications, Boston, VT.
Losses in Plastic Deformation and Fracture, Ottawa, Canada, 1989, National Research Council, Ottawa, Canada.
Fracture, The International Conference, IJFF, Advances in Fracture Research, Vol. 1, 1989, Elsevier, London, TN, March 1989, Pergamon Press, Oxford.
Fracture Technology and Proceedings of the 11th Symposium on Fracture in Technology, Vol. 1, 1989, Elsevier, London, TN, March 1989, Pergamon Press, Oxford.
High Power Lasers, Vol. 1, 1989, Pergamon, Oxford, 1987.
High Temperature Materials in Engineering, Metal Ceramics, Plastics, 1989 European Conference, London, UK, April 1989, IBC Technical Services, London, UK.
Ironmaking, 4th International Conference, IL April 1989, Iron and Steel Society, Warrendale, PA.
IL November-December 1988, American Society for Mechanical Engineers, New York, NY, 1988.
Materials and Engineering Design, 1988/1989, The Next Decade, B.E. Dym, 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, Ingeniørskolen Helsingør Teknisk, Helsingør, Denmark.
Process Gas Handling and Cleaning, Proceedings of the International Symposium, Vol. 11, 28th Annual Conference of Metallurgists of CIM, C. Two, Moncton, Canada, August 1989, Pergamon Press, New York.
Processing of Ceramic and Metal Matrix Composites, Proceedings of the International Symposium, 28th Annual Conference of Metallurgists of CIM, Vol. 17, Halifax, Canada, August 1989, Pergamon Press, New York.
Processing of Composites, 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 Nonferrous Metals Industry, Concentrates and Recycled Commodities, International Symposium, Hamburg, FRG, May 1989, Gesellschaft Deutscher Metallhütten- 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

1-11 Mar, Indianapolis, IN - 12th Int'l Treat- ing Conference/Exposition, ASM Heat Treat- ing Division.
24-29 Mar, Los Angeles, CA - WESTEC '89, Western Metal and Tool Exposition, ASM, SNE and AMTA.
24-29 Mar, Miramar Beach, FL - 1989 National Ap- plication of New Ultra Alloy, ASM.
11-16 April, Phoenix, AZ - LTA Association and Re- pair Technology and Materials in Turbine Engines Symposium, ASM.
10 May, Oak Ridge, TN - 4th Annual Com- posite Materials, ASM Specialty Materials Division.
21-24 May, Long Beach, CA - 3rd National Ther- mal Spray Conference/Exposition, ASM Thermal Spray Division.
21-24 May, Long Beach, CA - AER, MAT, Ad- vanced Aerospace Materials Processes Con- ference/Exposition, ASM.
21-24 May, Long Beach, CA - Lasers in Ma- terials Processing, ASM W. Coast Exten- sion Liaison Committee.
11-14 June, Glasgow, Scotland - 10th Inter- national 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 and Ann Arbor, ASM ESD (ERA/TEC), 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 Con- ference on Fossil Energy Materials. For more information contact D.N. Brack, Oak Ridge National Laboratory, P.O. Box 248, Oak Ridge, TN 37831-0248, 615-574-5792.
20-21 May, Cleveland, OH - Workshop on the Science and Technology of Diamond Thin Films, sponsored by Case Western Reserve University. For more information contact John C. Angus, Chemical Engineering Department, Case Western Reserve Univer- sity, Cleveland, OH 44106.
20-21 Aug, Wrightsville Beach, NC - 47th Sea Beach Institute Meeting. For more information contact L.E. Barker at Laque Center for Chemical Technology, Inc., P.O. Box 156, Wrightsville Beach, NC 28406, 919-256-2271.
21-22 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 Meeting and Metallurgical Coatings. For more information contact Prof. T. Shaojie, 10th ICM, The Chinese Society of Metals, 36 Dongsi Dajie, Beijing 10071, 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 248, Oak Ridge, TN 37831-0248.

