NISTIR 5198

Workshop on Characterizing Diamond Films II

February 24-25, 1993
Gaithersburg, MD

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National Institute of Standards and Technology

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Advanced Technology Materials

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Norton Diamond Film

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May 1993

U.S. DEPARTMENT OF COMMERCE
Ronald H. Brown, Secretary

NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY
Arati Prabhakar, Director

Organizing Committee:

Chairman – Albert Feldman, NIST
Charles Beetz, Advanced Technology Materials
Paul Klocek, Texas Instruments
Grant Lu, Norton Diamond Film

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WORKSHOP ON CHARACTERIZING DIAMOND FILMS II

Abstract

The second in a series of workshops was held at NIST on February 24th and 25th to discuss the characterization of diamond films and the need for standards in diamond technology. The audience targeted for this workshop were the 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: characterization of optical absorption and scattering for optical applications; characterization of electrical properties and electrical contacts for electronic applications; and, standardization of thermal conductivity measurement for heat spreading applications. A particular accomplishment of the workshop was the formation of a working group to evaluate methods of measuring the thermal conductivity or thermal diffusivity of CVD diamond. A round-robin is being organized to compare different measurement techniques. A set of specimens prepared voluntarily by producers of CVD diamond will be circulated among experts in the measurement methodologies. NIST will coordinate the circulation of the specimens among the measurement laboratories and will collate the results of the measurements for presentation at the next working group meeting.

Key Words: chemical vapor deposition, contacts, CVD, diamond, electrical properties, electronic properties, metallization, optical scattering, optical absorption, Raman spectroscopy, standards, thermal conductivity, thermal diffusivity.

1. Introduction and Conclusions

The second in a series of workshops was held at NIST on February 24th and 25th 1993 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 first workshop [1]. The audience targeted for this workshop was the producers and potential users of CVD diamond technology. University scientists and scientists from government laboratories were invited as experts in properties measurements. There were 44 attenders at the workshop.

We focussed on three technical topics for discussion: characterization of optical absorption and scattering for optical applications; electronic characterization — metallization and electronic contacts for electronic applications; and, standardization of thermal conductivity measurement. In addition, a short session presented some new developments in Raman measurements and in thermal conductivity measurements.

An important session of the workshop was devoted to the formation of a working group for standardizing thermal conductivity measurements. Grant Lu of Norton Diamond Film was informally chosen to chair the working group. At this session, a round-robin comparison of thermal conductivity and thermal diffusivity measurements was agreed upon. A set of specimens prepared voluntarily by producers of CVD diamond will be circulated among experts in the measurement methodologies. NIST will coordinate the circulation of the specimens among the measurement laboratories and will collate the results of the measurements for presentation at the next working group meeting.

All registrants have been asked to evaluate the workshop. The purpose for this evaluation was to determine the usefulness of the workshop, the desire for further workshops, topics for future workshops, and the need for additional standards related activities. The feedback received is given in Appendix A.

Sections 2 to 6 contain summaries of the main sessions of the workshop. Appendix B contains the workshop program, Appendix C contains the abstracts of the papers presented, and Appendix D contains a list of attenders.

The principal conclusions of the workshop include:

- There is no apparent need for special techniques to optically characterize CVD diamond. Techniques used on other materials appear to be adequate.

- Sessions on optical characterization and electrical characterization should be part of future workshops in order to maintain a free exchange of information among workers in the field.

- A working group to investigate standardization of thermal conductivity measurements on CVD diamond has been formed.

- Planning was begun for an interlaboratory round-robin comparison of thermal conductivity and thermal diffusivity measurements. NIST will coordinate this activity.

2. Characterization of Optical Absorption and Scattering

Seven presentations that discussed procedures for measuring the optical absorption and scattering in CVD diamond were given.

The first presentation was by P. Klocek of Texas Instruments who discussed and compared the physical properties of diamond with other optical materials. While the broadband transparency, low thermooptic constant, and low dispersion of diamond are very attractive, it is the combination of these properties with exemplary mechanical and thermal properties that make diamond compelling for passive optics, i.e., infrared windows, coatings, geometric optics, diffractive optics. Specific application requirements such as transmission, emission and optical phase were discussed in terms of measurable optical properties, i.e., n and k, absorption coefficient, scattering coefficient, and modulation transfer function. Microscopic theory (quantum theory of phonons) and macroscopic theory (Maxwell's equations) were used to introduce the various optical measurement techniques for the optical properties. Tolerances or variances were suggested for these properties for the various passive optical applications along with a simple statistical method for determining the required measurement technique accuracy.

J.M. Trombetta of Texas Instruments presented a discussion of the common methods for determining the infrared absorption coefficient spectrum of an optical material specimen. CVD diamond now under development is thin, typically less than one millimeter thick. This translates into a small material response and therefore low precision in transmission and emission measurements. While background noise is low in Fourier-transform infrared (FTIR) spectrometers, signal drift and reflection artifacts in the instrument cause errors in the absolute transmittance. Photoacoustic spectroscopy can assist in distinguishing absorption loss features from scattering loss but the technique is generally non-quantitative. Therefore, for highly accurate properties determinations, a combination of techniques would be most valuable. Dr. Trombetta indicated that a proper identification of the various contributions to transmission loss requires a complete optical analysis, including measurement of both scattering and absorption spectra.

C.A. Klein of Raytheon, discussed laser damage in diamond. He stated that the laser damage threshold of diamond is high but not uniquely so. While diamond's exceptionally large figure-of-merit for thermal shock resistance suggests an outstanding laser damage threshold for high average-power optical radiation, its large nonlinear refractive index n_2, suggests a low critical power for self-focusing and, hence, a low peak-power damage threshold. The low self-focusing threshold combined with the occurrence of surface damage due to graphitization will thus limit diamond's usefulness as a window for transmission of high peak-power laser radiation. Measured data from various sources was reviewed. Type IIa natural diamond crystals exposed to picosecond pulses of 355 nm radiation exhibited surface ablation at threshold intensities of roughly 60 GW/cm^2. Surface damage (melting) was observed at peak intensities of 6 TW/cm^2 when diamond was irradiated with femtosecond pulses at 620 nm. Single picosecond pulses of 1.06 μm radiation from a Nd:YAG laser resulted in internal damage due to dielectric breakdown. The large value of n_2 (2.3×10^{-13}) resulted in a self-focusing critical power of 1.7 MW and a breakdown intensity of 1 to 3 TW/cm^2. Another study showed that type IIa diamond, exposed to nanosecond pulses of CO_2 laser radiation at 10.6 μm, exhibited sub-surface damage at intensities in the low GW/cm^2 range. The results suggested that the breakdown intensity depended on laser wavelength and pulse characteristics. To date, the only laser damage studies reported on CVD diamond were performed on poor quality samples. Laser damage studies are needed on high-quality CVD diamond.

K.A. Snail of the Naval Research Laboratory discussed the need to determine the amount of bulk and surface light scattering in CVD diamond, particularly for infrared window/dome applications. Scattering measurements performed at 0.633 μm and 10.6 μm on polished specimens of poor quality CVD diamond revealed significant bulk scattering which was much greater than scatter exhibited by typical optical materials. A first order scattering theory was described which allows for distinguishing between bulk scatter and surface scatter. Studies with a microscope equipped FTIR spectrometer suggested that the grain boundaries of the CVD diamond are the major source of bulk scatter. Commercial light scattering equipment capable of measuring the bidirectional distribution function is available; however, their use is limited to only a few laser sources.

R.P. Miller of Raytheon discussed the use of laser calorimetry to measure optical absorption coefficients. The basic techniques for measuring optical absorption were discussed. Transmittance or photometric techniques possess spectral information but lack sensitivity; absorption coefficients not much less than 10^{-2} cm^{-1} can be measured with these techniques. Emittance techniques are sensitive to much smaller absorption coefficients (10^{-5} cm^{-1}) but are subject to background noise. Laser calorimetry is sensitive to small absorption coefficients (10^{-5} cm^{-1}) and relatively straightforward to perform. However, spectral information is limited to the wavelengths of the laser sources used; thus, the technique has limited usefulness if one requires spectral information about materials that exhibit complex absorption spectra. Because CVD diamond is thin, one has difficulty in separating the surface from bulk contributions to absorption. Bulk scattering in the diamond also complicates the calculation of absorption coefficient; if the scattering is not properly taken into account, one can overestimate the absorption coefficient. Data from several sources were discussed. A CO_2 laser was the optical source. Typical absorption coefficients for natural type IIa diamond were found to be 0.06 cm^{-1} at 9.2 μm and 0.04 cm^{-1} at 10.6 μm, although values as high as 0.4 cm^{-1} at 10.6 μm were found. This may result from sample to sample variability or from slight differences in the wavelength of measurement on a specimen with an absorption coefficient that has a strong wavelength dependence. (CO_2 lasers can operate at several closely spaced wavelengths such as 10.591 μm and 10.67 μm) Data at local spots in high quality CVD diamond showed absorption coefficients of 0.094 cm^{-1} at 9.27 μm and 0.067 cm^{-1} at 10.591 μm, without correction for surface absorption which was believed to be small.

