Characterization of CVD Diamond for Thermal Management Applications

R.S. Balmer, B. Bolliger, J.M. Dodson, D.J. Twitchen*

Element Six, 3901 Burton Drive, Santa Clara, California, 95054, U.S.A.

Email: Daniel.Twitchen@e6.com / Richard.Balmer@e6.com

Abstract

Data is presented on state-of-the-art microwave plasma assisted chemical vapour deposited (CVD) diamond films with thicknesses between 0.1 and 0.8 mm. Infrared transmission measurements are compared with through-thickness and in-plane thermal conductivities measured using thermal flash and heated bar techniques, respectively. A simple model is presented and discussed on the correlation between thermal conductivity and the integrated absorption in the infrared region of the spectrum between 2760 and 3030 cm^{-1}. This correlation opens the possibility to a cost effective, repeatable measurement methodology accurate enough for quality control and new recipe development.

Key words

Characterization, CVD diamond, Heat spreaders, Infrared absorption, Packaging, Thermal conductivity

I. Introduction

The ITRS Roadmap for semiconductors projects device power densities are on a trajectory to be well above $100W/cm^2$ at the 14 nm technology node. The advent of GaN devices, for high-voltage solid-state switching and high-power RF devices, are further enablers of this power-density trajectory. Thermal-management solutions for these high-power-density devices must go beyond today's commonly used materials to prevent forcing designers to compromise on performance, or reduce their design thermal margins, impacting product reliability and system efficiencies.

Synthetic diamond is an interesting material for thermal management in semiconductor packaging for advanced electronic systems driving towards higher power density, as it combines exceptionally high thermal conductivity with other relevant properties including electrical isolation, low density, low toxicity and mechanical stiffness/strength. Room temperature thermal conductivity values greater than 2000 W/mK are achievable for the highest quality polycrystalline synthetic diamond grown by microwave plasma assisted chemical vapour deposition (CVD) techniques [1]. This is the highest room temperature value of all known materials and exceeds that of copper, which is commonly regarded as an excellent thermal conductor, by a factor of more than five and by over a factor of 10 higher than commonly-used high *K* electrical insulators, such as aluminium nitride or beryllium oxide. The commercial availability of large area free standing CVD diamond has opened a host of possible options in which it can be used in the heat management of electronic and opto-electronic devices [1, 2]. Control of diamond grown by CVD has allowed the synthesis of material with optimized cost/performance for various thermal-management challenges from wafer bonding and device testing equipment to semiconductor packages and modules.

However, being able to tailor the thermal conductivity during synthesis dictates the requirement to measure the thermal conductivity, if not of every diamond heat spreader, then at least on a regular, on-going basis for quality control purposes and new recipe/grade development. Due to diamond's high values, measuring its thermal conductivity in a routine fashion is far from trivial, especially using methodologies that rely on direct physical contact to deduce *K* values. Any measurement methodology needs to be cost effective, repeatable, and accurate enough to ensure material meets or exceeds its specifications.

In this paper, thermal conductivity (through-plane and in-plane) data on three groups of CVD diamond samples of differing optical quality is presented, as judged by their absorption coefficient at an IR wave length of 10.6 µm. We report a correlation between the integrated absorption in the range 2760 and 3030 cm^{-1} and the measured *K* value using a non-contact

lab-oriented measurement methodology. This IR correlation provides a quick and reliable proxy method of ascertaining a film's thermal conductivity that can be used in routine testing.

II. Thermal Conductivity Mechanism in Diamond

In contrast to a metal, where thermal conductivity is provided by the mobility of conduction band electrons, heat transfer in the insulator diamond is solely carried by lattice vibrations, i.e. phonons. The reason for the outstanding thermal conductivity and the high Debye-temperature of 2000K of diamond is the stiffness of the sp^3 bonds forming its rigid structure together with the low mass of the carbon atoms. All contributions influencing thermal conductivity depend on the wavelength of the contributing phonons and, therefore, on the temperature of the sample. Hence, for understanding phonon scattering mechanisms and their relative contributions, measurements of the temperature dependent thermal conductivity are of basic importance. In most applications, however, the temperature is well below the Debye temperature and, hence, phonon-phonon scattering is small, resulting in little impedance for the phonon-mediated heat transport in high quality crystals.

