NISTIR 5418

Workshop on Characterizing Diamond Films III

February 23-24, 1994
Gaithersburg, MD

Albert Feldman
National Institute of Standards
and Technology

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Norton Diamond Film

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April 1994

U.S. DEPARTMENT OF COMMERCE
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TECHNOLOGY ADMINISTRATION
Mary L. Good, Under Secretary for Technology

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WORKSHOP ON CHARACTERIZING DIAMOND FILMS III

Abstract

The third in a series of workshops was held at NIST on February 23th and 24th to discuss the characterization of diamond films and the need for standards in diamond technology. The audience targeted for this workshop were producers and potential users of CVD diamond technology in the United States. Three technical topics that have relevance to applications of chemical vapor deposited (CVD) diamond were discussed: characterizing brazing and polishing, standardization of thermal conductivity measurement, and characterizing stress strain, and fracture.

Key Words: brazing, chemical vapor deposition, CVD, diamond, fracture, polishing, Raman spectroscopy, standards, strain, stress, thermal diffusivity, thermal conductivity.

WORKSHOP ON CHARACTERIZING DIAMOND FILMS III

1. Introduction and Conclusions

The third in a series of workshops was held at NIST on February 23th and 24th 1994 to discuss, in depth, specific topics deemed important to the characterization of diamond films made by chemical vapor deposition (CVD diamond) and to address the need for standards in diamond technology. The topics chosen for this workshop were based on feedback from the attenders of the previous workshop. The audience targeted for this workshop were producers and potential users of CVD diamond technology. University scientists and scientists from government laboratories were invited as experts in properties measurements. There were 55 attenders at the workshop.

We focussed on three technical topics for discussion: characterizing brazing and polishing, standardization of thermal conductivity measurement, and characterizing stress strain, and fracture.

The principal conclusions of the workshop include:

- The development and availability of reliable post growth processes, such as polishing and brazing, will contribute in a substantial way to realizing new applications of CVD diamond. It is important to characterize and evaluate the results of these processes in a uniformly accepted way.
- The first results of the interlaboratory round-robin comparison of thermal conductivity and thermal diffusivity measurements were presented. They showed considerable laboratory to laboratory variations although much of this variability may be due the manner in which the different measurement methods employed are affected by specimen inhomogeneity and specimen anisotropy. Additional laboratories will be making measurements that will add to present measurement data base.
- CVD diamond exhibits lower resistance to fracture than other forms of diamond. This is impeding the use of CVD diamond in applications where the material is subjected to high stresses such as stresses induced by thermal shock. The strength deficiency is attributed to surface flaws and high internal stresses that originate during growth. The relationship between growth conditions and internal state of stress has not yet been resolved.

2. Characterizing Brazing and Polishing

There were six presentations in this session. The first three presentations centered on techniques for polishing and surface figuring CVD diamond. The last three talks discussed issues and techniques for bonding diamond to other materials.

The development and availability of reliable post growth processes, such as polishing and brazing, will contribute in a substantial way to realizing new applications of CVD diamond. Being able to characterize and evaluate the results of these processes in a uniformly accepted way is very important. The quality of a brazed joint between a CVD diamond component and a ceramic or metal support structure, may be defined in a number of different ways, depending on the specific application. In one application the most important feature of a joint might be its heat transfer characteristics at cryogenic temperatures or across a broad temperature range; in another application its most important characteristic may be its mechanical strength which might be determined by the level of success in compensating for the thermal expansion mismatch between the substrate and the diamond. Optical applications will be driven by other requirements such as how a specific polishing process controls the surface micro-roughness and how closely can an accurate surface figure be attained.

The first presentation was by R. Miller of Raytheon who gave an extensive overview of diamond polishing technology. In his talk, he grouped the currently pursued polishing methods into contact type and non-contact type processes. Contact methods may be further divided into non-reactive and reactive methods. The non-reactive polishing methods discussed were the conventional and the abrasive jet techniques. Among the reactive polishing techniques, the hot metal polishing approach was emphasized. Polishing diamond against iron, manganese, lanthanum, and cerium metals has had variable success.

The iron plate method is usually a dynamic method in which the diamond is rubbed against the iron at an elevated temperature. It results in a smooth finish (20 nm peak-to-valley) when the plate temperature is low ($\approx$750 °C) and the polishing is done in a hydrogen environment; the material removal rate is relatively low ($\approx 0.5\ \mu$m/hr). The polishing process and the material removal rate may be speeded up ($\approx 7\ \mu$m/hr) by increasing the plate temperature to $\approx$950 °C. However, this results in a rough finish. An appropriate sequence of polishing temperatures appears to result in an acceptably smooth surface in a reasonable length of time. However some intergranular cracks may form during the processing which may or may not be acceptable, depending on the application. A method for characterizing the cracks in the polished CVD diamond surface must be used to in order to evaluate the seriousness of such cracks.

Molten lanthanum or cerium metals, used in a static procedure, minimizes the intergranular cracking in CVD diamond during polishing. In this procedure, the diamond is placed in contact with the metal, but no relative motion takes place, that is, no rubbing occurs. This process results in higher material removal rates than the previous method, but at the cost of increased surface roughness.

Other reactive contact polishing methods mentioned were float polishing employed at the Naval Air Warfare Center and amorphous silicon oxide techniques used by Edge Technologies, Inc.

Non-contact polishing methods fell into two groups, those that use laser beam etching and those that used ion beam etching. Polishing with YAG laser beam at either 1.06 μm or at 0.53 μm and with an excimer laser beam was discussed. Two different ion beam techniques have been used to polish of CVD diamond. In the first technique, diamond is removed by sputter-etching with an argon or oxygen ion beam. A second novel technique has been developed by the Spire Corporation. It uses ion implantation to soften a top layer of diamond about one μm thick, which is then removed by conventional polishing methods.

The second talk was given by T.S. Sudarshan of Materials Modification Inc. He summarized recent advances in the use of lasers for polishing diamond films. Special emphasis was placed on the difficulty associated with polishing large areas and on the interpretation of the characterization of the polished diamond surfaces. Technical areas in which surface roughness plays important role, such as tribological applications, were discussed.

The last talk on polishing was presented by S. Holly of Rockwell International, Rocketdyne Division. He highlighted the importance of surface shape control during polishing. Several applications require polished surface that are very flat. These include thermal applications, such as large area diamond plate heat-sinks for multichip module technology and optical applications such as infrared windows. Future applications of CVD diamond will require accurate control of non-flat surfaces, such as spherical, aspherical, cylindrical and toroidal shapes, that might be used in optical domes and lenses.

A polishing procedure that utilizes a combination of several polishing methods was then described. The procedure is based on interferometrically controlled ablation of diamond to produce a flat surface. The material removal proceeds in a manner similar to that used in single-point diamond turning; however, in this process, material removal is controlled in real time by continuous interferometric monitoring of the surface being ablated. The present status and recent results of this polishing procedure were discussed.

The first talk on CVD diamond brazing was presented by T.P. Thorpe of the Naval Research Laboratory (NRL). He focused on the importance of reliable brazed joints for producing high quality homoepitaxial diamond. These joints provide a thermal path between the diamond substrates and an underlying heat sink. The joints must survive high temperatures (up 1500 °C) for extended periods of time. Because the temperatures are so high, the conventional commercial brazing material (from Drukker International), a gold-tantalum composite which melts at $\approx$1060 °C, could not be used. As a result, several alternative brazes were investigated.

For NRL's purposes the selection criteria for a braze material were: 1) it should contain a refractory carbide-forming element in order to achieve satisfactory bonding to the diamond substrate. 2) It should form a refractory compound or alloy with the underlying molybdenum heat sink. 3) All products created during braze formation should have a melting point above 1300 °C. Among the brazes tried were several variations on the Drukker braze recipe, including substitution or alloying of gold with different members of the platinum group of metals. Greatest success was achieved with a Pd substitution. This was primarily due to its relatively low melting point of 1552 °C which helped to minimize graphitization of the diamond surface during braze formation. Platinum-gold alloys were also found to be effective but they were inherently more difficult to fabricate due to an unexpectedly complex Au-Pt interaction. Both of the above mentioned brazes were found to withstand growth conditions for several hours at temperatures up to 1400 °C without degradation.

Diamond-metal brazes employing Nichrome were also fabricated. They were able to withstand temperatures up to 1200 °C. Details of all of the fabrication techniques were discussed.

The second talk on brazing was given by R. Meilunas of the Grumman Corporate Research Center. The talk emphasized the importance of rigorous joint design procedures. A practical approach to braze design would include: 1) Consider the temperature of operation of the joint; select the melting point of the braze alloy to be 100 to 200 °C above the operation temperature. 2) Select the joint geometry. 3) Determine the mechanical properties of each component to be brazed. 4) Determine the thermoelastic/thermoplastic properties of the braze alloy (such as stress/strain *vs* temperature, strain hardening coefficient, elastic modulus, poisson's ratio). 5) Determine the wetting/bonding properties of the braze alloy to the components to be brazed. 6) Perform a stress analysis of the joint. 7) Perform experimental validation of the stress analysis. 8) Determine the environmental stability of the joint.

A list of practical braze alloys was presented that covered brazing temperatures between 280 °C and 1300 °C. The properties of several substrate materials, such as W, Be and Cu, were related to the brazing process. The value and importance of a finite element analysis of brazed joints was described. The following statements concluded the presentation: 1) The stability of diamond-metal joints depends critically upon the residual stresses developed during cool-down from the brazing temperature. 2) A finite element stress analysis can provide insights into the residual stress distribution and potential failure modes in the joints. 3) The design of CVD diamond-metal brazed joints requires knowledge of wetting, chemical bonding, and metallurgical interactions during brazing.