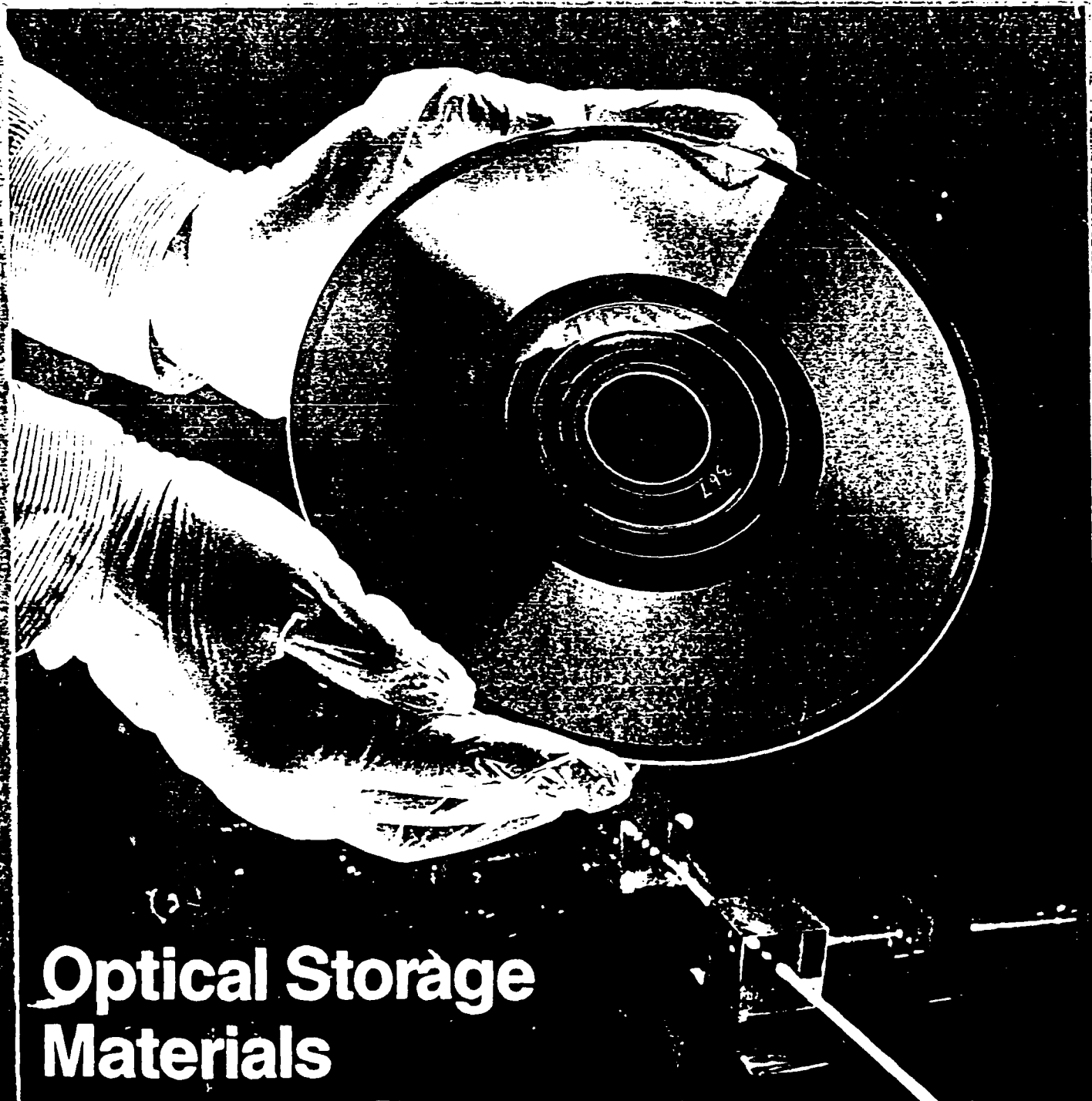
MRS

BULLETIN

April 1990

Volume XV, Number 4

Serving the International Materials Research Community



**Optical Storage
Materials**

- 11-14
19th Biennial Conference on
National Materials Policy
Williamsburg, VA
E. Houston, Federation of
Materials Societies, 1707 L St.,
NW, Suite 333, Washington, DC
20036, (202) 296-9282
- 11-15
Basic Course: SEM and X-Ray
Microanalysis
Bethlehem, PA
J. J. Goldstein, Dept. of Materials
Science and Engineering, Bldg. 5,
Lehigh University, Bethlehem, PA
18015, (215) 756-5133
- 11-15
Gordon Research Conference on
Condensed Matter Physics
Worcester, MA
A. M. Crosshank, Gordon
Research Center, Univ. of Rhode
Island, Kingston, R. 02881-0801
(401) 783-4211, fax (401) 783-
7644
- 11-15
10th International Conference on
Vacuum Metallurgy
Beijing, China
T. Shaojie, Chinese Society of
Metals, 46 Dongxixi, Dake, Beijing
100711, China, fax 512 4122
- 12-14
4th International Electronic
Materials and Processes
Conference
Albuquerque, NM
SAWPE, P.O. Box 2459, Covina,
CA 91722, (618) 331-0616,
fax (618) 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, 358-04512600,
fax 3580-462373
- 18-21
Advanced Topics: SEM and X-Ray
Microanalysis
Bethlehem, PA
J. J. Goldstein, Dept. of Materials
Science and Engineering, Bldg. 5,
Lehigh University, Bethlehem, PA
18015, (215) 756-5133
- 18-21
Analytical Electron Microscopy
Bethlehem, PA
J. J. Goldstein, Dept. of Materials
Science and Engineering, Bldg. 5,
Lehigh University, Bethlehem, PA
18015, (215) 756-5133
- 15-21
5th International Conference on
Metallurgical Labor Phase Epitaxy
Aachen, Germany
H. Henke, Institut für Halbleiter-
technik, RWTH Aachen, Templer-
graben 55, D-5100 Aachen, W.
Germany, 241 60 77 50, fax
(241) 80 77 51
- 15-22
C-MRS International '90
Beijing, China
Hengfu Dai, Dept. of Materials
Science & Engineering, Tsinghua
Univ., Beijing 100084, China
655646, fax (010) 25353
(See related article in
Vol. XX, No. 9)
- 16-Jun-29
Miniworkshop on Strongly
Correlated Electron Systems
Thessaloniki, Greece
Condensed Matter Group
Secretary, International Center for
Theoretical Physics, P.O. Box
586, 134100 Trieste, Italy, (040)
224241, fax 224531
- 21-22
Thin Specimen Preparation
Bethlehem, PA
J. J. Goldstein, Dept. of Materials
Science and Engineering, Bldg. 5,
Lehigh University, Bethlehem, PA
18015, (215) 756-5133
- 21-22
Workshop on MOMB, CBE,
GSMBE, and Related Techniques
Aachen, Germany
H. Henke, Institut für Halbleiter-