L.H. Robbins of NIST discussed the use of specular transmittance and reflectance to measure the optical constants of CVD diamond. Expressions for transmittance and reflectance in the presence of surface scatter and bulk absorption were presented. By fitting the measured transmittance and reflectance to these expressions, values are obtained for the sample thickness, root-mean-squared surface roughness, refractive index and extinction or absorption coefficient. The model was developed for the study of thin unpolished optical films, less than several micrometers thick, where the surface scatter only partially attenuates the specular beams. This corresponds to a surface roughness to wavelength ratio close to unity. Transmittance and reflectance measurement on CVD diamond samples 0.42 μm thick with surface roughness 10 nm, and 1.90 μm thick with surface roughness 30 nm were fit to the model. The calculated absorption coefficients were significantly higher than the absorption coefficients of type IIa diamond. Because most CVD diamond material produced is much thicker than the specimens measured, the typical roughnesses will be much greater. For these types of specimens, unless they are polished, the model has limited usefulness in the ultraviolet-visible range, but the model may prove useful in the infrared.

In the final presentation, M.E. Thomas of Johns Hopkins University discussed how emissivity measurements can be used to obtain optical properties of diamond. In the two-phonon region, 4 to 7 μm, diamond has a fairly high absorptivity and therefore a high emissivity. The emissivity of diamond in this region was found to be 0.8 and not very sensitive to temperature; thus, the emission signal is large. In the three- and four-phonon regions, 2 to 4 μm, diamond is weakly emissive. However, if the specimen is sufficiently thick, the emitted radiation in this spectral band can have a useful signal:noise ratio. Thomas pointed out that in the 7 to 12 μm region, which is of great interest, emissivity measurements are difficult to make because the background emission in this spectral band is large relative to the diamond emission. Because the optical phonon spectrum in diamond begins at wavelengths below this spectral range, emission is exceedingly week and the signal:noise ration is small. Work is now in progress to overcome this difficulty. Other difficulties with emission measurements on diamond include oxidation above 800 K when high temperature measurements are performed and light scattering within the sample. At this time, emission measurements on CVD diamond appear to be most useful in the 2 to 7 μm region and perhaps in the visible region in low scatter specimens. However, measurement of absorption by emissivity measurements in the 7 to 12 μm region is difficult.

In summary, the session on optical characterization of CVD diamond benefitted both speakers and other participants because of the free exchange of information.

3. Electronic Characterization — Metallization and Electronic Contacts

Seven speakers presented different aspects of the electrical properties of semiconducting diamond and the formation of ohmic and Schottky contacts.

The first paper was given by J. Vandersande from the Jet Propulsion Laboratory. He presented the results of recent electrical resistivity measurements on diamond between room temperature and 1200 °C. He described a special apparatus designed for making resistivity measurements up to 1200 °C and showed that resistivity values of $\sim 10^{16}$ Ω-cm typically reported in the literature for type IIa natural diamond represent a lower limit to the true values because of limitations in the measurement instrumentation. The resistivity of type IIa diamonds was found to drop from $\sim 10^{15}$ Ω-cm at 200 °C to 10^4 Ω-cm at 1200 °C, with an activation energy of ~ 1.5 to 1.6 eV. Results were also presented for CVD diamond films that showed electrical resistivities comparable to or greater than those for natural type IIa diamonds; the CVD films also had similar activation energies. Dr. Vandersande cautioned that during high temperature measurements, surface graphitization can occur, leading to a decrease in specimen resistance on cooling. The surface graphitization layer can be removed by cleaning in acid solutions, thus restoring the original specimen resistance.

C. Hewett from the Naval Command, Control and Ocean Surveillance Center discussed the importance of low resistance ohmic contacts to high power device applications of semiconducting diamond. Ohmic contact formation is based on a solid state reaction in which a transition metal reacts with the diamond to form a carbide layer during high temperature annealing. This carbide interface layer is in intimate contact with both the metal contact and the underlying diamond, thus promoting good adhesion between the metal contact to the diamond. Dr. Hewett described a technique for measuring the specific contact resistance using a circular transmission line model. This technique eliminates the need for mesa etching, a procedure that is usually needed for minimizing artifacts due to three dimensional current flow.

M. Geis of Lincoln Laboratories reviewed the device properties of diamond and discussed the advantages and disadvantages of diamond in high power, high frequency devices. He discussed the use of various surface treatments for passivating the diamond surface in order to eliminate surface leakage currents. Exposing diamonds to CF_4O_2 or N_2 plasmas gave the best results. Dr. Geis also presented interesting results which illustrated that artifacts in capacitance-voltage measurements can be caused by back surface contact resistance. He also discussed interesting approaches to achieving large area single crystal diamond substrates; a novel method was developed for placing of highly oriented diamond seed crystals on patterned Si substrates. He also discussed applications of diamond as a cold electron emitter.

J. von Windheim from Kobe Steel USA, Inc., discussed electronic transport measurements on natural single crystal diamonds, homoepitaxial CVD diamond, and polycrystalline CVD diamond films. He reviewed the results of various measurements such as high temperature resistivity, AC conductivity, DC current-voltage measurements, and space charge limited currents. In addition, he described the role of these measurements in identifying various trapping centers. Results of Hall effect and resistivity measurements indicate a complex conduction process in which 2 to 20 percent of the boron atoms used to dope the diamond specimens are compensated. The nature of the compensating center has not been elucidated but it is believed to be nitrogen, possibly in the A-aggregate form. Comparisons were made between the transport properties of polycrystalline diamond films and diamond single crystals. The transport properties of the polycrystalline films were much poorer that those of the single crystals.

J. Glesener of the Naval Research Laboratory presented additional results describing the electrical characterization of impurities in diamond. He employed admittance spectroscopy to characterize deep levels associated with boron impurities. The technique consisted of measuring the AC conductivity of a Schottky-barrier diode fabricated on the diamond. The conductance of the sample was measured as a function of temperature and as a function of the AC frequency. The AC voltage applied to the Schottky diode modulates the intersection of the Fermi level with the impurity level, providing a time dependent source of carriers. Dr. Glesener showed that the conductance peaked when the carrier emission rate from the trap became comparable to the AC frequency. The trap emission rate could be changed by lowering the temperature of the diamond. From these measurements, the energy level of the deep trap was found to be 0.33 eV and the hole capture cross-section was estimated to be $\sim 2\text{x}10^{-12}$ cm^2. The deep trap was believed to be due to boron that had been present in the gas used to grow the diamond.

K. Das from Kobe Steel USA, Inc. discussed contacts on diamond. He reviewed the results for a wide range of metals, semiconductors, silicides and metal carbides as rectifying contacts on semiconducting diamond. He showed that direct metallization on CVD grown films does not always produce good rectifying contacts; it is sometimes necessary to introduce an insulating diamond or dielectric film between the doped diamond and the metal in order to get a good rectifying characteristic. He also showed that the rectification properties of metal contacts can be improved by near surface implantation of boron into the diamond prior to the metallization step. Dr. Das also discussed the formation of low resistance ohmic contacts using carbide forming transition metals deposited on heavily doped diamond films. He also presented data on the chemical composition of the formed contact structures.

The last presentation was given by C.P. Beetz of Advanced Technology Materials, Inc. He discussed the measurement of Schottky-barrier heights of metals on diamond using the method of internal photoemission. He listed the Schottky barrier heights of various metals on diamond and discussed the observation of a region showing two thresholds in the photoyield of metals on type IIa natural diamond. Dr. Beetz pointed out that the upper threshold values presented in some of the literature must be corrected to take into account contributions from the lower threshold. He also discussed controlling the Schottky-barrier height of metals on diamond by using shallow near surface silicon implants. These implants would favor reactions with silicide forming metals. He showed results for platinum, molybdenum, and titanium contacts in which the barrier height decreased with increasing silicon implant dose.

4. Work in Progress and New Developments

A special session was organized for presentation of new results and to cover miscellaneous topics not covered by the principal sessions.

E. Etz of NIST presented recent results of Raman spectroscopy measurements on several specimens provided by two producers of CVD diamond. This work was presented in the context of a proposed Raman standard reference material discussed at the previous workshop. The Raman spectrum is being used as a measure of diamond quality. The quality of diamond is considered to decrease with increasing line width of the diamond Raman line at 1332 cm^{-3}, increasing background luminescence intensity, and increasing intensity of the sp^2 carbon peak near 1550 cm^{-1}. In high quality films, the sp^2 peak may not be observable. Freestanding diamond wafers of high quality with thicknesses ranging from 300 μm to 1.7 mm were examined. A cross-sectional examination by Raman spectroscopy indicated that the diamond in the bottom layer (the material closest to the substrate during deposition) was of poorer quality than the diamond in the top layer. The width of the diamond Raman line in one of the specimens was equal to the width of the diamond Raman line in a type IIa single crystal natural diamond. This result suggests that the specimen was essentially strain free. The Raman spectrum of a specimen deliberately doped with nitrogen indicated a deterioration in the quality of the diamond. A trace analysis of a cross-section indicated the presence of Na, K, Ca, and Mg, possibly due to contamination of the specimen during preparation.