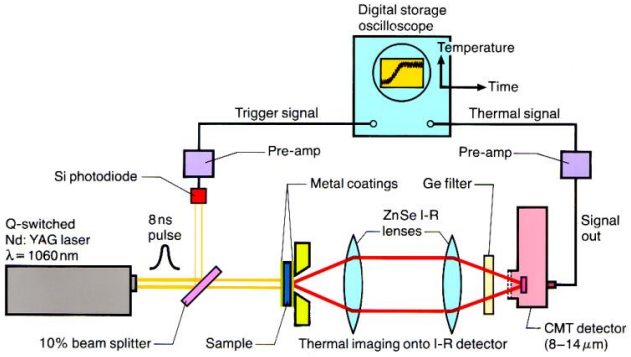

Fig. 1. Laser Pulse Measurement Methodology setup.

Extrinsic phonon scattering mechanisms impact the thermal resistance in less pure material at room temperature and dominate further at lower temperatures. For single-crystal diamond, scattering at the sample's boundaries and extrinsic impurities such as nitrogen impurities are the main contributors to thermal resistance. For polycrystalline materials, additional contributions arise from scattering at grain boundaries, dislocations and extended defects. In addition to these factors in both single crystal and polycrystalline materials the 1.1% natural isotopic abundance of ^{13}C further impacts the room temperature thermal conductivity by adding an additional phonon scattering mechanism.

Small changes in process parameters such as substrate temperature, gas purity and power can impact the properties of synthetic diamond grown by microwave plasma assisted CVD techniques. By tuning these synthesis conditions it has been possible to develop materials with varied properties and hence also thermal conductivities that can vary by more than a factor of two from 1000 to 2000 W/mK. The fact that the property of thermal conductivity can be so sensitive to changes in synthesis conditions warrants the need for relevant techniques to characterize this parameter against changes in synthesis.

III. Experiment Details

A laser-pulse technique (Fig. 1) is used as the reference laboratory methodology for through-plane thermal conductivity measurements. This technique makes use of a short, high-energy, laser pulse of approximately 8 ns in duration. The pulse impinges on one face of the diamond plate [3-7]. The temperature rise on the opposite face is measured via a fast (20 MHz), liquid nitrogen cooled far-IR point photo-voltaic detector. The temperature rise as measured by the detector is read into a digital storage oscilloscope from which the thermal diffusivity, and hence, thermal conductivity is deduced. The diamond is mounted in a cryostat to ensure that the temperature of the sample is known precisely. A 5K variation in the temperature can cause more than a 3% error in the determined thermal conductivity at 300K. This technique directly measures the thermal diffusivity D, which is related to the thermal conductivity K, via the specific heat capacity C_p and density ρ of the material by:

$$D = K / \rho C_p \,. \qquad (1)$$

In theory, any point on the rise curve (Fig. 2) can be analyzed to yield D:

$$D = W_x L^2 / \pi^2 t_x \qquad (2)$$

where L is the test piece thickness, t_x is the time for the test piece to reach a fraction of the maximum temperature, x is the fraction of the maximum rise in temperature, and W_x is a constant in the absence of radiation loss [8,9] and finite pulse corrections [10-13]. In practice, D is often calculated by measuring $t_{0.5}$ directly from the digital scope (for which $W_{0.5} = 1.37$). In the case of noisy data (Fig. 2), and where a small error in the measured rise time equates to a large uncertainty in the value of K, the entire rise curve can be fitted to the expression:

$$(3) \quad \Delta T\,(L,t) = \frac{Q}{\rho c_p L}\left[1 + \sum_{n=1}^{\infty}(-1)^n \, exp\frac{(-n^2\pi^2 Dt)}{L^2}\right]$$

The laser flash technique measures the thermal diffusivity perpendicular to the plane of the diamond

plate. It has been reported that, in some cases, CVD diamond exhibits anisotropy in *K* owing to its columnar grain structure; the thermal diffusivity parallel to the plane of the plate may be typically 10-20% less than that perpendicular to the plate surface [14]. A carefully designed and constructed steady state heated bar technique was used to measure the in-plane TC. The full details of the experimental set up are described by Wittorff et al. [15]. The measured *K* value was identical to that measured using the laser flash technique within the accuracy of the measurement (8%). A good fit to existing theoretical models [17] of the measured *K* as a function of temperature (10-300K, Fig. 3) could be obtained using only a point defect concentration and grain size as variables.