The final talk of the session was given by J. Intrater, Oryx Technology Corporation. The talk focused on specimen surface preparation and selection of methods for analyzing the brazed joint. In considering sample surface preparation, special emphasis was placed on the challenges of sectioning and polishing of diamond and the problems that arise from the vast differences in hardness between metals and diamond. Important to characterization of metallization on diamond is the determination of the elemental distribution throughout the interfacial region and an assessment of the carbon phases present (ie. the amount of sp^2 and sp^3 carbon present). The talk discussed use of a scanning electron microscope (SEM) equipped with an x-ray microprobe and a wavelength dispersive spectrometer and Raman spectroscopy for evaluating the joint.

3. New Developments

In order to foster international cooperation in the development of standards for CVD diamond, we invited Yoichiro Sato of the National Institute for Research in Inorganic Materials (also known as NIRIM) to discuss the need for standardized methods of characterization and property measurement in Japan. In the area of CVD diamond, no standards development is occurring in Japan at present. Dr. Sato expressed the view that the large property variations that occur in CVD diamond make standards development difficult at this time. He has agreed to inquire whether other laboratories in Japan might want to participate in the round robin measurements of thermal conductivity.

K. V. Ravi of Lockheed Missiles & Space Company discussed the optical transmission properties of diamond produced by a novel combustion flame method. Some in the audience questioned whether the transmissivity was as good as was claimed, based on certain features seen in the absorption spectrum. This issue was not resolved.

E. Etz of NIST compared conventional Raman spectra of CVD diamond (obtained with visible light excitation) with Fourier Transform Raman (FT-Raman) spectra obtained with an excitation wavelength of 1.06 μm. While no significant difference was found between the two types of spectra obtained from a type IIa single crystal diamond, radical spectral differences were observed between the two types of spectra from CVD diamond. CVD diamond specimens exhibiting extremely clean Raman spectra in the visible show a large number of spectral features in the infrared region. Thus, FT-Raman spectroscopy appears to be a much more sensitive probe of diamond quality than visible Raman spectroscopy. Of note was a pronounced spectral feature in the FT-Raman spectrum of CVD diamond that was not observed in the visible Raman spectrum.

4. Standardizing Thermal Conductivity Measurements

Four presentations were made during this session.

J. Graebner of AT&T reported the results of thermal conductivity measurements on an isotopically enriched (0.055% ^{13}C) CVD diamond plate. At room temperature, the in-plane thermal conductivity was 22 W/cm/K and the perpendicular-to-plane thermal conductivity was 26 W/cm/K. Not only are these values higher than any previously reported for CVD diamond, but the perpendicular value is higher than that for the best natural single crystal diamond with the normal abundance of ^{13}C. An analysis of the temperature dependence of the thermal conductivity was consistent with a reduction in point-defect scattering of phonons in the isotopically enriched CVD diamond. This would account for the higher thermal conductivity.

O. Käding of Daimler-Benz described thermal conductivity measurements using photothermal displacement spectroscopy at transient thermal gratings (PDS-TTG). In this method, a polished diamond surface is heated by two pulsed laser beams that interfere to form a transient periodic heating pattern (grating) on the specimen surface. The relaxation time for the heating pattern to dissipate is governed by the period of the grating and the lateral thermal diffusivity. The relaxation time is determined by measuring the change in the deflection angle of a cw laser beam that is reflected from an undulation in the sample surface caused by the heating. The depth dependence of the thermal diffusivity near the surface can be determined by varying the grating period.

A. Feldman of NIST presented the results of round robin measurements of thermal conductivity. Measurement where performed by six laboratories on ten specimens provided by four manufacturers. Three geometries were provided: squares, disks, and long/narrow strips. Most laboratories could not test every specimen because each measurement procedure usually required a specific specimen geometry. Typically, the highest value and the lowest value for a given specimen differed by a factor of two. However, such a comparison is not necessarily meaningful because the thermal conductivities of the specimens were inhomogeneous and anisotropic. Each of the techniques sampled the specimen properties in different ways so that different results were to be expected. However, even measurement results that should have yielded similar results showed variations up to 80%.

G. Lu of Norton Diamond Film presented the results of a survey that had been sent to users of CVD diamond for thermal management inquiring about their need for a standardized measurement method. When asked, if only one type of measurement could be performed, what would they prefer it to be, a clear majority preferred in-plane thermal conductivity rather than a perpendicular-to-plane measurement or an approximate average of the two. A clear majority also chose ±10% as the minimum level of accuracy needed. There was a strong preference for a less accurate, quality control tool that would be used on every lot rather than a more accurate measurement that sampled every fifth or tenth lot. However, there was no consensus on other questions such as: was it preferable to determine both the in-plane and perpendicular-to-plane thermal conductivity on an occasional basis; or, should the thermal conductivity of every lot be measured in one direction.

5. Characterizing Stress, Strain, and Fracture

Recent advances in the art of producing CVD diamond now make it possible to obtain free-standing millimeter-thick deposits that have elastic, optical, and thermal properties comparable to those of type-IIa natural diamond crystals. These deposits, however, exhibit fracture strengths that are substantially lower than anticipated judging from the reported strength values of single crystals (natural and synthetic) or polycrystalline high-temperature/high-pressure produced diamond compacts. Since many of the potential applications of CVD diamond, for example infrared transmitting windows or domes, critically depend on the ability to withstand stresses generated in a thermal shock environment, it has become essential to properly assess the fracture behavior of this material. Furthermore, the production of thick CVD diamond plates is often hindered by cracking of the deposit, which suggests that the CVD process gives rise to internal stresses that may initiate crack propagation. The purpose of this session was to explore how a proper description of the development of strains and stresses in CVD diamond may help us understand its strength and fracture characteristics. In this regard, it has been established that the deposition process itself generates highly localized stress concentrations at the grain boundaries, thus weakening the structure. These stress concentrations appear to result from the intrinsic elastic anisotropy, from the formation of high-order twins boundaries, and (perhaps) from the defects associated with the presence of residual hydrogen impurities. Still, the issue of how to control process-induced stresses, in effect, establishing the relationship between growth conditions and state of stress, has not yet been resolved. Ten presentations at this sessions addressed these questions.

Evidence of internal strains in CVD diamond films was first reported by Japanese workers[1] based on Raman spectroscopy work. Y. Sato of the National Institute for Research in Inorganic Materials indicated that measurements performed on films 10-30 μm thick deposited on silicon showed peak-position displacements up to 3 cm^{-1} in addition to substantial line broadening, which points to inhomogeneous strain distributions. Microscopic birefringence patterns seen on polished surfaces also demonstrate that, besides gradual stress variations between top and bottom layers, there were steep stress gradients, perhaps up to 5 GPa/μm, within regions comparable to the grain size. At Norton, K. Gray obtained Raman spectra at various locations on an optical quality 0.5 mm thick CVD diamond bar uniaxially stressed in a three-point bending fixture and observed that the Raman peak shifts in accord with the hydrostatic pressure coefficient, 2.9 cm^{-1}/GPa, previously recorded for single crystals. Because of the large beam spot-size (30 μm), the Norton spectra do not provide the resolution required to detect highly localized stresses as was done at the Naval Research Laboratory (NRL). J. Butler reported that the micro-Raman instrument used at NRL, which operates at a wavelength of 514.5 nm, provides spatial resolutions as low as 1 μm in addition to exceptional spectral resolution. Thus, the stress can be assessed not only in terms of the shifting and the broadening of the diamond Raman line but also from the splitting of the line that occurs due to the lifting of the longitudinal-optic/transverse-optic phonon degeneracy. In accord with the NIRIM observations, this important work leads to the conclusion that residual stresses in CVD diamond films are highly localized and exhibit a spatial distribution that correlates well with surface morphological features; peak stresses exceeding 3 GPa have been recorded.

At this point, it becomes desirable to examine what causes the stress concentrations, and three papers addressed that issue.

S. Kurtz and collaborators at the Pennsylvania State University are making use of the Poisson-Voronoi tessellation model, in conjunction with finite-element methods, to calculate both the effective elastic modulus of random aggregates of diamond grains and the microstresses that develop at the periphery of individual grains in textured diamond deposits. Their result for Young's modulus was shown to be in remarkable agreement with the value obtained elsewhere[2] upon using the Hershey-Kröner-Eshelby averaging procedure. More importantly, these numerical simulations show that, near grain triple points in textured thin films, there are very large stress concentrations, or stress singularities, which derive from the elastic anisotropy of the diamond lattice and depend on the degree of preferred orientation.

On a more visual level, D. Shechtman of the Technion (at present, guest scientist at NIST and NRL) considered the impact of low-order twin boundaries that evolve during the deposition of CVD diamond and that play a role in providing suitable nucleation sites. The intersection of these low-order twin boundaries leads to the formation of higher-order twin boundaries that may contribute to creating locally stressed regions. The columnar structure of CVD diamond, specifically, the presence of grain boundaries as well as twin boundaries, thus can provide a direct fracture path and, therefore, contribute to lowering the fracture resistance.

Very comprehensive investigations of the relationships between growth conditions, microstructure, and residual stresses in microwave-plasma CVD diamond deposits were reported on by A. Harker of Rockwell International. The characterization tools he uses to examine microstresses include angle-resolved x-ray diffraction, channeling electron microscopy, and stimulated fluorescence. One of the conclusions of his work is that even if there are wide fluctuations in local stress levels, the average residual bulk stress appears to be rather insignificant with the growth surface generally under tension and the nucleation surface under minor compression.

The latter work corroborates some of the results of R. Hallock and C. Klein of Raytheon, who performed wafer-curvature experiments on diamond/silicon laminates for the purpose of characterizing the average intrinsic strain of CVD diamond as a function of the diamond thickness and deposition temperature. In this connection, they emphasized that if the proper thin-film conditions are not satisfied, commonly used formulas for obtaining the coating stress from the wafer curvature involve semi-empirical approximations of questionable validity. The model they are using to interpret their data is based upon a general theory of elastic interactions in multi-layer laminates[3] that assumes isotropic relationships in the layer planes, in other words, texture-free polycrystalline deposits on (111) or (100) Si substrates. Errors originate primarily from some unavoidable uncertainty in assessing the growth temperature and, hence, in determining the thermal mismatch strain; in addition, Si creep may cause problems at growth temperatures in excess of ~950°C. For these reasons, wafer-curvature experiments were also carried out with diamond on diamond systems, which not only eliminates the thermal mismatch but yields direct evidence on intrinsic strains since the wafer curvature is related to the coating strain through a very simple equation. In both types of experiments (diamond on silicon as well as diamond on diamond), the average process-induced strain was found to be relatively small but strongly dependent upon the deposition temperature, the sense of the strain changing from compressive at lower temperatures to tensile at temperatures above 1030°C.