At the previous workshop, D. Morelli of the General Motors Research Laboratory discussed the thermal conductivity of CVD diamond as a function of temperature. The curve representing the temperature dependence at low temperature showed a kink that could not be explained satisfactorily. At this workshop, Dr. Morelli presented the results of an experiment that appears to explain the effect. In this experiment, thermal conductivity measurements were made on single crystal diamond specimens before and after exposure to neutron radiation. Prior to irradiation, the specimens did not exhibit the kink in the thermal conductivity whereas after irradiation and heat treatment, a kink appeared. The temperature at which the kink occurred was correlated with the expected sizes of the defects produced. At low temperatures, the mean wavelength of thermal phonons is greater than the size of the defect so that scattering is reduced. As the temperature increases, the mean phonon wavelength decreases and scattering increases resulting in a decrease in the expected thermal conductivity behavior. The result is a kink in the dependence of thermal conductivity on temperature. The larger the size of the defect, the lower the temperature at which the kink will occur. The work also demonstrated that grain boundaries are transparent to phonon propagation, at least at the low temperatures.

L. Wei of Wayne State University described the method of photothermal deflection for measuring the thermal diffusivities of diamond. Measurements had been performed on a large number of diamond specimens over the last several years at Wayne State. Dr. Wei discussed the measurement of thermal diffusivity as a function of temperature of diamond crystals containing higher ratios of C^{12}:C^{13} than the natural abundance ratio. She found that the thermal conductivity increased with decreasing C^{13} content. The temperature dependence of the thermal conductivity could be explained by a theory that took into account both Umklapp phonon scattering processes and normal phonon scattering processes.

5. Thermal Conductivity of Diamond: Standardization Issues

Six presentations were given that discussed general standardization issues and specific measurement techniques related to measuring thermal conductivity. R. Tye from Ulvac Sinku-Riko reviewed the ideal requirements for a standard measurement method, standard methods now in use for determining thermal conductivity, and related international standards. Some of the ideal requirements for a standard method are: a generally accepted and proven technique; the availability of a related current standard; relative simplicity in the concept, design and operation of the equipment; rapid and minimal specimen preparation; a capability of providing absolute values to a known precision or a required precision. The advantages and disadvantages of techniques such as axial rod heat flow, 3 omega, flash, converging wave, and ac calorimetry were discussed. The flash method is used in three international standards (ASTM, UK/BS and Japan/JIS) for thermal diffusivity measurements. However, these standards would need modification to be applicable to CVD diamond.

R. Taylor from the Thermophysical Properties Research Laboratory at Purdue University stressed the difficulty of accurately measuring thermal transport properties. He showed that published thermal conductivity values of 99.9+% pure tungsten and TiC show very large variations; values differing by factors of two to three were observed. Professor Taylor then described a new measurement technique developed at Purdue University. In this technique, a thin strip of diamond 50 mm long × 4 mm wide is partially masked. The unmasked portion is uniformly exposed to a step input of heat from an infrared lamp by means of a shutter. Three thermocouples, attached along the length of the masked portion of the sample, monitor the rise in temperature as heat flows from the unmasked portion of the specimen to the heat sink at the other end. The time dependence of the temperature is used to compute the thermal diffusivity.

D. Slutz from General Electric Superabrasives discussed the development of two methods suitable for quality control monitoring of thermal conductivity rather than for obtaining absolute accuracy. The first is based on Ångström's method [2]. A modulated laser beam focused to a line at one edge of the specimen provides the heat source. An infrared detector monitors the phase lag of the traveling thermal wave as a function of the distance from the heating source. The thermal diffusivity is calculated from the data. In the second method, the specimen is heated in the same manner as above but data is collected at a single point on the specimen. A Fast Fourier Transform analyzer is used analyze the collected data, from which the thermal diffusivity is calculated. The measurement time for each specimen is 20 minutes.

J. Graebner of AT&T Bell Laboratories described measurement techniques to measure the thermal conductivity in the plane of a specimen and the thermal diffusivity perpendicular to the plane of the specimen. The in-plane measurement is performed with a two-heater steady state technique; one of the heaters allows for a correction due to radiative heat loss and conductive heat loss through the electrical leads. The perpendicular thermal diffusivity is measured by the laser flash technique. A thermal conductivity of 26 W/cm/K has been calculated from laser flash measurements on high quality CVD diamond.

S. Preston described laser flash measurements of thermal diffusivity at AEA Technology in Great Britain. A high power Q-switched ruby laser was used as the heating source. A relatively thick metallic coating (10 μm thick) was deposited on the diamond to absorb the laser beam without being ablated away. In order to account for the transient delay due the coating, a measurement was performed on a piece of high purity copper foil coated along with the diamond films. Because the thermal diffusivity of the copper foil was known, he was able to calculate the thermal diffusivity of the coating; this value was used in calculating the thermal diffusivity of the diamond.

G. Lu of Norton Diamond Film described the results of thermal modelling to determine the relative importance of in-plane thermal conductivity vs. perpendicular thermal conductivity for lowering the temperatures of junctions of diamond with other materials. In most cases, a higher perpendicular thermal conductivity led to a lower junction temperature. The one exception was the case of a small circular heat source having a diameter much less than the diamond thickness; in this case, in-plane heat spreading plays the major role in removing heat from the junction region. Results were also presented which showed that incremental decreases in junction temperature were minimal when the diamond thermal conductivity increased beyond three to four times the thermal conductivity of the heat sink on which it is placed.

6. Organization of Working Group

Thermal management applications are leading the way in large-scale commercialization of CVD diamond. Recent press announcements [3] show the incorporation of CVD diamond into the production of high power electronic packages. However, not only is there no accepted method of measuring the thermal conductivity of CVD diamond, but different methods can frequently yield significantly different results. Therefore, a working group has been formed to examine the issues and formulate a recommendation on standardizing thermal conductivity measurements of CVD diamond. The members of the working group are:

Grant Lu, Norton Diamond Film - Chairman
Albert Feldman, NIST
John Graebner, AT&T
Ronald Tye, ULVAC Sinku-Riko

David Slutz, General Electric
Pao-Kuang Kuo, Wayne State University
(Steven Preston, AEA Technology - Associate Member)

As one of the first steps in the process, an interlaboratory round-robin test will be conducted to assess differences in the results of measurements made at different laboratories using different methods. A set of samples will be fabricated by several manufacturers and sent to different laboratories for measurement of thermal conductivity. At the workshop, Norton Diamond Film, General Electric, and Raytheon agreed to supply specimens. AT&T, Wayne State University, Purdue University, AEA Technology, Sinku Riko, General Electric, and Norton Diamond Film offered to perform the measurements. Other manufacturers and measurement laboratories will be asked to participate. The results will be compiled by NIST and presented at the next workshop.

7. References

[1] "Workshop on Characterizing Diamond Films", NISTIR 4849, A. Feldman, C.P. Beetz, M. Drory, and S. Holly, 1992.
[2] M.A. Ångström, "A New Method of determining the Thermal Conductibility of Bodies", Philos. Mag. **25**, 130-142 (1863); Annln Phys. **114**, 513-521 (1861).
[3] Photonics Spectra, November 1992, Laurin Publishing Company, Inc.

Appendix A - Workshop Evaluation

Workshop attenders were asked to evaluate the workshop. 24 evaluations were received. Almost all of the attenders found at least one of the discussion topics useful. Below are listed the suggestions received for future workshop topics and for possible subjects for standards. Most suggestions and comments received are presented.

What topics would you like covered next year?

	Number of responses and comments
Optical properties	✓✓✓✓✓✓✓, temperature dependence, absorption and scattering
Electronic properties	✓✓✓✓✓✓✓✓✓✓, transport, contact barrier heights
Doping characterization	✓✓✓✓✓✓✓, implant doping
Defect characterization	✓✓✓✓✓✓✓✓✓, electrically active defects
Thermal properties	✓✓✓✓✓✓✓✓✓✓✓✓✓, heat transfer issue, new developments, thermal stability
Tribological characterization	✓
Other:	✓✓✓✓✓✓ Mechanical properties Structural-mechanical damage due to polishing-finishing and effects on optical products like domes and windows. Stresses and strain, fracture Joints, contacts, contact resistance, etc. Adhesion characteristics Effect of surface preparation on material and characterization

In your view, what specific standard specimens and standard measurement procedures are needed?

> "Chemical impurity levels at concentrations of parts per billion, especially light elements."
>
> "Thermal diffusivity"
>
> "Procedures for thermal and electronic properties would benefit from standardization. Standard specimens need to be of sizes relevant to applications."
>
> "Round robin thermal conductivity measurements"
>
> "Standardization of the electrical measurements are probably not so critical at this stage. Developing a basic understanding is more important."

"Working group and round robin are good starts."

"This area needs more work." (Temperature dependence of optical properties) "Most researchers are applying standard techniques that can be optimized better. Also, better CVD samples are needed for accurate measurements."

"Thin film hardness"

"I don't feel that a strong push toward standard methods for thermal conductivity is in order yet. We need to explore the applicability of various techniques and arrive at accurate values before settling on a method or methods."