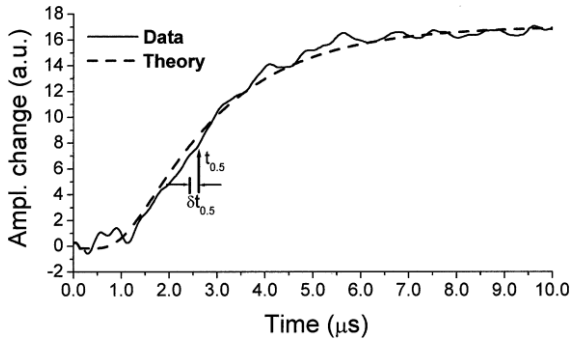

Fig. 2. Oscilloscope readout showing T rise on the diamond rear surface after being hit with a short laser pulse on the front. The dashed line shows fit to Eq. 3.

IV. Correlation Results for IR Measurements

The samples (Fig. 4) used in this study were polycrystalline CVD diamond grown using a microwave assisted process. For the measurements reported here, 30-40 μm of material was removed from both the growth and nucleation surfaces. The infrared optical properties were measured using an interferometer in a simple bench top setup. The *K* measurements were made using the laser-pulse methodology described earlier.

Table 1 shows the absorption coefficients and *K* values of the three samples compared to those of a high quality single crystal natural type IIa diamond where the total point defect density measured by FTIR was known to be less than 5 parts per million.

Table 1.	S1	S2	S3	IIa
IR CH_x Abs. Coeff (cm^{-2}) between 2760 and 3030 cm^{-1}	0.03	0.26	0.48	0
K ($W\ cm^{-1}K^{-1}$)	2220	1914	1646	2265

Assuming no heat losses, *K* is related to the diffusivity measured using the laser flash method through Eq. (1), i.e. it depends on the specific heat capacity C_p. Fig. 5 shows the room temperature IR spectra of samples S1-S3. The absorption near the range 2760-3030 cm^{-1} is shown enlarged; this has been associated with stretch modes of CH_x species within the film [16]. In Fig. 6, the integrated absorption between 2760 and 3030 cm^{-1}, measured after subtracting a linear baseline, is plotted against the thermal conductivity measured at 300K using the laser flash technique. The data points, which correspond to the samples S1-S3, (Fig. 4) are labelled. The other data points are taken from samples, with as-grown thicknesses varying from 100 to 800 μm, which were grown under similar conditions to samples S1-S3.

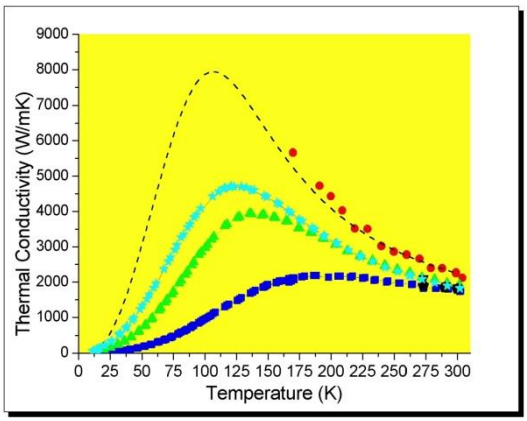

Fig. 3. Measured thermal conductivity for four different synthesis recipes.(S1 - red dots [Laser Flash], S2 - aqua stars [Heated bar], and S3 - green triangles [Heated bar]) as a function of temperature. Dashed lines show a theoretical curve based on a phonon scattering model [17].