C. Klein of C.A.K Analytics commented that in evaluating the fracture-strength of CVD diamond it is essential to keep in mind that the crack propagation mechanism appears to be controlled by surface flaws. Consequently, the stress at failure cannot be considered indicative of an intrinsic fracture strength because it obeys a probability law. In effect, the failure probability at a given applied stress obeys the Weibull distribution. An analysis of fracture-strength measurements performed on CVD diamond films[4] made by hot filament CVD, 10 to 100 μm thick, yielded a characteristic strength of ~485 MPa at the growth surface and 1030 MPa at the nucleation surface.

J. Mecholsky of the University of Florida confirmed that polycrystalline diamond indeed fails from the surface and outlined current approaches to describing the fracture behavior, which include fracture mechanics considerations, the fractal geometry description of a fractured surface, and molecular dynamics modeling. Fracture mechanics experiments were used to determine the critical fracture energy and the fracture toughness. Using the characteristic strength values reported above, one can estimate the flaw sizes to range from 30 μm at the nucleation surface to 150 μm at the growth surface; these dimensions are roughly equal to the estimated grain sizes at these surfaces. Also of interest is Mecholsky's observation, using the $\sin^2(\psi)$ x-ray diffraction technique, that the stress pattern in diamond coatings deposited on silicon shows evidence of growth stresses, i.e., stresses that cannot be accounted for by thermal expansion mismatch alone. This conclusion is in accordance with the wafer-curvature work done at Raytheon.

Finally, M. Drory of Crystallume obtained a fracture toughness value of 5.3 $\mathrm{MPa{\cdot}m^{1/2}}$ for CVD plates thicker than 200 μm that had been subjected to a uniaxial tensile stress. This value, which is typical of high-strength ceramic materials, agrees with Drory's earlier number derived from indentation testing but appears to be lower than values obtained by other workers and may reflect specimen-to-specimen variations in microstructural features. How such variations would affect the fracture toughness is not really understood.

5. References

1. S. Matsumoto, Y. Sato, M. Kamo, and N. Setaka, *Jap. J. Appl. Phys.* 21, L183 (1982).
2. C. Klein, *Mater. Res. Bull.* 27, 1407 (1992).
3. P. Townsend, D. Barnett, and T. Brunner, *J. Appl. Phys.* 62, 4438 (1987).
4. G. Cardinale and C. Robinson, *J. Mater. Res.* 7, 1432 (1992).

Appendix A — Workshop Program

WORKSHOP on CHARACTERIZING DIAMOND FILMS III
National Institute of Standards and Technology
Gaithersburg, MD 20899
February 23, 24, 1994

FINAL PROGRAM

Wednesday Morning, February 23
Administration Building, Lecture Room B

8:00am *Registration and Refreshments*

8:50am Welcome

Steve Freiman, Chief, Ceramics Division, Materials Science and Engineering Laboratory, *NIST*

Characterizing Brazing and Polishing

Chairman, Sandor Holly, *Rockwell International*

9:00am Review of CVD Diamond Polishing Technology
Richard P. Miller, *Raytheon Company*

9:20am Polishing of Diamond and Hard Carbon Films
T.S. Sudarshan, *Materials Modification Inc.*

9:40am Control of Surface Figure in Diamond Polishing
Sandor Holly, *Rockwell International*

10:00am Discussion

10:10am *Refreshments*

10:30am Development of New High Temperature Diamond to Metal Brazes
T.P. Thorpe, K.A. Snail, and R.G. Vardiman, *Naval Research Laboratory (NRL)*

10:50am Residual Stresses and Microstructural Effects in Brazed CVD Diamond
R. Meilunas, A. Levy, and A. Tobin, *Grumman Corporate Research Center*

11:10am Aspects of the Characterization of Metallization/Diamond Interfaces
James Intrater, *Oryx Technology* and T.S. Sudarshan, *Materials Modification Inc.*

11:30am Discussion

New Advanced Technology Programs

11:50am John Gudas, *NIST/ATP*
Discussion

12:30pm *Lunch*

(continued)

Wednesday Afternoon, February 23
Administration Building, Lecture Room B

New Developments
Chairman, Albert Feldman, *NIST*

1:30pm Need for Standardized Methods of Characterization and Property Measurement in Japan
Yoichiro Sato, NIRIM

1:50pm High Rate Synthesis of High Quality Diamond for IR Optics
K.V. Ravi, *Lockheed*

2:10pm Improved Characterization of CVD Diamond by FT-Raman Spectroscopy
Edgar Etz, *NIST*

Working Group on Standardization of Thermal Conductivity Measurement
Chairman, Grant Lu, *Norton Diamond Film*

2:30pm Improved Thermal Conductivity in Isotopically Enriched CVD Diamond
John Graebner, *AT&T Bell Labs*, T.M. Hartnett and R.P. Miller, *Raytheon Company*

2:50pm Determination of Depth-Dependent Lateral Thermal Diffusivities
O. Kāding and R. Zachai, *Daimler-Benz*

3:10pm *Refreshments*

3:30pm Consideration of Uniformity of Property of CVD Diamond Films
Ronald P. Tye, *ULVAC Sinku Riko*

3:50pm Results of Industrial Survey
Grant Lu, *Norton Diamond Film*

4:10pm Results of Round-Robin Measurements
Albert Feldman, *NIST*

4:30pm Discussion

5:30pm *End of Session*

6:30pm Dutch Treat Dinner at Golden Bull Restaurant

Meeting of Working Group on Standardization of Thermal
Conductivity Measurement

(continued)

Thursday Morning, February 24
Administration Building, Lecture Room B

8:00am *Refreshments*

Characterizing Stress, Strain, and Fracture
Chairman, Claude A. Klein, *C.A.K. Analytics*

9:00am Characteristic Features of Strain in CVD Diamonds
Yoichiro Sato, *NIRIM*

9:20am Formulas for Characterizing Strains, Stresses, and Fracture Strength: How to do it Right ...
Claude A. Klein, *C.A.K. Analytics*

9:40am Strains and Stresses in Thick Diamond Deposits: The Wafer-Curvature Method
Robert A. Hallock, *Raytheon Company* and Claude A. Klein, *C.A.K. Analytics*

10:00am Investigations of Stress in Polycrystalline Diamond
Alan B. Harker, *Rockwell International Science Center*

10:20am *Refreshments*

10:40am Measurement of Stress in CVD Diamond by Raman Spectroscopy
Kevin Gray and Henry Windischmann, *Norton Diamond Film*

11:00am Characterization of Localized Stresses in Polycrystalline Diamond
D.J. Vestyck, Jr., D. Shechtman, and J.E. Butler, *Naval Research Laboratory*

11:20am Elastic Properties and Microstresses in Polycrystalline Diamond Films
S.K. Kurtz, *Pennsylvania State University*, and S. Kumar, *University of Cincinnati*

11:40am Discussion

12:20am *Lunch*

1:30pm Stress and Fracture in Diamond Films
J.J. Mecholsky, Jr., and L.P. Hehn, *University of Florida*

1:50pm Fracture Behavior of CVD Diamond
M.D. Drory, *Crystallume*, J.W. Ager, *Lawrence Berkeley Laboratory*, and R.O. Ritchie, *University of California at Berkeley*

2:10pm Defect Induced Brittleness in CVD Diamond
Dan Shechtman, *Technion*, and guest scientist at *NIST* and *NRL*

2:30pm Discussion

3:10pm *Refreshments and Adjournment*

Appendix B — Workshop Evaluation

Workshop attenders were asked to evaluate the workshop. 19 evaluations were received. The vast majority of the attenders found at least one of the session topics useful. Below are listed the topics recommended for the future. Nearly all of the suggestions and comments received are presented.

What topics would you like covered in depth next year?

	checked responses
Optical Properties	xxxxxxxxxx
Electronic Properties	xxxxxxxxxx
Doping Characterization	xxxx
Defect Characterization	xxxxxxxx
Thermal Properties	xxxxxxxxxxx
Mechanical Characterization	xxxxxxxxxxxxxx
Other:	
Polishing Update	x
Standards of characterization methods	x

Comments:

"Finally reliable data .... No more hype!" (in regard to standarization of thermal conductivity measurements)

"The standardization for thermal conductivity of diamond should concentrate on having well measured standard samples which can be requested by and industry of lab for calibration of equipment. This will allow many methods to be used. Also, the lab in industry can determine to what level of precision or accuracy their equipment needs to be. Calibration is then traceable to NIST, by this set of standards. Another suggestion is to use single crystal SiC as a test sample, $\alpha \cong 2.3\ \mathrm{cm}^2/\mathrm{s}$"

"We are not really doing intensive studies ourselves, but I would be interested in trace impurity analysis (hopefully quantitative or semiquantitative), including standard sample preparation and calibration of simpler methods. Defect and impurity characterization are going to be a primary requirement at a higher level."

"Well run, could have sent out the program earlier."

"The session was very informative as to the progress of processes and potential applications. (observed as an end user, costomer.)"

The stress, strain and fracture session was well organized and well conducted. I applaud Claude!

"I found the meeting to be very informative ...."