"In terms of electrical characterization, it is probably too early to identify measurement methods and it is likely that these will evolve as the technology matures. However, we have found that sample preparation is critical for all types of electrical measurements. Hall effect measurements, C-V measurements and I-V measurements are all affected by the quality of the ohmic contact and the method of surface preparation (cleaning). Another major issue, which people are starting to recognize, is the fact that annealing (CVD) samples at high temperatures is generally necessary to obtain reliable electrical data. It may still be too early to address these issues for diamond but, on the other hand, it is important that people who do electrical measurements are made aware of basic requirements for proper diamond sample preparation."

"A standard measurement technique for measuring thermal diffusivity parallel and perpendicular to plane on free standing diamond films ~300 μm thick. A round robin interlaboratory exercise."

"Thermal conductivity, impact strength and other mechanical properties"

Comments

"To continue to emphasize the electronics industry needs will focus a large group of people on defects, a topic of interest to us."

"It was suggested that a committee be formed to investigate the need for standards in diamond electronics. I am interested in participating in this effort."

"A good workshop which satisfied my need to keep up to date on measurement techniques being developed to measure the thermal properties of diamond films in the U.S.A. I was pleased to see a round robin exercise put forward on these types of measurements and would like to see an international effort in this area."

"Based on the diversity of today's discussion, it appeared to me that at this time it is unclear that the industry is looking for standards — each of the participants are (sic) still looking for confirmation that their efforts are valid and useful for the establishment of the industry/market applications. Leadership and discussion to encourage CVDD to emerge into the industrial arena may be healthy for this country's participation in the "new Mat'l Industry" market place — Congratulations to NIST for taking on this Big Job!"

Appendix B - Workshop Program

WORKSHOP on CHARACTERIZING DIAMOND FILMS II
National Institute of Standards and Technology
Gaithersburg, MD 20899
February 24, 25, 1993

FINAL PROGRAM

Wednesday Morning, February 24
Administration Building, Lecture Room D

8:30am Refreshments

9:00am Welcome

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

9:10am Characterization of Optical Absorption and Scattering — Chairman, Paul Klocek, Texas Instruments

Requirements, Issues, Standards Needs for Optical Property Measurements of CVD Diamond
P. Klocek
Texas Instruments

Spectral Measurements of Absorption in CVD Diamond: Issues and Standards
J.M. Trombetta, J.T. Hoggins, T.A. McKenna, and P. Klocek
Texas Instruments

Laser Induced Damage Thresholds of Diamond
Claude A. Klein
Raytheon

Light Scattering Measurements of CVD Diamond
K.A. Snail, D. Chenault, C. Merzbacher, and C.F. Hickey
Naval Research Laboratory

10:45am Refreshments

11:00am Characterization of Optical Absorption and Scattering (Continued)

Optical Absorption Coefficient of CVD Diamond Determined by Laser Calorimetry
Richard P. Miller
Raytheon

Determination of the Optical Constants of Thin CVD Diamond Films by Specular Transmittance and Reflectance Spectroscopy
Lawrence H. Robins
NIST

Optical Properties of Intrinsic Diamond and Experimental Emissivity of CVD Diamond
Michael E. Thomas and William J. Tropf
Applied Physics Laboroatory

Discussion

12:30pm Lunch

(continued)

Wednesday Afternoon, February 24
Administration Building, Lecture Room D

1:30pm Electronic Characterization — Metallization and Electrical Contacts, Chairman, Charles Beetz, ATM

Electrical Resistivity Measurements of Diamond and Diamond Films Between Room Termperature and 1200 C; Results and Some Pitfalls.
Jan W. Vandersande — Jet Propulsion Laboratory

Ohmic Contacts to Semiconducting Diamond
C.A. Hewett — Naval Command, Control and Ocean Surveillance Center

Electronic Transport in Natural and CVD Diamond
Jesko von Windheim, Brad Fox, Dean Malta, Henry Wynands — Kobe Steel USA, Inc.

Electrical Investigation of Impurities in Diamond
John W. Glesener — Naval Research Laboratory

3:00pm Refreshments

3:15pm Electronic Characterization — Metalization and Electronic Contacts (Continued)

Metal Contacts on Diamond
K. Das — Kobe Steel USA, Inc.

Internal Photoemission Measurements of Schottky Barrier Heights of Metals on Diamond
Charles Beetz — Advanced Technology Materials

Diamond Transistor Performance and Fabrication
M.W. Geis and J.C. Twichell — Lincoln Laboratory

Discussion

5:00pm End of Session

6:30pm Dutch Treat Dinner

(continued)

Thursday Morning, February 25
Administration Building, Lecture Room D

8:30am	Refreshments	
9:00am	Work in Progress and New Developments — Chairman, Albert Feldman, NIST	
	The Raman Spectrum of CVD Diamond as a Measure of Diamond Quality and Performance	
	Edgar S. Etz	NIST
	Influence of Defects on Thermal Conductivity	
	Donald Morelli	General Motors Research
	Mirage Effect Measurement of the Thermal Conductivity of Diamond	
	Lanhua Wei, P.K. Kuo, and R.L. Thomas	Wayne State University
10:00am	Standardization of Thermal Conductivity Measurement — Chairman, Grant Lu, Norton Diamond Film	
	Standardization of Thermal Conductivity Measurements: Anisotropy and Accuracy Issues	
	Grant Lu	Norton Diamond Film
	Thermal Conductivity of Diamond: Standardization Issues	
	R. P. Tye	ULVAC Sinku Riko, Inc.
10:45am	Refreshments	
11:00am	Standardization of Thermal Conductivity Measurement (Continued)	
	Determination of Thermophysical Properties	
	R.E. Taylor	Purdue University
	A Simple Method for the Determination of Thermal Diffusivity in Free-Standing Diamond Sheet	
	P.G. Kosky	GE R&D Center
	D.E. Slutz	GE Superabrasives
	Techniques for Measuring $\kappa_{\parallel}$ and $D_{\perp}$ in CVD Diamond Plates	
	John E. Graebner	AT&T Bell Laboratories
12:30am	Lunch	

(continued)

Thursday Afternoon, February 25
Administration Building, Lecture Room D

1:30pm Standardization of Thermal Conductivity Measurement (Continued)

The Thermal Diffusivity of Diamond Films Using Parker's Method
S.D. Preston AEA Technology

Discussion and Organization of Working Group

3:00pm Refreshments

3:15pm Standardization of Thermal Conductivity Measurement (Continued)

Time available as needed

5:00pm Adjourn

Abstracts

Characterization of Optical Absorption and Scattering

Chairman — Paul Klocek
Texas Instruments

REQUIREMENT, ISSUES, STANDARDS NEEDS FOR OPTICAL PROPERTY MEASUREMENTS OF CVD DIAMOND

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The continued development and improvement of CVD diamond is encouraging an increased focus on the specific requirements and the concomitant physical properties necessary for specific applications. One such application is optics. This paper will present an overview of the optical property requirements of CVD diamond for various optical component applications with emphasis on passive optical elements such as windows, domes, lenses and coatings. These requirements, such as transmission, emission, optical intensity and optical phase, will be used to identify the necessary measurable optical physical property such as index of refraction (both n and k), absorption coefficient, scattering coefficient, laser damage threshold, and modulation transfer function (MTF). Potential areas of measurement technique and data analysis that might benefit from standardization will be reviewed. A simple statistical methodology will be reviewed that could be used for any specific requirement of an optical component application allowing selection of a proper measurement technique and data analysis based upon their variances. This methodology also has utility as the measurement or observation function in the basic synthesis development of CVD diamond.

SPECTRAL MEASUREMENTS OF ABSORPTION IN CVD DIAMOND: ISSUES AND STANDARDS

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A means of obtaining a precise and accurate determination of the absorption coefficient spectrum of an optical material specimen is a requirement for understanding its physical structure and for directly predicting its performance as a window. Due to technological limitations, CVD diamond is costly both to polish and to deposit in thickness and tends to scatter light from bulk sites to some degree. When used to study thin samples which scatter light, each of the spectral techniques commonly employed suffer some new incorporation of error. For this reason, it is best to use a combination of techniques aimed at an accurate and complete determination of optical properties, including both the scattering coefficient and the absorption coefficient and their local variation with structure. Several methods including transmission, photoacoustic and integrating-sphere measurements will be reviewed. The information provided by each technique and its limitations for a variety of sample properties will be discussed.

LASER INDUCED DAMAGE THRESHOLDS OF DIAMOND

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The contemplated utilization of CVD diamond windows for high-power free-electron lasers [1] critically depends on properly characterizing potential damage mechanisms as a function of laser wavelength, pulse duration, and spot size. Until very recently, relevant information has been fragmentary and contradictory. Some authors [2] claim that, since diamond has an exceptionally good figure of merit for tolerance to thermal shock, this material should exhibit outstanding resistance to damage from intense optical radiation. Others [3] contend that, owing to the high value of the non-linear refractive index n_2, the critical power for self-focusing is relatively low, which, in conjunction with the occurrence of surface damage due to graphitization, makes diamond "unsuitable" as a high-peak-power laser window material. In fact, both statements are misleading: The optical damage resistance of diamond is among the highest of all materials but by no means exceptional. It is the purpose of this presentation to discuss the situation in the light of recent laser-damage threshold measurements performed on type-IIa natural diamonds and to speculate on performances (standards) that may be achievable with synthetic CVD diamonds.