technik, RWTH Aachen, W.
Germany, Templergraben 55, D-
5100 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 546-664138
- 25-29
Gordon Conference on Defects in
Glass
Tilton, NH
R. J. Egan, 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. Futers, Computational
Mechanics Institute, Ashurst
Lodge, Ashurst, Southampton
SO4 2AA, United Kingdom,
(0421)291 3223, (0421)291 2853
- 27-29
Electronic Materials Conference
Santa Barbara, CA
V. G. Karamidas, Bellcore, 331
Newman Springs Rd., Red Bank,
NJ 07071, (201) 756-3353, fax
(201) 756-9526
- JULY 1990
- 2-5
7th CIMTEC Satellite Symposium
4, High T Superconductors
(See June 24-30 CIMTEC listing)
Trieste, Italy
7th CIMTEC Satellite Symposium
4, P.O. Box 174, 48018
Faenza, Italy, 545-664143,
fax 546-664138
- 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
Brookside Plaza Drive, West-
erville, OH 43081, (614) 890-4700,
fax (614) 899-6109
- 11-13
Optoelectronics Conference
Chiba, Japan
K. Ito, DEC 90, c/o Business
Center for Academic Societies
Japan, Conference Dept.,
Crocevia Hongo 2F, 3-23-1
Hongo, Bunkyo-ku, Tokyo 113,
Japan, 81-3-617-5831, fax 81-3-
617-5836
- 15-20
8th American Conference on
Crystal Growth
Vail, CO
B. L. Sopon, Solar Energy
Research Institute, 1617 Cole
Bldg., Golden, CO 80401-3393;
(303) 231-1383
- 17-19
Low Temperature Engineering and
Cryogenics Conference, LTCEC 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) 278-2603
- 22-3
NAT Advanced Study Institute on
Diamond and Diamond-Like Films
Castelvecchio Pascoli, Italy
C. J. McManus, Metals and
Ceramics Div., Oak Ridge National
Lab., P.O. Box 2008, Oak Ridge,
TN, 37831-2008, (615) 574-4344,
fax (615) 574-7559
- 23-26
Conference on Advances in
Cementitious Materials
Gathensburg, MD
American Ceramic Society, 757
Brookside Plaza Drive, West-
erville, OH 43081, (614) 890-4700,
fax (614) 899-6109
- 23-27
5th International Conference on
Scanning Tunneling Microscopy/
Spectroscopy and 1st Interna-
tional Conference on Nanometer
Scale Science & Technology
Baltimore, MD
J. S. Murray, Code 6100, Naval
Research Lab., Washington, DC
20375-5000, (202) 767-3026, fax
(202) 424-7139
- 24-26
Conference on Polymer Blends
Cambridge, United Kingdom
D. C. Vane, 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, Albuquer-
que, 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. Hemment, Dept. of
Electronic & Electrical Engineer-
ing, Univ. of Surrey, Guildford,
Surrey GU2 5XH, (0483) 571281;
fax (0483) 300803