Appendix C
Specifications for Thermal Conductivity Round Robin

C1. Specimen Specifications

Listed below are the specifications for the round robin thermal conductivity specimens. We attempted to obtain three specimens from each supplier, prepared preferably from a single wafer 300-400 μm thick. The other dimensions of the specimens were to be:

specimen 1: disk, 40 mm in diameter
specimen 2: rectangular strip, 4 mm wide × 50 mm long.
specimen 3: square wafer, 10 mm × 10 mm

Specimens were to be polished to a surface roughness of 0.3 μm Ra or less. The thickness uniformity was to be 1% or less over 5 mm; however, an attempt to maintain this uniformity over as large an area as possible was considered highly desirable. The approximate thermal conductivities of the specimens were to fall near one of the following values: 700 W/m/K, 1000 W/m/K, and greater than 1300 W/m/K. A unique code provided by NIST was to be inscribed or etched by the producer near an edge or corner of each specimen for identification purposes.

The following identifies the number of specimens received in each geometry:

small square (SQ) - 5 pieces
long bar (LB) - 3 pieces
large disk (LD) - 2 pieces

C2. Laboratories Reporting Thermal Conductivity Results

AT&T Bell Laboratories
Daimler-Benz
General Electric
Norton Diamond Film
Sinku-Riko
Wayne State University

C3. Companies Supplying Specimens

Diamonex
General Electric
Norton Diamond Film
Raytheon

Abstracts

Characterizing Brazing and Polishing

Chairman — Sandor Holly
Rockwell International

REVIEW OF CVD DIAMOND POLISHING TECHNOLOGY

Richard P. Miller

Raytheon Company, Research Division
Advanced Materials Department
Lexington, MA 02173

High quality bulk diamond plates have been grown up to 5" diameter and 1 mm thick. Films have been grown on a variety of substrates and over very large areas. A major bottleneck impeding the military or commercial use of CVD diamond is the difficulty in economically planarizing or polishing the surfaces and meeting the specifications of large area components.

Diamonds resistance to mechanical abrasion is unmatched by any other engineering material known today. Traditional methods for polishing single crystals use porous cast-iron scaifes charged with diamond powder where rates can vary by two orders of magnitude depending on the crystallographic plane and abrading direction on the crystal.[1] These methods are unsuitable for polishing CVD diamond deposits. On the other hand conventional methods using modern machinery, techniques and specialized lapping media have been quite successful at polishing CVD diamond with the stipulation that the process suffers from being unacceptably slow and creates subsurface damage in the material.

In recent years new techniques are undergoing development to overcome the limitations of conventional polishing. To accelerate the rate of stock removal most methods rely on some form of chemical reaction with diamond. Contact and non-contact systems comprise the two classes of non-conventional finishing techniques being explored today:

Contact Systems

The majority of labs are working with hot metal systems in lap, foil or powder form.[2,3,4,5] The accepted mechanism is a combination of catalyzed graphitization of the diamond phase followed by solid state diffusion of carbon into the metal. Background atmosphere is an important factor in controlling the reactions. The dominant metal under study is iron followed by other metals exhibiting carbon solubility.

Other more specialized approaches that are being tested include the SiOx chemical machining process[6] and abrasive liquid jets.[7]

Non-contact Systems

Nd:YAG and Excimer lasers are being explored as sources to planarize or polish CVD diamond.[8,9] Nd:YAG lasers operate in the near IR and visible well below the diamond band gap where coupling thresholds are high and grazing incidence is typically employed. Excimers operate in the UV slightly below or above the band gap where surface absorption is high and depth control can be managed more effectively.

Ion beams have been effective at smoothing CVD diamond.[10] Using oxygen ions and a matching planarizing layer Bovard et al. have improved a 5 cm diameter film from 1 µm p-v to 55 nm p-v roughness.[11] Based on work in Japan and the United States, Spire Corp. has proposed two complimentary techniques.[12,13] One uses low energy, high current density beams with high rates of stock removal and improved surface finish. The second uses high energy ion bombardment to soften the surface making it suitable for conventional finishing with standard abrasives.

The non-conventional techniques with reported high stock removal rates and smooth surfaces have not yet demonstrated uniform high quality finishes over useful areas. In spite of there drawbacks the best results to date have been accomplished with conventional methods although ongoing development of new techniques holds much promise for the future.

In our work at Raytheon I wish to acknowledge Rob Hallock for his efforts in development of reactive techniques. Joe Zanco and Paul Morissette have been invaluable in pursuing conventional methods.

References

[1] J. and E. Wilks, "Polishing and shaping diamond," in *Properties and Applications of Diamond* (Butterworth/Heinemann, 1991), pp. 228-264

[2] A. B. Harker, "Reactive Polishing of Polycrystalline Diamond and Measured Spectroscopic Properties," in *Applications Of Diamond Films and Related Materials* (Tzeng et al., Elsevier, 1991), pp. 223-225 (1991)

[3] S. Jin et al., "Thinning and Polishing of Diamond Films by Diffusional Reaction with Metals," *SPIE Proc.* 1759, Diamond Optics V, pp. 57-67 (1992)

[4] S. Jin et al., "Shaping of Diamond Films by Etching with Molten Rare-earth Metals," *Nature* 362, pp. 822-824 (1993)

[5] H. Tokura et al., "Study on the Polishing of Chemically Vapour Deposited Diamond Film," *Thin Solid Films*, 212, pp. 49-55 (1992)

[6] K. Snail, "Growth, Processing and Properties of CVD Diamond for Optical Applications," *Optical Materials* 1 No. 4, pp. 235-258

[7] M. Hashish and D. Bothell, "Polishing of CVD Diamond Films with Abrasive-Liquidjets," *SPIE Proc.* 1759, Diamond Optics V, pp. 97-105 (1992)

[8] L. Bouilov et al., "Excimer Laser Etching and Polishing of Diamond Films," *Proc. 2nd Int. Symposium on Diamond Materials* 91-1, pp. 357-364 (1991)

[9] K. Ravi and V. Zarifis, "Laser Polishing of Diamond," *Proc. 3rd Int. Symp. on Diamond Materials* 93-17, pp. 861-867 (1993)

[10] A. Hirata et al., "Smoothing of Chemically Vapour Deposited Diamond Films by Ion Beam Irradiation," *Thin Solid Films*, 212, pp. 43-45 (1992)

[11] B. Bovard et al., "Oxygen-ion beam Polishing of a 5-cm-diameter Diamond Film," *Applied Optics* 31 No. 13, pp. 2366-2369 (1992)

[12] N. Efremow et al., "Ion Beam Assisted Etching of Diamond," J. Vac. Sci. Tech. B3(1), pp. 416-418 (1985)

[13] H. Funamoto et al., "Planing of Synthetic Diamond Film by the Penning Discharge Microsputtering Method," *Surf. & Coat. Tech.*, 47, pp. 474-480 (1991)

POLISHING OF DIAMOND AND HARD CARBON FILMS

T. S. Sudarshan
Materials Modification Inc.
2929-P1, Eskridge Road
Fairfax, VA 22031

Synthesis of diamond and diamond-like films have achieved a reasonable degree of maturity over the last two years and there is an increasing emphasis for the application of these films on products. One of the major areas that does pose some limitations in applications involving tribology, thermal management or optics is the roughness of the as-deposited film surface.

Over the years, various techniques have been proposed to reduce the surface roughness of hard carbon films. These have ranged from mechanical polishing methods using abrasives to chemical and mechanochemical methods. More recently, techniques have been developed that use thermochemical means (molten metals) to reduce the surface roughness. Other techniques that are non-contact in nature and are increasingly being researched include laser and ion beam methods.

In this talk, a summary of the research efforts based on the above techniques coupled with the recent advances in the use of lasers for polishing diamond films will be highlighted. Specific importance will be provided to the difficulties associated with the polishing of large areas and the interpretation of results obtained by current characterization techniques. The final emphasis of this talk will be on the impact of surface roughness in determining the tribological properties of diamond films.

CONTROL OF SURFACE FIGURE IN DIAMOND POLISHING

Sandor Holly
Rocketdyne Division
Rockwell International Corporation
6633 Canoga Ave
Canoga Park, CA 91304

Characterization of a polished surface includes description of the degree of accuracy of its surface figure. The application itself determines how accurate the surface figure of a polished surface has to be. In conventional polishing processes using typical optical materials it is necessary to use substrates with diameter to thickness ratios not more than 6 to 8 in order to be able to produce and maintain an acceptable figure of the polished surface.

Since CVD grown diamond is available primarily in forms of thin plates, typically less than 2 millimeters in thickness, any applications that require large flat polished areas (2" to 3" diameter and larger) must deal with less than perfect figures of the polished surfaces when any of the conventional polishing methods are employed.

The present discussion focuses on this difficult issue of how to produce surface figures on polished CVD diamond wafers which are acceptable for various applications. Optical methods to characterize and measure the feature of optically polished surfaces are briefly reviewed.

A new method to figure flat and non-flat surfaces of thin, wafer-like CVD substrates by using a non-contact material removal method based on interferometrically controlled diamond surface ablation is described. Potential advantages and new opportunities presented by this method are discussed. Some of the difficulties and challenges that must be overcome to take full advantage of this noncontact surface figuring technique in various applications are presented.

DEVELOPMENT OF NEW HIGH TEMPERATURE DIAMOND TO METAL BRAZES

T. P. Thorpe, K. A. Snail, and R. G. Vardiman
Naval Research Laboratory, Code 5622
Washington, D. C. 20375

In order to initiate and maintain high quality homoepitaxial diamond growth strict temperature control is critical. This can pose an extremely difficult practical problem for high growth rate methods, such as the use of an oxygen-acetylene torch, where the energy flux delivered to the substrate may approach 1 kw/cm^2. The substrate must be in excellent thermal contact with a heat sink capable of absorbing energy at those rates. Typically, it is necessary to braze the diamond substrate to such a heat sink in order to achieve the necessary thermal contact. This braze must simultaneously withstand for multi-hour periods temperatures sufficient to achieve high quality homoepitaxial growth (up to 1300 °C) as well as the corrosive effects of typical growth conditions. Initial growths made by our group utilized polished natural diamond substrates commercially brazed (Drukker International) to a molybdenum rod with a gold-tantalum composite. This particular braze melts at ~ 1060 °C, however, and therefore proved insufficient for our application. We have investigated several alternative brazes as a result, and will discuss our results at this presentation(1).