At 355 nm, work in progress at CREOL [4] points to surface ablation at threshold intensities (I_{th}) of roughly 60 GW/cm^2, for picosecond pulses, presumably caused by two-photon processes since the relevant absorption coefficient is about 0.3 cm/GW. Surface damage (melting) has also been observed in the three-photon absorption regime (620 nm), at much higher intensities ($I_{th} \simeq 6$ TW/cm^2), upon using femtosecond "pump" pulses and detecting front-surface reflectivity enhancements by means of a "probe" beam [5]. Perhaps more significant are the results of experiments performed at 1.06 µm with picosecond single pulses from a Q-switched mode-locked Nd:YAG laser [3,4], which show clear evidence of internal damage initiated by dielectric breakdown. Based on n_2 values derived from Z-scans ($n_2 = 2.3 \times 10^{-13}$ esu and not 7.2×10^{-13} esu as reported in Ref. 3), the critical power for catastrophic self-focusing should be approximately 1.7 MW, which leads to estimated breakdown intensities in the 1 to 3 TW/cm^2 range. Early experiments on CVD diamond using differential reflectometry [2], which yielded orders of magnitude lower thresholds ($I_{th} = 620$ MW/cm^2) at the Nd:YAG laser wavelength, are not indicative of the performance of high-quality material since the films were damaged by surface graphitization/ablation resulting from absorption due to the presence of sp_2-bonded carbon. Finally, we note that damage studies at the CO_2-laser wavelength (10.6 µm) on type-IIa diamonds[6] also point to a sub-surface field-induced electron-avalanche ionization mechanism but at threshold intensities in the low GW/cm^2 range, for nanosecond pulses, which suggests that the breakdown field strength may exhibit a fairly strong dependence on laser wavelength and/or pulse characteristics.

I am indebted to Rick DeSalvo (University of Central Florida) for making his data available prior to publication, to Prof. M. Downer (University of Texas at Austin) for an enlightening discussion, and to Dr. J. Savage (UK Defense Research Agency) for a preprint of Ref. 6.

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Light scattering measurements of CVD diamond

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ABSTRACT

Diamond grown with chemical vapor deposition (CVD) processes is currently being considered for use as a long wave infrared (LWIR) dome/window material for super- and hyper-sonic missiles and as a sensor window material for supersonic aircraft. In order to assess diamond's suitability for these applications, a complete understanding of the optical properties of CVD diamond is needed. This includes a determination of the relative amount of bulk and surface scattering, and a measurement of the absorption in thick CVD diamond films. In this paper, we present scattering data for visible (0.633 μm) and infrared (10.6 μm) wavelengths from optically smooth thick (200-500 μm) diamond films. Scattering data from the aluminized front and back surfaces of the films is also reported. These measurements, together with first order scattering theory, provide a means for determining the component of scattered radiation which is due to bulk scattering. For the diamond samples analyzed, the visible scattering ($\lambda = 0.633$ μm) is strongly dominated by bulk phenomena, and the infrared scattering level was found[1] to be significantly higher than a ZnSe flat. In the visible, the films were photographed in transmission with an optical microscope. The grain boundaries clearly showed up as being darker than the grain centers, indicating higher levels of either absorption or scatter. In the infrared, an FTIR with a microscope accessory was used to show that the transmittance is significantly higher on some grain centers compared to the adjacent grain edges.[2] These observations suggest that grain boundaries are a major source of scatter in polycrystalline diamond films.

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[2] This technique was first reported by John Trombetta (Texas Instruments) at the tri-service DoD diamond conference held at Raytheon in October, 1992.

OPTICAL ABSORPTION COEFFICIENT OF CVD DIAMOND DETERMINED BY LASER CALORIMETRY

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In the late 60's there was a need to develop better techniques to accurately measure low levels of residual absorption in infrared transmitting materials. This effort was driven by advances in high power CO_2 gas laser research and the need for window components with very low optical absorption coefficients.[1,2] The basic techniques can be broken down into three classes: transmission measurements, measurements based on emittance and calorimetric measurements. Of the techniques applied, laser calorimetry has became the most widely used primarily because of its simplicity, low detection limits and relatively low sensitivity to scattered radiation.[3] Laser calorimetry has been useful in assessing both bulk and surface optical absorption coefficients in bulk materials as well as films. Most of the low loss materials have the advantage that they can be fabricated into an almost unlimited variety of sample sizes and geometries. Diamond on the other hand poses a much greater restriction such that the ability to separate out the contributions from surface an bulk effects is more difficult.

Characterization of diamond absorption by CO_2 laser calorimetry has been conducted in several labs. Most of the work has concentrated on assessing single crystal natural material. J. Zar[4] has done 10.6 µm laser calorimetry on 17 natural clear type Ia and IIa single crystals with bulk coefficients ranging from 0.021 cm^{-1} to 1.95 cm^{-1}. The range of values reported for type IIa material at 10.6 µm are from 0.015 cm^{-1} to 0.400 cm^{-1}.[5] More recently S. McGeoch et al.[6] have used laser calorimetry to evaluate four specimens of type IIa diamond at four wavelengths from 9.24 µm to 10.67 µm. Their results fall within the range of previously reported data with an average value of 0.027 cm^{-1} at 10.6 µm. At Raytheon, we have measured the optical absorption coefficient at 9.27 µm and 10.591 µm on both natural type IIa diamond and a number of high quality CVD specimens. After separating the surface from the bulk absorption based on a plot of total fraction absorbed vs thickness, the type IIa bulk values were 0.062 cm^{-1} and 0.047 cm^{-1} at 9.27 µm and 10.591 µm respectively. The best average values obtained to date for CVD diamond on a single sample without separating out the surface contribution are 0.094 cm^{-1} and 0.067 cm^{-1} at 9.27 µm and 10.591 µm respectively.

This review will present a detailed discussion of the strengths and weaknesses of laser calorimetry for determining the optical absorption coefficients of CVD diamond in the intrinsically transparent regions. The sources and magnitude of the errors will be examined along with the details of the measurement technique applied at Raytheon. Finally the most up to date results on our MPCVD diamond will be presented. Laser calorimetry is an excellent technique with many advantages for the development of standards to characterize the optical absorption coefficients of CVD diamond bulk material as well as films.

I wish to thank Keith Harris of Dubbeldee Harris Diamond Corporation for providing the single crystal type IIa samples and Tom Varitimos of Raytheon Company for making the laser calorimetry measurements.

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DETERMINATION OF THE OPTICAL CONSTANTS OF THIN CVD DIAMOND FILMS BY SPECULAR TRANSMITTANCE AND REFLECTANCE SPECTROSCOPY

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Polycrystalline diamond films produced by chemical vapor deposition generally have rough, faceted surfaces. A collimated light beam may be weakly or strongly scattered when it interacts with such a surface, depending on the ratio of the root-mean-squared (r.m.s.) surface roughness to the wavelength. If this ratio is much smaller than unity, then most of the light will undergo specular transmission or reflection; if the ratio is unity or larger, then the light will be almost entirely scattered away from the specular directions. This talk will concentrate on the analysis of the transmittance and reflectance spectra of free-standing diamond films for intermediate values of the roughness-to-wavelength ratio, where the specular beams are partially but not completely attenuated by surface scatter.

Quantitative expressions for the effects of surface scatter were developed by Filinski[1]. According to his model, for light of wavelength λ normally incident on the surface of a free-standing film with refractive index equal to n and r.m.s. surface roughness equal to σ, the electric field amplitudes of the specular beams are reduced by factors s_t for transmission, s_x for external reflection, and s_n for internal reflection (from inside the film), where

$$s_t = exp\{-2\pi^2(n-1)^2(\sigma/\lambda)^2\} \qquad s_x = exp\{-8\pi^2(\sigma/\lambda)^2\} \qquad s_n = exp\{-8\pi^2 n^2(\sigma/\lambda)^2\}$$

From the above equations, combined with the standard equations for the optical properties of a weakly absorbing film, expressions can be derived for transmittance and reflectance in the presence of both surface scatter and bulk absorption. By fitting these expressions to the experimental transmittance and reflectance data, values can be obtained for the film thickness d, the r.m.s. roughnesses σ of both film surfaces, the refractive index $n(\lambda)$, and the extinction coefficient $k(\lambda)$ (or the absorption coefficient $\alpha(\lambda) = 4\pi k(\lambda)/\lambda$).

Data from several diamond films with thicknesses between 0.42 and 1.90 μm, and r.m.s. surface roughnesses between ~10 and ~30 nm, were analyzed according to this model. The absorption spectra of these films are found to differ significantly from the absorption spectrum of a perfect diamond crystal. Although most CVD diamond films have surface roughnesses too large for the method presented here to be applicable, at least in the UV-visible range, it may prove useful for other types of optical thin films. A version of this work has been published previously.[2]

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OPTICAL PROPERTIES OF INTRINSIC DIAMOND AND EXPERIMENTAL EMISSIVITY OF CVD DIAMOND

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Since current CVD diamond samples show absorption close to the intrinsic absorption of type IIa single crystal diamond, it is worthwhile to discuss the frequency and temperature dependence of the intrinsic optical properties. Direct emission measurements are sensitive to background radiation which is always present to some level in the spectrometer and sample chamber. Thus, knowledge of the intrinsic emissivity can be used to determine the necessary background suppression for achieving a reasonable signal to noise ratio. This is important because sample temperatures currently of interest are not high enough to easily overwhelm the background radiation in the long wavelength (8 to 12 μm) spectral region. This point is a major design consideration for an emissometer that is to be used for measurements on diamond and other materials that transmit at long wavelengths.