- 30-3
POLYSE 90: Polycrystalline Semi-
conductors
Schwabach, 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, Greece
A. Christou, Code 5830, Naval
Research Laboratory, 4555
Overlook Ave. SW, Washington,
DC 20375-5000, fax (202)
767-0546
- 30-3
Porous Ceramics Processing
The Future for Manufacturing
Cambridge, MA
Director of the Summer Session
M.I.T. Rm. E15-356, Cambridge
MA 02139, (617) 253-2101
- 31-2
4th International Conference on
Shallow Impurities in Semicon-
ductors
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 53,
Westbury House, Bury St.,
Guildford, Surrey, GU2 5BH,
United Kingdom, 0483 300966,
fax 0483 301563
- 12-18
12th International Congress to
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. Duffell, IRC in Super-
conductivity, Madingley Rd.,
Cambridge CB3 0HE, UK, (0223)
337472, fax (0223) 337074

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)

FINAL SCIENTIFIC PROGRAM

Page 2

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 ($\frac{1}{2}$ hr)
C. J. McHargue (Oak Ridge National Laboratory, USA)

Process Characterization of a-C:H Plasma Deposition ($\frac{1}{2}$ hr)
Ch. Wild (Fraunhofer Institut, FRG)

In Situ Characterization of a-C:H Films and Film Structure
Interfaces by Photoelectron Spectroscopy (1 $\frac{1}{2}$ 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 ($\frac{1}{2}$ 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)

FINAL SCIENTIFIC PROGRAM

Page 3

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 Universität 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.

DIAMOND AND DIAMOND-LIKE FILMS AND COATINGS
NATO ADVANCED STUDY INSTITUTE, IL CIOCCO HOTEL
CASTELVECCHIO PASCOLI, ITALY

July 22 - August 3, 1990

PARTICIPANTS

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Moscow 117915, U.S.S.R.
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Pittsburgh, PA 15232
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Bat 108 Campus D'Orsay
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Phone: 33-69415212 FAX: 33-169415268

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Universitat Della Basilicata
85100 Potenza, Italy
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Department d'Etudes des Materiaux
Section de Genie des Surfaces
BP-85X
38041 Grenoble, Cedex, France
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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
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