Among the approaches tried were several variations on the Drukker braze, including substitution or alloying of the gold with various members of the platinum group of metals. Greatest success was achieved with Pd substitution, primarily due to its relatively low melting point (1552 °C), which helped to minimize graphitization of the diamond surface during braze formation. Results from an Auger depth profile analysis of a Pd-Ta braze will be presented. Use of Pt-Au alloys was also found to be effective, but inherently more difficult to fabricate due to an unexpectedly complex Au-Pt interaction. Both of the above mentioned brazes were found to withstand growth conditions for several hours, at temperatures up to 1400 °C, without noticeable degradation. Additionally, diamond-metal braze joints employing Nichrome have been fabricated which can withstand growth conditions at temperatures up to 1200 °C. Details of fabrication procedures will be discussed.

(1) T.P. Thorpe et. al., Proc. 3rd Int. Sym. Diamond Mat., p. 468, (1993).

RESIDUAL STRESSES AND MICROSTRUCTURAL EFFECTS IN BRAZED CVD DIAMOND

R. Meilunas, A. Levy, and A. Tobin
Grumman Corporate Research Center
Bethpage, NY 11714

The outstanding physical properties of CVD diamond have the potential to significantly enhance performance in electronic, optical, and tribological systems. Integration of CVD diamond into many of these advanced system designs will require methods of joining a CVD diamond layer to dissimilar materials. For example, integration of CVD diamond heat spreaders into laser diode packages requires joining methods for the chip/diamond/package. CVD diamond inserts brazed to conventional carbide tooling faces for non-ferrous machining applications also require highly reliable joining techniques. Certain optical applications of CVD diamond such as in high powered lasers require a metal/diamond joint that is vacuum tight with a high thermal conductivity.

This paper addresses the critical issues associated with joining CVD diamond to non-diamond materials using conventional brazing techniques. The importance of the thermo-physical, mechanical and chemical properties of the braze, metal, and diamond materials on the successful joining of CVD diamond to metallic substrates will be demonstrated with several metal/braze/diamond systems of engineering interest. Finite element modeling and closed form solutions are utilized to evaluate the residual stress distribution developed in the braze, diamond, and metal substrate for different metal/braze/diamond combinations and configurations. The importance of the braze yield strength and work hardening in determining the residual stresses developed during cool-down from the brazing temperature is discussed. These results are compared to experimental findings of interface microstructure for several representative brazed joints. Comparison between analytic results and experimental observation of failure modes at the interface are discussed.

Aspects of the Characterization of Metallization/Diamond Interfaces

James Intrater
Oryx Technology Corporation
47341 Bayside Parkway
Fremont CA 94538

T.S. Sudershan
Materials Modification Inc.
2929-P1 Eskridge Road
Fairfax, VA 22031

The microanalytical investigations into metallization/diamond interfaces requires particular focus on both sample preparation and selection of analytical methods. In the first case one needs to maintain such considerations as the anticipation of the difficulty of sectioning and polishing diamond and the need to contend with the vast differential hardness between metals and diamond.

On the front of probing into the bondline analysis, the researcher would like to determine, principally, the elemental distributions throughout the interfacial region followed by the more ambitious assessment of actual phase identification (*e.g.* sp^2 *vs* sp_3 carbon). Such techniques as scanning electron microscopy with x-ray microprobe, wavelength dispersive and Raman spectroscopies will be discussed.

New Developments

Chairman — Albert Feldman
National Institute of Standards and Technology

NEED FOR STANDARDIZED METHODS
OF CHARACTERIZATION AND PROPERTY MEASUREMENT IN JAPAN

Yoichiro Sato
National Institute for Research in Inorganic Materials
1-1 Namiki, Tsukuba, Ibaraki 305, Japan

At present, in spite of the potential needs, there appears to be neither an immediate official program for investigating the needs or possibility for the standardized methods of characterization nor a call for a nation-wide meeting for the related discussion in Japan. However, it seems obvious that the call for standardized methods will become stronger sooner or later. I hope to present some of the factors that lead to the needs for such methods.

1.A wide variety in CVD diamond in terms of structural features:

It is well known that "diamond" obtained by CVD can be highly variable in "structure" depending on growth techniques and growth conditions. For example, meaningful comparisons of samples prepared in different laboratories require standardized characterization, and we have often witnessed frustrated discussion and mutual disbelief.

2.Versatile potential application - Various properties of interest:

Specialists from entirely different fields of application may get together at a meeting:From hard coatings to optical and electronic application. Properties ranging from mechanical to electrical: Different properties can have different structure sensitivity, which in turn requires different levels of impurity and/or defect controls. Could there be a common scale to rely on?

3.Constraints imposed by sample geometry.

In many cases, the samples are either too small or too thin to permit reliable property measurements which is essential for mutual comparisons. New methods or evaluation of different methods are required since there may be, e.g., systematic deviation in data from one method to another.

4."Japan Industrial Standard":

With the development in commercial productions, the Japanese government, Ministry of International Trade and Industry, will require to establish standardized methods for important properties.

In the present stage, it seems important to know the characteristic features of the measurement methods, and what kind of combinations of simple methods is useful for characterizing CVD diamonds. We should also try to draw attention of specialists to develop new methods or modify conventional methods which form the basis of science and technology of diamond together with the known methods of characterization and synthesis.

High rate synthesis of high quality diamond for IR optics

K.V. Ravi
Lockheed Missiles & Space Company
Research & Development Division
3251 Hanover Street, Palo Alto, CA 94304-1191

Diamond IR windows synthesized by low pressure activated vapor deposition techniques have been demonstrated by a number of organizations in recent times. Most of the optical properties of such windows have been shown to be identical to those of natural diamond. However for the practical utility of such windows the economics of manufacture have to be considerably improved. Among the techniques being developed for the synthesis of diamond films and bulk diamond slabs the combustion flame synthesis process has some distinct advantages in terms of achieving low manufacturing costs attended by high quality. The combustion reaction between acetylene and oxygen is utilized to generate the requisite energy to activate excess acetylene in the gas mix leading to the deposition of diamond films on a temperature controlled substrate brought into contact with the flame. Oxygen and oxidizing specie (such as OH radicals) in the flame ambient are much more effective than atomic hydrogen in promoting the growth of diamond over the growth of graphite and other non- diamond forms of carbon. In addition this technique enables the growth of diamond at high rates and is readily scaled for large area synthesis. In this presentation the current status of this technology will be discussed with a presentation of relevant physical properties such as IR transmission characteristics of large area diamond windows. Some of the key issues involving *in-situ* measurement of relevant process variables in combustion synthesis will also be discussed in this presentation.

Improved Characterization of CVD Diamond by FT-Raman Spectroscopy

Edgar S. Etz
Chemical Science and Technology Laboratory
National Institute of Science and Technology
Gaithersburg, Maryland 20899

Diamond deposited by CVD methods represents one of the most exciting new material products to emerge in several decades. The remarkable progress in this technology made over the past two years has led to the commercial production of high quality CVD diamond suitable for the most demanding applications, such as optical window material or for thermal management tasks. A major issue that has emerged in the industrial production, processing, and application of diamond films is the measurement of diamond quality and consistency, specifically the crystallinity, structural perfection, and purity. Major efforts focus on the identification and the mapping of the distribution of the various forms of non-diamond carbon and the principal trace element impurities, namely hydrogen and nitrogen. At present there are no standards or standardized measurement techniques to support this important emerging technology.

Following our proposal [1] for the development of a Raman standard for CVD diamond, we have examined the capabilities (and limitations) of Raman spectroscopy, as embodied in commercially available instrumentation, for characterizing polycrystalline diamond deposited by several CVD methods. We have examined specimens in various physical forms, such as supported and free-standing films, coatings, wafers, both polished and unpolished. This work, by early 1993, resulted in the conclusion, also recognized by other workers in the field, that Raman characterization employing visible excitation (commonly the 488.0, 514.5, and 647.1 nm lines from Ar and Kr lasers), was no longer sensitive enough to monitor the purity and perfection of highest quality CVD diamond, as the spectra of such samples were virtually indistinguishable from the best type IIa natural diamond. Corroborating conclusions were arrived at also from optical transmission measurements by FT-IR spectroscopy in the mid-IR range (1-20 μm).

With the recent acquisition of a comprehensive macro-/micro- Fourier transform infrared and Raman system, we have re-examined the potential of Raman scattering, now through excitation in the near-IR at 1.064 μm (Nd:YAG laser), as a diagnostic analytical technique for all types and grades of commercially produced CVD diamond. We are reporting on the initial results of these investigations obtained from high-quality research samples of several producers where the FT-Raman spectra provide new information on relative diamond quality previously not discernable from the spectra excited in the visible. These new observations are interpreted as resulting from resonance enhancement [2,3] of non-diamond carbon through excitation in the near-infrared, whereby new "carbon signatures" are observed due to enhanced scattering intensities from amorphous or disordered sp^2-bonded carbon components, relative to the ~1333 cm^{-1} Raman line from sp^3-bonded diamond. These spectral variations are discussed for a range of "poor" and "highest-quality" CVD diamond illustrating the increased sensitivity of FT-Raman microspectroscopy to trace impurities of carbon (and possibly hydrogen and nitrogen) over conventional Raman microprobe methods. These results are correlated with data on several of the same specimens examined in the FT-IR microscope for which transmission measurements were possible.

Industrial CVD diamond research materials were kindly provided by Crystallume, Norton Diamond Film, and Raytheon Research Division.

1. E. S. Etz, "Requirements of a standard for the chemical characterization of CVD diamond by Raman spectroscopy," in *Applications of Diamond Films and Related Materials*, Y. Tzeng et al., Eds., Elsevier Science Publishers, New York (1991), pp. 603-609.
2. M. Yoshikawa et al., "Characterization of crystalline quality of diamond films by Raman spectroscopy," Appl. Phys. Lett. **55** (25), pp. 2608-2610 (1989).
3. J. Wagner et al., "Resonance effects in Raman scattering from polycrystalline diamond films," Appl. Phys. Lett. **59** (7), pp. 779-781 (1991).