Experimental and theoretical results from several spectral regions will be presented and implications discussed. The 7 to 12 μm region exhibits low emission in the presence of a potentially high background radiation. Thus, a cooled emissometer or signal discrimination techniques are required. The 4 to 7 μm region covers the diamond two-phonon absorption band and this is a region of high emissivity. A noninvasive pyrometric technique can be used to directly measure the sample temperature. The 2 to 4 μm region covers the three and four phonon bands, which are weakly emissive depending on the sample thickness. The last two spectral regions have low to modest background radiation contamination levels and are easier emission measurements to make than far infrared emission measurements. Also, the intrinsic absorption of diamond near the band gap will be discussed.

A review of experimental techniques for measuring the infrared emissivity of CVD diamond will be presented. Since diamond begins to oxidize at temperatures above 800 K in air, a high-vacuum emissometer must be used above this temperature.

Electronic Characterization — Metallization and Electrical Contacts

Chairman — Charles Beetz
Advanced Technology Materials

Electrical Resistivity Measurements of Diamond and Diamond Films Between Room Temperature and 1200 C; Results and Some Pitfalls.

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The electrical resistivity of insulating natural type IIa diamond is very high at room temperature and can be difficult to measure, similarly with the resistivity of undoped diamond films. An apparatus was specifically designed and built to be able to measure very high resistivity insulators up to 1200 C. The high temperature data are very useful specifically to determine activation energies.

The resistivity of natural type IIa diamond is reported in the literature to be 10^{16} Ω-cm but that has been found to be an "apparatus-limited" value [1]. Values greater than 10^{16} - 10^{17} Ω-cm cannot be measured. The resistivity of natural type IIa diamond drops from approximately 10^{+15} Ω-cm at 200 C to 10^{+4} Ω-cm at 1200 C with an activation energy in the 1.5 - 1.6eV range. Undoped diamond films which only two years ago had room temperature resistivities typically in the 10^{10} - 10^{16} range now have resistivities almost as good or in a few cases higher than that for natural type IIa diamond. Just about all good undoped diamond films have high temperature activation energies that are also in the 1.5 - 1.6 eV range, indicating that the same impurity (maybe nitrogen) is responsible.

Most electrical resistivity measurements of diamond films that go up in temperature above at least 400 C and then back down to room temperature, give different up and down curves. These differences are usually in the literature attributed to changes in the film itself. This belief is only correct if the resistivity is higher on the down curve [2]. Lower resistivities on down curves are due to graphitization of the surface which is not optically visible and takes place even in a vacuum as good as 10^{-5} to 10^{-6} Torr. The original resistivity can easily be restored by cleaning the diamond or film in an acid solution. The rate at which the data is taken is also important. Sitting at a temperature above 400 C for several hours in a vacuum of 10^{-4} to 10^{-6} Torr will result in a lower resistivity, again due to surface graphitization.

Several examples with data will be presented for the various cases.

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Ohmic Contacts to Semiconducting Diamond

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The unique material and electronic properties of diamond make it a potentially very important candidate for use in high power or high frequency applications, as well as in high temperature and corrosive environments. The performance of any electronic device, however, is determined by a combination of device structure and the materials properties of the structure. The development of ohmic electrical contacts is an integral stage in the implementation of a new material technology. A low contact resistance is the primary requirement for such contacts; however, they must also be strongly adherent, able to withstand the high temperatures for which diamond devices are intended, and as much as possible, they should be compatible with conventional device processing techniques.

The formation of low resistance ohmic contacts to any wide band gap semiconductor is a difficult problem due the large potential barrier which arises when a metal is deposited on the semiconductor. To further complicate the problem, diamond has a large surface state density, effectively pinning the Fermi level far from the band edges. In spite of these difficulties, techniques have been developed to produce ohmic contacts to naturally occuring p-type semiconducting diamond. Ohmic contacts produced via a solid state annealing process have been studied extensively and are believed to satisfy all four conditions [1]. In this process a thin film of a transition metal carbide forming metal is deposited on the diamond surface. Annealing at high temperature (950°C) leads to the formation of a carbide layer at the interface. This layer provides an intimate contact to the diamond and promotes good adhesion. Auger electron spectroscopy studies indicated that the decrease was associated with the formation of a carbide phase. Similar results have been observed for Ti/Au, V/Au and Ta/Au contacts. In contrast, non-carbide forming metals tend to exhibit poor adhesion, and poor ohmic contact behavior [2].

Ohmic contacts are characterized by measuring the series resistance arising at the contact-semiconductor junction, R_c. Normalizing this resistance to the contact area yields the specific contact resistance, r_c. For the ideal case of uniform current flow perpendicular to the contact $r_c=R_c/A$, with A being the contact area. In reality, however, the current flow is rarely perpendicular, and the finite resistance of the semiconductor leads to current crowding. Utilizing an array of contact pads of equal size, but varying separation, contacting a thin conducting layer allows one to deconvolve the current crowding and semiconductor bulk resistance from R_c, thereby uniquely determining the specific contact resistance. The primary drawback to this transmission line model is the need to perform a mesa etch in order to reduce the analysis of current flow between contacts to a two dimensional problem. Using a circular test pattern consisting of a central dot and concentric ring contacts eliminates the need for a mesa etch. The measurements are interpreted using a circular transmission line model [3].

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Electronic Transport in Natural and CVD Diamond

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Diamond is considered to have a unique combination of electronic properties that make it an optimal material for high frequency/high power electronic devices. Additionally, the radiation hardness and chemical inactivity of diamond make it attractive as an electronic material for harsh environments. The electronic characterization of diamond via Hall effect and resistance measurements as well as capacitance-voltage (C-V) and current-voltage (I-V) measurements is critical for the development of diamond as an electronic material.

Various trap levels have been determined in undoped diamond using space charge limited current (SCLC), ac conductivity, and dc resistivity measurement techniques. High temperature resistivity measurements indicate an activation of ~1.5 eV for high quality polycrystalline diamond, as well as for type IIa natural crystals. This activation is generally attributed to a nitrogen donor, although there is some question as to whether it is substitutional nitrogen (with an ionization energy of ~2 eV relative to the conduction band), or possibly the A-aggregate of nitrogen (with an ionization energy of ~ 4 eV). Other trap levels have been determined by SCLC and ac conductivity to lie at ~0.4 and 0.6 eV, while dc resistivity measurements on many polycrystalline materials reveal an activation at ~1 eV. The nature of these various trap levels is still under investigation.

Results from Hall effect and resistivity measurements consistently support a complex conduction mechanism involving valence band conduction (i.e., due to B ionization), impurity band conduction (due to overlap of B orbitals), and hopping conduction (due to transition of a hole from an occupied to an unoccupied acceptor site). Calculations based on high temperature Hall measurements, as well as C-V measurements, indicate that the level of compensation is typically ~10^{15}-10^{17} cm^{-3}. Thus, depending on the B doping level, compensation ratios range from ~2-20%. The nature of the compensating center has not been investigated in detail; however, optical measurements support a nitrogen donor, possibly in the A aggregate form. Although some success has been reported in obtaining n-type diamond, no singular method has gained wide acceptance, indicating that reproducibility may still be a problem.

Comparison of polycrystalline and homoepitaxial diamond indicates that transport is substantially degraded in the polycrystalline material. Mobilities for polycrystalline diamond range from ~10-33 $cm^2/V{\bullet}s$ compared to ~560 $cm^2/V{\bullet}s$ for similarly doped homoepitaxial material. It has been speculated that charge trapping at the grain boundaries, similar to what has been observed in polycrystalline Si, is primarily responsible for the degradation in transport properties, although the role of intragranular defects cannot be discounted. At the same time, complex conductivity behavior is observed in polycrystalline diamond at lower doping levels, relative to the homoepitaxial samples, indicating that grain boundaries may be responsible for an enhancement of impurity conduction or hopping conduction.

In summary, a better understanding of the electrical transport in undoped and B doped diamond is being developed. Future work needs to concentrate on the role and the nature of specific trap levels, and the development of active devices that are viable within the constraints set by the transport properties of diamond materials.

The authors would like to Dr. K. Das and Mr. V. Venkatesan (Kobe Steel USA Inc.) for their help in carrying out this work.

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Electrical investigation of impurities in diamond

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Impurity detection is an important part of the semiconductor process control cycle because of the feedback provided in tracking down sources of contaminants. Many techniques are available to detect impurities in traditional semiconductors. Electrical techniques such as DLTS are widely applied because of their ease of implementation and their low cost; they can detect impurity concentrations as low as $10^{10}/cm^3$.