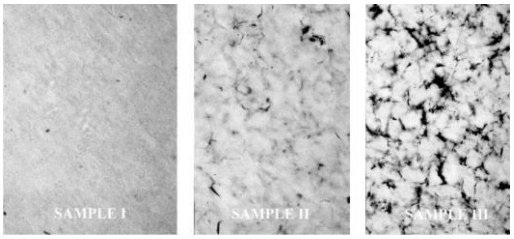

Fig. 4. Samples S1, S2, and S3 with parallel polished faces: back-lit transmission photographs.

A simple heuristic explanation, based on the work of Callaway [17], can be used to give an insight into the relationship between the CH_x absorption and the measured *K*. Simple kinetic theory gives the following expression for *K* in terms of the phonon collision time, T:

$$K = \rho C_p \ v^2 T / 3 \qquad (4)$$

where v is the mean phonon velocity. The model assumes that the total effective scattering rate for phonons is simply the sum of the individual scattering processes [17]:

$$1 / T_S = 1 / T_{CH} + 1 / T_R \qquad (5)$$

where T_S is the total effective collision time for phonon scattering, T_{CH} is the collision time for phonon scattering due to CH_X related defects [or whatever defect(s) correlates with this and affects the thermal resistance], and T_R is the effective collision time for all other phonon scattering processes (e.g. Umklapp phonon processes, point defects, dislocations, etc.).

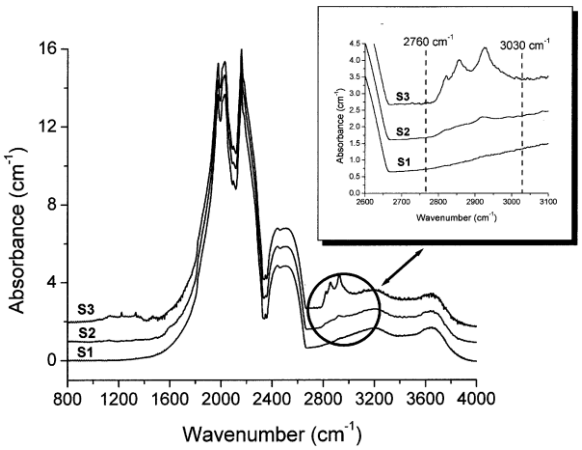

Fig. 5. Samples S1, S2, and S3 IR absorption spectra measurements.

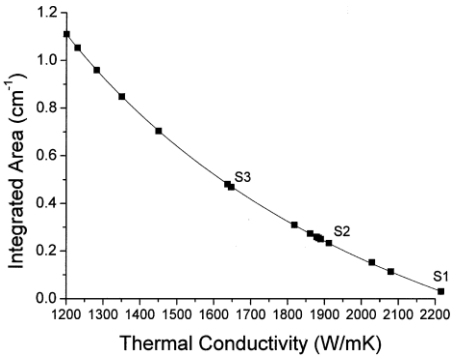

Fig. 6. The measured integrated absorption between 2760 and 3030 cm^{-1} plotted against the thermal conductivity measured using the laser flash technique. Samples S1-S3 are marked; other data points are measured from a range of material with as-grown thicknesses varying from 100 to 800 µm. All data points are fitted to the solid-line curve.

The phonon mean free path for scattering from CH_x defects λ_{CH} can be written as:

$$\lambda_{CH} = 1 / n_{CH}\sigma_{CH} \qquad (6)$$

where n_{CH} is the density of CH_x related defects and σ_{CH} is the cross-section for phonon scattering from these centers. Assuming that the IR absorption α_{CH} is proportional to its effective density, using Eq. (6), it follows that λ_{CH} is proportional to $1/\alpha_{CH}$ giving the following relationship between the phonon collision time and absorption coefficient:

$$\lambda_{CH} = 1 / A\alpha_{CH} \qquad (7)$$

where A is a constant. Combining this with Eqs. (4) and (5) gives the following expression for K in terms of the IR CH_x absorption coefficient:

$$K = (\rho C_p v^2 / 3)\,(1 / (1 / T_R + A\alpha_{CH})) \qquad (8)$$

Fitting this expression to the data shown in Fig. 6 (shown as solid line) yields:

$$K\ (Wm^{-1}K^{-1}) = 2270 / (1 + 0.803\alpha\ (cm^{-1})) \qquad (9)$$

for the dependence of K on the CH_x absorption coefficient. That this relationship holds for all the data points, irrespective of the as-grown thickness of the film, means that this is a quick and reliable method of ascertaining a film's thermal qualities at room temperature. However, it is worth emphasizing here that a minimum of 25 µm of material had been removed from the nucleation side of all the samples measured. Further work is required to understand the origin of the thermal resistance which is associated with the CH_x absorption. That the relationship holds for films of thickness varying from 100 to 800 µm, suggests that the defects responsible for the thermal resistance must be uniformly distributed over this range of thickness. It is worth noting however that certain synthesis parameters were fixed in this study, for example the substrate temperature and substrate diameter. For CVD diamond grown using different techniques, for example plasma torch or hot filament, the correlation would need to be tested again.

V. Summary

Current state-of-the-art CVD synthesis can reproducibly yield thick (100-1000 micron) high-quality polycrystalline diamond plates up to 140 mm diameters, with identical values of through- and in-plane K, with properties tailored for thermal management of high-power-density semiconductor devices. This study concludes there is a strong relationship between the integrated absorption in the IR spectrum between 2760 and 3030 cm^{-1}, associated with stretch modes of CH_x, and the thermal conductivity measured at 300K. Thus the measurement of the integrated IR absorption coefficient provides a quick and reliable method of assessing a microwave grown CVD film's thermal qualities. Because this measurement technique is easy to implement with a bench top interferometer, it provides an excellent quality-control methodology for recipe development and control. Since the power, efficiency, and lifetime of high-power semiconductor devices are significantly impacted by their associated thermal-management solution, module makers can be ensured they are getting the specified thermal conductivity of their synthetic diamond heat spreaders.

References

[1] R.S. Balmer et al, J. Phys. C, 21, 2009, p. 364221
[2] R.S. Sussmann, in 'Handbook of Hard Ceramic Materials' Ed. R. Riedel, Wiley VCH 2000. p. 573.
[3] C.J.H. Wort, C.G. Sweeney, M.A. Cooper, G.A. Scarsbrook, R.S. Sussmann, Diam. Relat. Mater. 3, 1994, p. 1158.
[4] W.J. Parker, R.J. Jenkins, C.P. Butler, G.L. Abbot, J. Appl. Phys. 32, 1961, p. 1679.
[5] R. Taylor, Br. J. Appl. Phys. 16, 1965, p. 509.
[6] K. Beedham, P. Dalrymple, Re. Hautes Temp. Reft. 7, 1970, p. 278.
[7] R. Righini, A. Cesairliyian, High Temps. High Press. 5, 1973, p. 481.
[8] L.M. Clark III, R.E. Taylor, J. Appl. Phys. 34, 1963, p. 714.
[9] R.D. Cowan, J. Appl. Phys. 34, 1963, p. 926.
[10] J.A. Cape, G.W. Lehmann, J. Appl. Phys. 34, 1963, p. 1909.
[11] R.C. Heckman, J. Appl. Phys. 44, 1973, p. 1455.
[12] R.E. Taylor, L.M. Clark, III, High Temp. High Press. 6, 1974, p. 65.
[13] K.B. Larsen, K. Koyama, J. Appl. Phys. 39,1968, p. 4408.
[14] J.E. Graebner, J. Wide Bandgap Mater. 7, 1999, p. 105.
[15] V.W. Wittorff, N.E. Hussey, J.R. Cooper, Research Review, High Temperature Superconductivity, University of Cambridge, 1998, p. 70.
[16] K.M. McNamara, B.E. Williams, K.K. Gleason, B.E. Scruggs, J. Appl. Phys. 76, 1994, p. 2466.
[17] J. Callaway, Phys. Rev. 113, 1959, p. 1046.