Working Group on Standardization of Thermal Conductivity Measurement

Chairman — Grant Lu
Norton Diamond Film

IMPROVED THERMAL CONDUCTIVITY IN ISOTOPICALLY ENRICHED CVD DIAMOND

J. E. Graebner
AT&T Bell Laboratories
Murray Hill, N. J. 07974

T. M. Hartnett and R. P. Miller
Raytheon Company
Lexington, MA

The thermal conductivity κ of an isotopically enriched (0.055% ^{13}C) polycrystalline diamond plate made by chemical vapor deposition (CVD) has been measured for heat flowing in a direction either parallel ($\kappa_{\|}$) or perpendicular ($\kappa_{\perp}$) to the plane of the plate. The room-temperature conductivities ($\kappa_{\|} = 21.8$ and $\kappa_{\perp} = 26$ $\mathrm{Wcm^{-1}K^{-1}}$) are higher than for any CVD diamond previously reported[1], and the $\kappa_{\perp}$ value is higher than the best gem-quality single crystal with the natural abundance (1.1%) of ^{13}C. Analysis of the temperature dependence of $\kappa_{\|}$ reveals that the point-defect scattering of phonons is in fact significantly lower than expected for the natural abundance of ^{13}C and that this is responsible for the improved conductivity. The observed anisotropy $\kappa_{\|}/\kappa_{\perp} = 0.84$ at room temperature is associated with the anisotropic grain structure.

1. J. E. Graebner, S. Jin, G. W. Kammlott, J. A. Herb, and C. F. Gardinier, Appl. Phys. Lett. **60,** 1576 (1992); Nature **359,** 401 (1992).

Determination of Depth-Dependent Lateral Thermal Diffusivities

O.W. Käding, R. Zachai, Daimler-Benz AG, Wilhelm-Runge-Straße 11, 89013 Ulm
(Germany)

At the present state of development of CVD diamond fabrication, layer thickness inhomogeneities in crystallite size and phase purity in the diamond material cannot be avoided. For CVD diamond heat spreading applications, the influence of such inhomogeneities on the heat transfer must be taken into account. Therefore, spatially resolved investigations of the thermal properties are of great interest.

Photothermal Displacement Spectroscopy (PDS) at Transient Thermal Gratings (TTG) was used to determine lateral thermal diffusivities of CVD diamond films with high spatial resolution. The results are compared with phase purity information obtained from micro Raman spectroscopy.

Heating of the specimens is realized by surface absorption of a two-beam interference pattern of a pulsed laser source. The surface displacement grating, caused by the laser-heating-induced thermal expansion, is probed by a strongly focused cw-laser beam. The transient angular deflection is measured by a position sensitive photodetector. The analyzed relaxation time is governed by the grating period and the lateral thermal diffusivity. The grating period (between 30 and 300µm) determines the information volume in the sample. Thus, by varying the period, depth resolved lateral thermal diffusivities can be obtained.

Measurements on CVD diamond substrates with a thickness of several hundred microns, prepared by different suppliers, were performed in the frame of the thermal conductivity round-robin. The films had been lapped or polished on both sides with an unknown amount of removed material. The lateral diffusivity of the investigated films depends on the height within the films. The top side of high-grade diamond films showed lateral diffusivities comparable to the natural type IIa value. Up to three times lower values, however, were measured at the bottom side. Also significant in-plane inhomogeneities were observed for some films. As expected, the thermal diffusivity variations observed are in agreement with the phase purity behaviour as determined by micro Raman spectroscopy.

CONSIDERATION OF UNIFORMITY OF PROPERTY OF CVD DIAMOND FILMS

R. P. Tye
Ulvac Sinku Riko, Inc.
Andover, MA

For practical applications, particularly for electronics, the thermal properties of potential heat spreaders and heat sink materials such as CVD diamond need to be both uniform and reproducible.

The modified ac calorimeter technique is a widely used technique to measure the in-plan thermal diffusivity of CVD diamond films having different thicknesses from tens of micrometers to the order of a millimeter. It has been found that reproducible and uniform results are obtained on thin films (e.g. $< 50\ \mu m$). However, recent experience with thicker films (up to 0.6 mm) indicate that highly reproducible but different average values can be obtained at different local positions on a specimen.

These variations have been examined in more detail by undertaking measurements at smaller distance intervals than the standard 0.1 mm. Results of such studies indicate that while average reproducible values are obtained over a given distance, significantly different higher and lower "spot" values are seen. It would appear that these are due to very local effects of grain boundaries, crystal size etc.

Characterizing Stress, Strain, and Fracture

Chairman — Claude A. Klein
Raytheon Company

CHARACTERISTIC FEATURES OF STRAIN IN CVD DIAMONDS

Yoichiro Sato, National Institute for Research in Inorganic Materials, 1-1 Namiki, Tsukuba,
Ibaraki 305, Japan

In this paper, it is intended to present the results of our observation which show the presence and characteristic features of strain in various forms of CVD diamonds.

1.Polycrystalline films

One of the earliest evidence of strain has been reported by us on polycrystalline films based on Raman scattering measurements: Peak shifts and broadening of the diamond Raman line as compared with natural or high-pressure synthetic diamond single crystals have been noted[1]. Observations on films of 10-30μm thickness grown on Si with grain size of 0.2-5μm (grain size is smallest at the substrate side and largest at the surface side) show peak displacement of up to 2-3cm^{-1} to higher Raman shift side and broadening of the linewidth(FWHM) up to 8cm^{-1} which may be compared with, e.g., 1.7cm^{-1} for Type Ib single crystals. The Raman microprobe measurements on fractured cross sections prove that the displacement in peak position is higher at the substrate side than at the surface. No detectable displacement (greater than 0.2cm^{-1}) of Si Raman peak has been observed. Further, no appreciable change in peak position and linewidth is found when the films are isolated from the substrate. These results indicate that the internal strain in the films is inhomogeneous and bending of the films is governed primarily by the inhomogeneity.

There are other evidences which show strain distribution: Microscopic observation on polished films under crossed polarizers reveals minute patterns in which the size of the birefringent units is comparable to the apparent grain size as defined by SEM images[2]. Similar patterns are observed by acoustic microscopy. These results indicate that, apart from the gradual gradient in strain between the top and bottom layers, a steep gradient in strain , probably of 0.2-5GPa/μm, within a small region comparable to the grain size is also present.

2. Single crystals

The only X-ray diffraction study made by our group that shows the presence of strain is on a homo-epitaxial film grown on (111) face of natural diamond[3], but no determination of the lattice parameter has been made due to inhomogeneity. Although single crystals, or individual crystals, grown under optimum conditions are substantially free from strain[2], some can show remarkable Raman peak displacement of up to 10cm^{-1} corresponding to a stress of about 3GPa.

3. Concluding remarks

More detailed studies of strain are necessary for the better understandings of how it is brought about and of the effects of strain and strain gradient on various properties, as well as for finding better means of control.

References

1)S.Matsumoto, Y.Sato, M.Kamo and N.Setaka, *Jpn.J.Appl.Phys.*21,L183(1982).
2)Y.Sato and M.Kamo, Chapt. 11 in J.E.Field (ed.), *Properties of Natural and Synthetic Diamond*, Academic Press, London, 1992, p.423.
3)M.Nakazawa, Y.Kanazawa, M.Kamo and K.Osumi, *Thin Solid Films*, **151**, 199(1987).

Formulas for Characterizing Strains, Stresses, and Fracture Strengths: How to do it Right...

Claude A. Klein[*]
Raytheon Research Division, 131 Spring Street, Lexington, MA 02173

Chemical vapor deposition at elevated temperatures creates strains and stresses in the substrate as well as the coating. If the thin-film conditions ($t_c << t_s$ and $E'_c t_c << E'_s t_s$, where *t* is the thickness and *E*' the biaxial modulus) do not apply, commonly used procedures for obtaining the coating stress from the wafer curvature[1] involve semi-empirical approximations and may yield results of questionable validity. The main purpose of this presentation is to provide conceptually correct equations for describing both the room-temperature curvature ($1/\rho$) of a two-layer composite and the stress distribution, $\sigma(z)$, across the entire thickness. The model is based upon a general theory of elastic interactions in multi-layer laminates[2] but assumes isotropic relationships in the layer planes. In this context, it will be shown that the stresses are best described in a manner such as

$$\sigma_i(z) = E'_i\left[\varepsilon_i - \langle\varepsilon\rangle + \left(z_o - z\right)/\rho\right] , \qquad (1)$$

where the subscript *i* refers to the substrate or the coating. $\langle\varepsilon\rangle$ represents an appropriately weighted average strain, and z_o locates the position of the "neutral" plane as measured from the substrate's bottom surface. Two areas of interest in terms of characterizing CVD diamond (diamond on diamond and diamond on silicon) will be discussed in a companion paper[3] and should provide relevant illustrations.

With regard to fracture-strength evaluations of CVD diamond, it is essential to keep in mind that surface flaws control the process; the measured stress at failure, therefore, cannot be identified with an "intrinsic" fracture strength. The fracture probability at a stress level σ obeys the Weibull distribution

$$P(\sigma) = 1-\exp\left[-A\left(\sigma/\sigma_c\right)^m\right] \qquad (2)$$

where σ_c is the characteristic strength (or strength of a unit area specimen), *m* is the Weibull modulus and *A* is given by the following expression

$$A = \left[\Gamma(1+1/m)\right]^m \times m^{0.45} \times \pi\left(r_o/1\mathrm{cm}\right)^2 \qquad (3)$$

if r_o is the radius of the uniformly stressed area. Properly processed fracture-strength measurements performed on Raytheon-made CVD diamond films[4] yield $\sigma_c \sim 1050$ MPa ($m \sim 9$) and $\sigma_c \sim 490$ MPa ($m \sim 11$) for 100-µm thick specimens experiencing peak stresses at the substrate and the growth surface, respectively.