Currently, boron is the only useful electrically active impurity in diamond. Because the boron impurity level is not shallow, compensation by electrically active donors, particularly nitrogen, can be a problem. Adaptation of electrical techniques that require the measurement of a capacitance or conductance of a diamond Schottky barrier device may not be straight forward because of measurement complications due to series resistance in the sample. A recent adaptation of admittance spectroscopy to diamond Schottky barriers is discussed.[1] Results from the admittance measurements are presented.

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Metal Contacts on Diamond

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Metal contacts on semiconductor surfaces are of great scientific and technological interest. Establishing suitable ohmic and rectifying contacts on semiconducting diamond is of particular interest since this material has a number of attributes making it very desirable for the fabrication of electronic devices for operation at high frequencies, voltages and power levels. Although adhesion can be a problem, good rectifying contacts can be established on naturally occurring semiconducting crystals with evaporated or sputtered films of almost any conducting material. Elemental metals, semiconductors, silicides and metallic carbides have all been reported as rectifying contacts on semiconducting diamond crystals. Conventional current-voltage (I-V) and capacitance-voltage (C-V) measurements on these rectifying contacts have yielded information pertaining to dopant concentration, contact barrier heights, and deep-level states in the crystal. However, in the case of chemical vapor depostion (CVD) grown diamond films, direct metallization does not always produce acceptable rectifying contacts. It has been necessary to introduce a layer of an insulating diamond or a dielectric film on a previously deposited doped film in order to obtain rectification using a metal semiconductor structure. In these structures the metal film can be replaced by a heavily doped layer of diamond as the conductor. In a recent study an ion implantation step has been used to modify the surface and the subsurface region of a B doped diamond film. It has been demonstrated that a subsequently deposited metal contact exhibits a significant improvement in the rectifying characteristics from that of a similar contact without the implantation step. Ohmic contacts on diamond have been formed by depositing metals such as Ti, Ta and Mo with an overcoating of Au and a post-deposition anneal. Low-resistance contacts have also been obtained by placing metal contacts on highly doped diamond films. The high doping levels can be achieved either by *in-situ* doping during CVD film growth or by ion implantation at elevated tempertures. A combination of a highly doped films and metallization with a carbide forming metal has also been used for obtaining low resistance ohmic contacts on diamond. Apart from electrical characterization using conventional TLM patterns, these contacts have been analysed and chemical composition established by techniques such as Auger electron spectroscopy and X-ray photoelectron spectroscopy.

Acknowledgements
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Internal Photoemission Measurements of Schottky Barrier Heights of Metals on Diamond

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We re-examine the interpretation of barrier height measurements using internal photoemission and attempt to explain the appearance of two barriers and resolve the wide range of reported barrier heights of metals on diamond. We apply the technique of internal photoemission to study the effects of shallow Si implants on modifying the barrier heights of various metals deposited over the implant region. We find that the barrier height of metals such as Pt, Ti and Mo were reduced when deposited on shallow Si implants and given a heat treatment at 500°C. The barrier height of Pt on diamond was reduced from 1.89 eV to 0.97 eV by annealing of a sputtered Pt contact on a Si implanted dose of 10^{15} cm^{-2} that peaks at ~120Å into the diamond surface. Using the same approach, the barrier height of Ti on diamond was reduced from 2.00 eV to 1.29 eV, while the barrier height of Mo remained essentially unchanged. Although we have no direct evidence for silicide formation at this time, the reduction of the barrier height scaled inversely to the temperature of formation of the metal silicide. This is an extremely interesting observation and points to the possibility of achieving very low resistance contacts.

DIAMOND TRANSISTOR PERFORMANCE AND FABRICATION

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This presentation reviews some of the device properties of diamond as well as recently developed diamond device fabrication techniques. Diamond as a semiconductor in high-frequency, high-power transistors has unique advantages and disadvantages. Two advantages of diamond over other semiconductors are its high thermal conductivity and high breakdown field. The high thermal conductivity allows for higher power dissipation over similar devices made in Si or GaAs and the higher breakdown field makes possible the production of substantially higher-frequency higher-power devices than can be made with other commonly used semiconductors.

The lack of large-area single-crystal diamond substrates is the one largest technical obstacles to the development of diamond transistors. Boron is the only known p-type diamond dopant and because of its high activation energy (0.36 eV) only a fraction of the boron atoms contribute carriers to the valance band at room temperature. This makes even moderately doped, $10^{16}cm^{-3}$, diamond considerably more resistive, 10 to 100 Ω cm, than Si, 0.5 Ω cm, doped to the same level. However, even with these disadvantages high-voltage diamond transistors will still have a lower on-resistance than similar devices in Si or GaAs, because of diamond's high breakdown field.

Much of the technology necessary for the production of diamond devices already exists. Doping by homoepitaxy, etching diamond, preparing device quality SiO_2-diamond interfaces and ohmic contacts, will be reviewed. The remaining problems are the development of large-area single-crystal diamond substrates and improvement of doping techniques.

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Work in Progress and New Developments

Chairman — Albert Feldman
National Institute of Standards and Technology

The Raman Spectrum of CVD Diamond as a Measure of Diamond Quality and Performance

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The Raman spectrum of CVD diamond remains the most widely used analytical measure of ascertaining the quality of diamond with respect to its principal performance characteristics. The purity of the diamond phase determines many critical properties demanded by a wide range of applications. Raman scattering provides good sensitivity toward the detection and characterization of sp^2-bonded amorphous and graphitic carbon, if present in a matrix of sp^3- bonded diamond carbon. The spectra of such carbon composites are understood qualitatively , but not quantitatively. The ability of Raman spectroscopy to quantify these different carbon structures arises from several factors, among them optical absorption, resonance Raman effects, and optical scattering due to particle or grain boundaries and surface roughness.

The usefulness of the Raman spectrum beyond the identification of the different carbon phases has limitations. No correlations have appeared that relate the Raman spectrum to the principal elemental impurities, such as nitrogen and hydrogen commonly present below the 100 ppm level in high-quality CVD diamond. Diamond films and wafers of highest optical quality are now produced which furnish a Raman spectrum closely matching the spectrum of single-crystal natural diamond. For these forms of CVD diamond, the Raman spectrum appears to have reached its limit as a diagnostic measure of phase purity and structural perfection.

To further clarify the response of the Raman spectrum to the various differences in the compositional purity of CVD diamond, a broad range of samples from different sources (including specimens from industry) are examined by Raman microprobe spectroscopy. These studies examine the effects of grain size and grain boundary composition on the spectrum, in measurements mapping any sample heterogeneity in directions both parallel and perpendicular to the growth. The results shed light on the qualitative differences of diamond composition with growth, and are illustrated for optical quality thin films and free-standing wafers of varying thickness. Where possible, these data are related to the known performance properties of these materials. These new findings from the measurement of high-quality diamond films give us cause to re-examine the various requirements of a CVD diamond standard characterized by Raman spectroscopy.

Thermal Conductivity of Neutron-Irradiated Diamond Single Crystals and Films

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Neutron irradiation of diamond produces two common types of defects which can occur in vapor deposited material: vacancies and disordered carbon. These defects degrade the thermal conductivity and also induce absorption in the one-phonon region of the infrared spectrum [1]. We will discuss the similarity of the thermal conductivity of unirradiated CVD diamond containing growth-related defects and irradiated natural single crystals. We will also present new data on irradiated hot filament and microwave plasma assisted CVD material.

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Mirage Effect Measurement of the Thermal Conductivity of Diamond

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The mirage-effect/thermal wave technique has been successfully applied to the measurement of the thermal conductivity of a large variety of materials, especially to single crystal and CVD diamond which have unusually high values of thermal diffusivity. These measurements are absolute and involve only the measurement of a length and a time. The technique has been used to measure thermal diffusivity values over a range of seven orders of magnitude. Other than the accessibility of one flat surface. the technique has very little restriction for sample geometry, measurements can be made on sample areas as small as one square millimeter. It is equally applicable to bulk materials, thin films (free standing or on a substrate), and multilayered structures. Experimental results for CVD diamond films and quantum well structures are shown as examples of the applications.

We also present the latest experimental results on the thermal conductivity of isotopically enriched diamond crystals at low temperatures. By applying an existing theoretical model, we have obtained a very good fit for the thermal conductivity *vs.* temperature and isotope concentration. The extrapolation of our fit predicts that the thermal conductivity of a 99.999% ^{12}C diamond crystal would exceed 2000 W/(cmK) at its peak value.

Standardization of Thermal Conductivity Measurement

Chairman — Grant Lu
Norton Diamond Film

Standardization of thermal conductivity measurements: anisotropy and accuracy issues

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The measurement of thermal conductivity of CVD diamond poses a number of special challenges: anisotropic thermal conductivity, uniquely high thermal conductivity and size limitations. The different techniques which have been applied to CVD diamond measure the thermal conductivity in different directions: in-plane, (e.g. steady-state), perpendicular (e.g. laser flash) or a combination of the two (e.g. mirage wave). This makes it very difficult to compare the results of different measurement techniques. The question arises as to which direction is most important in determining the temperature rise of the heating source. Diamond's high in-plane thermal conductivity helps to spread the heat flux and therefore lower the temperature rise. However, the perpendicular thermal conductivity is also important because the thickness of the diamond represents a thermal impedance which is inversely proportional to the perpendicular thermal conductivity.