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[*] Present address: *c.a.k.analytics*, 9 Churchill Lane, Lexington, MA 02173.

[1] A. Brenner and S. Senderoff, J. Res. NBS 42, 105 (1949).

[2] P. Townsend, D. Barnett, and T. Brunner, J. Appl. Phys. 62, 4438 (1987).

[3] R. Hallock and C. Klein, this Workshop and to be published.

[4] G. Cardinale and C. Robinson, J. Mat. Res. 7, 1432 (1992).

STRAINS AND STRESSES IN THICK DIAMOND DEPOSITS: THE WAFER-CURVATURE METHOD

Robert B. Hallock and Claude A. Klein

Raytheon Research Division, 131 Spring St., Lexington, MA 02173

The fabrication of diamond windows of millimeter thickness is often hindered by cracking of the diamond deposit, suggesting stresses associated with the deposition process. Although a variety of techniques have been applied to the measurement of stresses in CVD diamond, a review of the literature revealed very little agreement between different laboratories in terms of relating deposition conditions to process-induced stresses in the deposits.

Initially, a series of experiments was carried out in which diamond layers up to several hundred microns in thickness were grown on 0.1" thick Si substrates. Process-induced stresses were estimated using the wafer-curvature method and correlated to deposition conditions. The wafer-curvature method is widely used to estimate average biaxial stress in thin films via Stoney's equation:

$$\sigma_c = E'_s t_s^2 / 6 t_c \rho$$

where ρ is the radius of curvature of the composite, σ is the average stress, E' is the biaxial modulus, t is the thickness, and the subscripts c and s refer to the coating and substrate respectively. However, Stoney's equation is valid only in the thin film limit defined as:

$$E'_c t_c << E'_s t_s$$

This condition is not satisfied in the case of thick diamond layers grown on Si, especially considering the high modulus of diamond as compared to Si. Therefore, a series of equations were derived based on a general theory of elastic interactions in multilayer laminates (1). The accurate determination of growth temperature, and therefore thermal mismatch strain, proved to be a primary source of error in these experiments. In addition, creep in Si has been shown to be a significant problem affecting wafer curvature measurements at growth temperatures in excess of 950°C (2). Therefore, a second series of experiments was carried out in which diamond layers were deposited on CVD diamond substrates. In this case, errors due to thermal mismatch calculations and substrate creep were eliminated and the average layer strain was calculated according to:

$$1/\rho = 6 t_s t_c (\varepsilon_c - \varepsilon_s) / (t_s + t_c)^3$$

where ε_c and ε_s refer to the average strain in the coating and substrate, respectively. The results of both experiments were in reasonable agreement; the process-induced (growth) strain in the diamond layers was strongly dependent on deposition temperature and changed from compressive at lower temperatures to tensile at temperatures above ca. 1030°C.

(1) P.H. Townsend, D.M. Barnett, T.A. Brunner, J. Appl. Phys. 1987, 62(11), 4438.
(2) L. Schäfer, X. Jiang, C.-P. Klages, in *Applications of Diamond Films and Related Materials*, Y. Tzeng, M. Yoshikawa, M. Murakawa, A. Feldman, Eds.; Elsevier Science Publisher B.V., 1991; p. 121.

INVESTIGATIONS OF STRESS IN POLYCRYSTALLINE DIAMOND

A. B. Harker
Science Center
Rockwell International
P.O. Box 1085
Thousand Oaks, CA 91358

ABSTRACT

Relationships between growth conditions, microstructure and residual stress in microwave plasma assisted CVD grown polycrystalline diamond are being studied by a range of techniques. Characterization tools include angle resolved x-ray diffraction, channeling electron microscopy, convergent beam electron diffraction, and stimulated fluorescence. Thick and thin film samples with one dimensional crystalline orientation are being characterized to isolate microstructural effects.

Abstract submitted for presentation in the NIST Workshop on Stress in Polycrystalline Diamond in February, 1994.

Measurement of Stress in CVD Diamond by Raman Spectroscopy

Kevin Gray, Henry Windischmann
Norton Diamond Films
Goddard Rd., Northboro, MA 01532

In order to understand the strength and fracture behavior of CVD diamond it is necessary to understand the stress state of the material. Because of the polycrystalline nature of most CVD diamond, it is desirable to examine the stress state with resolution sufficient to detect highly localized stress concentrations, such as might exist at grain boundaries or near defects. Raman spectroscopy provides both a technique which is sensitive to stress and which can achieve resolution on the order of 1 μm.

Stress induced shifts in the 1332 cm^{-1} diamond Raman line are well known from measurements of single crystal diamond in high pressure experiments. Under hydrostatic pressure the first order diamond Raman line exhibits a pressure dependence of 2.9 cm^{-1}/GPa (1 cm^{-1}/350 MPa).[1] Under non-hydrostatic conditions, this line, which is triply degenerate, shifts and also splits into singlet and doublet lines. The singlet and doublet lines split with a pressure dependence of 0.7 cm^{-1}/GPa.[2] The magnitude of the shift is dependent on the nature of the imposed stress and may be determined from a decomposition of the stress tensor. Consider a stress tensor representing a uniaxial stress. This tensor may be decomposed into two components, a diagonal component representing hydrostatic stress and a traceless component representing shear, as is seen below.

$$\begin{pmatrix} \sigma & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} = \frac{1}{3}\begin{pmatrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & \sigma \end{pmatrix} + \frac{1}{3}\begin{pmatrix} 2\sigma & 0 & 0 \\ 0 & -\sigma & 0 \\ 0 & 0 & -\sigma \end{pmatrix}$$

Thus for a given uniaxial stress only $\frac{1}{3}$ of the hydrostatic Raman line shift will be observed. The same is true for the splitting of the line, as is seen from the shear component.

We have obtained Raman spectra for a CVD diamond sample subjected to a known uniaxial stress. The sample was an optical quality CVD diamond bar of dimensions $25 \times 1.3 \times 0.50$ mm from Norton diamond deposition run TD1043. The sample exhibited a strong $\langle 110 \rangle$ preferential orientation. Both the substrate and growth surfaces were polished to an optical finish. Uniaxial stress was induced by loading the sample in a 3 point bend fixture (growth surface in tension). Raman spectra were obtained at known locations on the sample in both the stressed and unstressed states. A large spot size (30 μm) insured that the spectra were averaged over several crystallites. The observed shifts in the Raman peak agreed well with the shifts expected based on the above discussion. Observation of splitting of the triply degenerate lines was not possible due to the small stresses, typical Raman linewidth of 2.6 cm^{-1}, and instrument spectral slit width of 0.75 cm^{-1}.

1. H.Boppart, J. van Straaten, I.F. Silvera, *Phys. Rev. B*, **32**, 1423 (15 July 1985).
2. M.H. Grimsditch, E. Anastassakis, M. Cardona, *Phys. Rev. B*, **18**, 901 (15 July 1978).

Characterization of Localized Stress in Polycrystalline Diamond

D.J. Vestyck, Jr. , D. Shechtman*, and J.E. Butler
Gas/Surface Dynamics Section, Code 6174
Naval Research Laboratory
Washington DC 20375

Localized stress has been observed in CVD diamond films using micro-Raman spectroscopy. This stress is observed qualitatively as a broadening or shifting of the diamond phonon peak near 1332 cm^{-1} and occasionally as multiple peaks. Splitting of the Raman band due to defect induced stress grown into the crystal has been observed previously (*Applied Physics Letters* 62, 1227(1993)) in single crystal CVD diamond . Scanning electron microscopy is used to examine the surface morphological features in the stressed region. The micro-Raman instrument used for this study used 514.5 nm radiation (35 mw.) with a spatial resolution ca. 1 micron and a spectral resolution (FWHM) > 2.5 cm^{-1}. Multiple phonon peaks were not observed when macro-Raman (spot size > 30 microns) was employed. Thick CVD Diamond films from various sources and deposition techniques were examined. The highly stressed regions were found to be very localized and spatial maps of the splitting/stress are correlated with the surface morphology. Shifts exceeding 10 cm^{-1} (3 GPa) have been observed.

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* The Technion, Haifa, Israel, and The Johns Hopkins University, Baltimore MD

ELASTIC PROPERTIES AND MICROSTRESSES IN POLYCRYSTALLINE DIAMOND FILMS

S. K. Kurtz, The Pennsylvania State University
Susmit Kumar, University of Cincinnati

We have used a recently developed Poisson-Voronoi tesselation model[1] of polycrystalline materials and a new finite element method[2] for space filling arrays of irregular convex polyhedra to calculate both the effective elastic moduli of uniaxial, untextured bulk polycrystalline diamond and the microstresses around individual grains in textured films. The results for Young's modulus are in reasonable agreement with the results of Beetz et al.[3] ($E_{eff} = 874 \pm 400$ GPa) for fine (0.5 μm) grained polycrystalline diamond films. Our results for the microstresses in six sided grains in textured thin films of the same geometry studied by Tvergaard and Hutchinson[4], show very large stress gradients near grain triple points, with peak stresses well in excess of the mean applied stress. These large stress gradients extend well into the body of the grain and are a sensitive function of the crystallographic orientation of the neighboring grains relative to the central grain being studied. Results for the microstresses near grain corners (vertices) in a three dimensional aggregate will also be shown. The dependance on Zener elastic anistropy and texture will be discussed.

[1] S. Kumar, S. K. Kurtz, J. R. Banavar, and M. G. Sharma. 1992. *J. Statistical Physics* 67:523-557. S. Kumar and S. K. Kurtz. 1993. *Materials Characterization* 31:55-67. S. Kumar, S. K. Kurtz, J. R. Banavar, and H. Zhang. 1993. Normal grain growth in metals and ceramics: Constraints of statistical topology and geometry. In *Modeling of Coarsening and Grain Growth* edited by C. S. Pande and S. P. Marsh, 165-182. TMS.

[2] S. Kumar. 1993. Ph.D. Thesis, The Pennsylvania State University. S. Kumar and S. K. Kurtz. Preprint. Simulation of material microstructure using a 3D Voronoi Tesselation: Calculation of effective thermal expansion coefficient of polycrystalline materials. *Acta Metallurgica*. In Press

[3] C. P. Beetz Jr., C. V. Cooper, and T. A. Perry. 1990. *J. Materials Research* 5:2555-2560.

[4] V. Tvergaard and J. W. Hutchinson. 1988. *J. American Ceramic Society* 71:157-166.

STRESS AND FRACTURE IN DIAMOND FILMS

J. J. Mecholsky, Jr and L. P. Hehn

Department of Materials Science and Engineering, University of Florida

Gainesville, FL 32611

Abstract

Many of the potential applications for the use of diamond as a coating on microelectronic substrates, structural materials, etc., and as a bulk infrared transmitting window involve diamond as a structural material or, at least, diamond that can withstand the necessary stresses of fabrication and normal handling. Thus, crack propagation and fracture become critical elements in the design of any component. However, until recently, very little study has been reported on the fracture of diamond. This presentation outlines the current approach to determining the fracture behavior of diamond based on fracture mechanics, fractal geometry and molecular dynamics (MD) modeling and an approach to obtaining stresses in films. The relationship of bond breaking on the atomic scale is related to the macroscopic fracture features observed on the fracture surface of diamond disks.

We have determined that the critical fracture energy for polycrystalline diamond is about 25 J/m^2. Most fracture paths proceed across the grains, i.e., transgranularly, and appear to fail from the surface. Most of the crack sizes have been in the range of 50 to 200 μm. The strength appears independent of thickness.

Residual stresses in polycrystalline CVD diamond coatings deposited on the (110) surface of silicon were measured using the $\sin^2\psi$ X-ray diffraction technique. Over the range of thicknesses examined (4-25 μm) the stresses appeared to be independent of thickness. Preliminary results indicate the presence of growth stresses, i.e., stresses unaccounted for by thermal expansion mismatch alone. It is clear that large stresses can be present in diamond films. The potential of diamond as a structural material is assessed and the potential for reducing the existing stresses is discussed.

References:

"Fracture Studies of Diamond Films on Silicon," J. J. Mecholsky, Y. L. Tsai and W. R. Drawl, JAP 71 (10) 4875, 1992

"Fracture and Mechanical Properties of Diamond," J. J. Mecholsky, Jr., 2nd International Conference on the Applications of Diamond Films and Related Materials (ADC '93) Japan, Nov. 1993.

FRACTURE BEHAVIOR OF CVD DIAMOND

M. D. Drory,[1] J. W. Ager,[2] and R. O. Ritchie[2]

[1]Crystallume
125 Constitution Drive
Menlo Park, California 94025

[2]Center for Advanced Materials
Materials Sciences Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

Abstract

The fracture properties of CVD diamond are explored by uniaxial tension testing of relatively large plate specimens. Standard disk-shaped compact tension specimens were used to measure the fracture toughness of CVD diamond with plate specimens of >200μm thickness. Attempts were made at placing a sharp pre-crack in the specimen by laser cutting. The fracture toughness was estimated as 5.3 MPa√m, which is a value consistent with previous measurements by indentation techniques. Effects of pre-crack geometry and residual stress on fracture toughness testing of diamond will be discussed.

DEFECT INDUCED BRITTLENESS IN CVD DIAMOND

Dan Shechtman

Technion, Haifa
Guest Scientist at NIST and NRL

Structural defects in the form of $\Sigma=3$ twins which evolve during the deposition of CVD diamond play an important role in the growth process. They relieve a portion of the stress which develop due to an integration of foreign atoms in the growing rigid diamond lattice and enable rapid growth of new layers by providing nucleation sites along reentrant corners. Intersection of $\Sigma=3$ twins cause the formation of higher order twins ($\Sigma=9$, $\Sigma=27$ and $\Sigma=81$) and are, therefore, responsible in part to the locally stressed regions which accompany non-coherent high order twins. The columnar structure of diamond wafers offers a straight fracture path along the grains. Grain and high order twin boundaries are found along the fracture path. Twin boundaries may thereby contribute to lowering the fracture toughness of diamond wafers.

Appendix E

List of Attenders

Final Participants List

Workshop on Characterizing Diamond Films III
February 23-24, 1994
National Institute of Standards and Technology (NIST)
Gaithersburg, Maryland

James E. Butler
Naval Research Lab.
Code 6174
Washington, DC 20375

Arvio Casler
John Crane, Inc.
6400 W. Oakton St.
Rm. G1-614
Morton Grove, IL 60053

Jack Daugherty
Thermotrex
9550 Distribution Ave.
San Diego, CA 92121

Brian Davidson
Naval Research Lab.
4555 Overlook Ave., NW
Code 6604
Washington, DC 20375-5345

Mark Develyn
GE
P.O. Box 8
Schenectady, NY 12309

Michael D. Drory
Crystallume
125 Constitution Dr.
Menlo Park, CA 94025

Edgar Etz
NIST
Bldg. 222, Rm. A113
Gaithersburg, MD 20899-0001

Edward Farabaugh
NIST
Bldg. 223, Rm. A329
Gaithersburg, MD 20899

Roy Fauber
Kobe Steel USA, Inc.
79 TW Alexander Dr.
4401 Bldg.
Rsch Triangle Park, NC 27709

Albert Feldman
NIST
Bldg. 223, Rm. A329
Gaithersburg, MD 20899-0001

Renee G. Ford
Materials & Technology
23 Park Drive South
Rye, NY 10580

Steve Freiman
NIST
Bldg. 223, Rm. A256
Gaithersburg, MD 20899-0001

Roy Gat
Applied Science & Technology
35 Cabot Rd.
Woburn, MA 01801

Paul D. Goldman
Norton Diamond Film
Goddard Rd.
MC NNB-106
Northborough, MA 01532

John Graebner
AT&T Bell Labs.
Rm. 1D-157
Murray Hill, NJ 07974

Kevin Gray
Norton Diamond Film
Goddard Rd.
Northboro, MA 01532

John Gudas
NIST
Bldg. 101, Rm. A415
Gaithersburg, MD 20899-0001

Rob Hallock
Raytheon Company
131 Spring St.
MC L144
Lexington, MA 02173

Alan B. Harker
Rockwell International
1049 Camino Dos Rios
Thousand Oaks, CA 91360

Thomas Hartnett
Raytheon Company
131 Spring St.
MC L168
Lexington, MA 02173

Sandor Holly
Rockwell International
6633 Canoga Ave.
Mail Stop FA03
Canoga Park, CA 91304

James Intrater
Oryx Technology
47341 Bayside Pkwy.
Fremont, CA 94538

Olaf Kaeding
Daimler-Beuz AG
Wilhelm-Runge Str 11
89081 Ulm, Germany

Dan Kennedy
TI Group, Inc.
2001 Jeff. Davis Hwy.
Ste. 607-A
Arlington, VA 22202

Fred Kimock
Diamonex, Inc.
7150 Windsor Dr.
Allentown, PA 18106

Claude Klein
9 Churchill Lane
Lexington, MA 02173

Pao-Kung Kuo
Wayne State Univ.
666 W. Hancock
279 Physics Bldg.
Detroit, MI 48201

Stewart Kurtz
Penn State Univ.
State College, PA 16803

Robert Linares
Linares Mgmt Assoc, Inc.
93 West St.
Medfield, MA 02052

Grant Lu
Norton Diamond Film
Goddard Rd.
Northboro, MA 01532

Jack Mecholsky
Univ. of Florida
256 A Rhines Hall
Gainesville, FL 32611

Raymond Meilunas
Grumman Aerospace
MS A01-26
Bethpage, NY 11714

Richard Miller
Raytheon Company
131 Spring St.
MC L126
Lexington, MA 02173

Lawrence Mizerka
Night Vision & ES Direct.
MC AMSEL-RD-NV-LPD
Fort Belvoir, VA 22060

Dave Pickrell
Diamonex, Inc.
7150 Windsor Dr.
Allentown, PA 18106

K. V. Ravi
Lockheed Missiles & Space
3251 Hanover St.
Palo Alto, CA 94304-1191

Lawrence Robins
NIST
Bldg. 223, Rm. A329
Gaithersburg, MD 20899

Yoichiro Sato
NIRIM
Namiki 1-1, Tsukuba
Ibaraki 305 Japan

Liselotte Schioler
BDM Technologies
7915 Jones Branch Dr.
McLean, VA 22102-3396

Jan Schreurs
Westinghouse STC
1310 Beulah Rd.
Pittsburgh, PA 15235

Dan Shechtman
NIST
Bldg. 223, Rm. B309
Gaithersburg, MD 20899-0001

Jogender Singh
Applied Research Lab.
P.O. Box 30
State College, PA 16804

David Slutz
GE Superabrasives
6325 Huntley Rd.
Worthington, OH 43085

T. S. Sudarshan
Materials Modification
2929-P1 Eskridge
Fairfax, VA 22031

Robert Thomas
Wayne State Univ.
666 W. Hancock
281 Physics Bldg.
Detroit, MI 48201

Thomas Thorpe
Naval Research Lab.
Code 5622
Washington, DC 20375

Kevin Turner
Naval Research Lab.
4555 Overlook Ave., SW
Code 5622
Washington, DC 20375

Ronald Tye
ULVAC Sinku Riko
6 Riverside Dr.
Andover, MA 01810

Y. Tommy Tzeng
Auburn Univ.
200 Broun Hall
Auburn, AL 36849

Jan Vandersande
JPL
4800 Oak Grove Dr.
Pasadena, CA 91109

Ronald Weimer
Naval Research Lab.
Code 5622
Washington, DC 20375

C.B. Willingham
Raytheon Company
131 Spring St.
Lexington, MA 02173

Robert W. Woolfolk
Southwest Rsch Institute
1235 Jeff. Davis Hwy.
Arlington, VA 22202-3293

Edward Yu
3M Center
CRTDL, 219-18-01
St Paul, MN 55144