Finite element modelling was used to determine the temperature rise in a variety of situations, including circular and line heat sources, large and small heat sources, $k_{\perp} < k_{\parallel}$ and $k_{\perp} > k_{\parallel}$. For a line heat source, and a large circular heat source, the situation $k_{\perp} < k_{\parallel}$ leads to the lowest temperature rise. For a small circular heat source, $k_{\perp} > k_{\parallel}$ leads to the lowest temperature rise. Only in the latter case does heat spreading have full opportunity to take effect. In the other cases, rapid transit of heat through the diamond is still most important.

Thermal modelling was also used to examine the effect of (isotropic) thermal conductivity on temperature rise. If the diamond heat spreader is located on a copper heat sink, there is little difference in performance between diamond with a thermal conductivity of 1200 W/m/K and 1600 W/m/K. Although there is a greater performance difference between diamonds of lower thermal conductivity, such performance difference is minimized when solder between the heat source and diamond is considered. Therefore, in practice, an accuracy of ± 10% may be sufficient for predicting the temperature rise in a packaging system which includes diamond.

THERMAL CONDUCTIVITY OF DIAMOND: STANDARDIZATION ISSUES

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During recent years there has been a phenomenal increase in research and development devoted to the fabrication of CVD diamond and diamond-like carbon materials and coatings in forms varying from thin films on substrates to thick free-standing wafers. The immediate probability of these products being manufactured in commercial quantities has encouraged more attention to be paid to the development of new applications and markets and the corresponding need for standardization within the diamond community.

One of the most desirable attributes of diamond is its potential to be an extremely good thermal conductor while being an electrical insulator. However, for many have applications uniformity of thermal property is a most-necessary attribute. During the various stages of research and development it has been found that thermal conductivity is highly dependent on a number of material variables. In addition, different workers have used a variety of measurement methods to measure or derive the thermal conductivity. The resultant values, obtained in some cases on the same specimen or material, have show significant divergence.

The present paper reviews and discusses the various dependent and interdependent materials and measurement factors involved and their impact on the development of an acceptable standard test method(s) to determine the thermal conductivity, and/or its uniformity of diamond materials.

The material factors will include the impact due to effects of production variables, size and form, thickness, anisotropy, and temperature.

The measurement methods, both steady-state and transient techniques, will include longitudinal heat flow, flash diffusivity, thermal wave, modified ac calorimetry, 3-omega and will address particularly their applicability to the desired property requirement and also its direction relevant to specimen orientation. It will also include a brief outline of current national/international standards that may be applicable or that could be modified.

The discussion will conclude with recommendations concerning transfer standards (well characterized materials) to be used in interlaboratory, inter-method, studies both for determination of the precision and bias of the chosen method(s) and for comparative verification of other techniques.

DETERMINATION OF THERMOPHYSICAL PROPERTIES

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The measurements of thermal transport properties are among the most difficult measurements to perform accurately (for example see "Things Mother Taught Me - about Thermophysical Properties of Solids",R.E. Taylor,Thermal Conductivity 21, edited by C.J. Cremers and H.A. Fine, Plenum Press, New York, 1990 and Volume 1, Thermal Conductivity - Metallic Elements and Alloys or Volume 2, Thermal Conductivity - Nonmetallic Solids. Y.S. Touloukian, Series Editor, Plenum Press (1970). This is true even for favorable cases where available sample geometries are not severely limited and where seasoned experimenters using techniques developed over many years are employed. However, in the case of diamond films, we are faced with samples of limited and undesirable geometries of materials with unusual properties and for which standard techniques and apparatuses are not applicable. Furthermore, many of the attempts to make measurements are being performed by experimenters with limited background in thermophysical property determinations. Thus the potential for unreliable results is substantial.

At TPRL, a technique (patent applied for) to measure the thermal diffusivity of thin diamond films in the in-plane direction has been investigated (Y. Li, "Thermal Diffusivity of Highly Conductive Thin Films, PhD Thesis, Mechanical Engineering, Purdue University, 1991). Free-standing strip-shaped samples are used. One end is clamped to a heat sink whose temperature can be controlled from sub-ambient to above ambient. Transient heat flows are generated using step-heating applied to the other end. Temperatures are monitored at three locations along the sample. The temperature outputs from the two outer locations are used as boundary conditions to solve for the thermal diffusivity using parameter estimation techniques. Results have been obtained for several metal foils and diamond samples from -190 to +50 C.

A SIMPLE METHOD FOR THE DETERMINATION OF THERMAL DIFFUSIVITY IN FREE-STANDING DIAMOND SHEET.

by

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Free-standing diamond films are a new form of matter; the characterization of their properties requires new variants on the standard methods of measurement. Specifically, diamond crystals have the largest known thermal diffusivities and conductivities and the extended 2-dimensional form of free-standing diamond films manufactured via chemical vapor deposition methods pose additional difficulties. In particular, unlike single diamond crystals (which are isotropic), their properties may be non uniform and spatially varying[1], especially across the growth direction.

The current work has two intents: the development of a simple instrument which can be operated as a laboratory facility (and not as a research project) and secondly that the measurement be representative of the whole sample and not a narrowly localized area. The chosen technique is the travelling wave method of Ångstrom in which the phase lag β of a thermal wave of frequency Ω at a distance x along the diamond sheet is measured and which simply relates to the thermal diffusivity, α, by[2]

$$\beta = \frac{\pi}{4} + \sqrt{\frac{\Omega}{2\alpha}}\,x$$

A fully automated instrument has been contructed using a Fast Fourier Transform signal analyzer to detect the phase difference between an IR laser diode exciter and the resultant wave. Data routinely take 20 minutes to produce and compare well to those obtained by the "mirage" method[3].

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TECHNIQUES FOR MEASURING $\kappa_{||}$ AND $D_{\perp}$ IN CVD DIAMOND PLATES

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Because of the typically columnar growth of CVD diamond, it is often important to measure two components of thermal conductivity: for heat flow in a direction either parallel or perpendicular to the plane of the plate. For high accuracy (2-3%), the parallel conductivity $\kappa_{||}$ is measured with the two-heater heated-bar steady-state technique[1]. This is an improvement on the standard four-probe method in that it uses a second heater near the thermal ground to detect and correct for loss of heat by thermal radiation or by conduction through the electrical leads of heaters or thermometers. For the perpendicular case, the thermal diffusivity $D_{\perp}$ is measured by a flash technique[2] which differs from the traditional approach because of the short time scale encountered with thin diamond plates. For a 100 μm −thick plate with a thermal diffusivity of 18 cm^2/sec (for isotopically purified diamond single crystals at room temperature), the time of arrival of the pulse at the rear face is ~ $0.8 \mu s$. This requires the use of fast heating (8 ns pulse) and fast thermometry (100 MHz infrared detection). A number of precautions must be observed regarding sample thickness and width, initial temperature rise, and optically dense coatings on the front and rear surfaces. Results for high-quality CVD diamond will be described, with a room-temperature diffusivity of 14.7 cm^2/sec corresponding to a thermal conductivity of 26 W/cmK. This is higher than has been observed for the best gem-quality single-crystal diamond of natural isotopic abundance that has been reported in the literature.

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THE THERMAL DIFFUSIVITY OF DIAMOND FILMS USING PARKER'S METHOD

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AEA Technology has been measuring the thermal diffusivity of diamonds at room temperature since 1984 using Parker's method[1,2]. The types of material measured include polycrystalline diamond, synthetic diamond, natural diamond and more recently, various types of free standing diamond film with thicknesses ranging between 0.3 and 1.2 mm. Parker's method has been adopted as the British standard for measuring the thermal diffusivity of engineering ceramics, providing a thermal diffusivity through the plane of the material (see BS 7134: Section 4.2).

Parker's method consists of applying a short duration heat pulse to one side of a homogeneous, parallel sided sample and monitoring the temperature rise on the opposite side with an infra-red detector as a function of time. The thermal diffusivity can then be calculated from the transit time of the heat pulse and the thickness of the sample. The application of the technique to thin, high conductivity samples is limited only by the sample size and the measurement technology. To measure free standing diamond films it is necessary to coat the samples on both side with a thin metallic coating to make them opaque, so that the heat pulse is entirely absorbed at the surface and the infra-red detector monitors only the rear surface temperature. The high thermal conductivity of diamond makes it necessary to determine the transient delay caused by the coating and this is done by coating a piece of high purity copper foil along with the diamond films. Knowing the thermal diffusivity of the copper foil, we can determine the delay due to the coating. A Q-switched laser is used to provide a short heat pulse and a fast infra-red detector is used to monitor the rear surface temperature rise.

To prove the technique is applicable to diamond, we measured a 6 mm square of natural type IIa diamond[3], 0.6 mm thick. A thermal diffusivity of 13.9 ± 1.8 cm^2s^{-1} was obtained at 22°C which compares favorably with the estimated value of 13.5 cm^2s^{-1} at 22°C given in the TPRC[4] data manuals.

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Appendix D

List of Attenders

Final Participants List

WORKSHOP ON CHARACTERIZING DIAMOND FILMS
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