

Local variation of room-temperature thermal conductivity in high-quality polycrystalline diamond

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Local thermal conductivity inside grains of high-quality polycrystalline diamond grown by chemical vapor deposition is measured at room temperature with micrometer spatial resolution. An effective conductivity is determined by choosing experimental conditions where the measured heat flow extends over adjacent grains. It is found that the effective conductivity may vary by a factor of 2, depending on the averaged volume and position on the sample. These variations are attributed to different grain structures present at the investigated locations. Local conductivity within a single grain varies by $\pm 30\%$ and a maximum value of 2350 W/mK is found. Local thermal conductivity data are related to the crystalline quality and impurity content determined by micro-Raman measurements. © 1998 American Institute of Physics. [S0003-6951(98)02732-6]

Recently, we analyzed the room-temperature thermal conductivity of high-quality chemical vapor deposited diamond with micrometer resolution¹ and demonstrated that the macroscopically averaged conductivity is mainly limited by thermal resistances at grain boundaries² while the conductivity inside diamond grains is that of natural type IIa diamond. The photothermal microscopy method utilized in these investigations measures hemispherical heat flow, and when operated with modulation frequencies in the MHz range averages over typically 1000 μm ;³ i.e., a volume that is much smaller than that of a typical diamond grain at the surface of a sample of some hundred micrometers thickness. A thermal conductivity obtained in this way is referred to here as a *local conductivity*.³ When reducing modulation frequency to values below about 100 kHz, the heat flow across grain boundaries to adjacent grains enters the measurement and the resulting average, hereafter, called *effective conductivity* is strongly reduced compared to the value inside the grain.¹ For the measurement of an effective conductivity we assume a pointlike heat source and heat flow within a hemisphere with a radius equal to the thermal diffusion length⁴ for the average material properties and modulation frequency.

In the present letter we use averaging experiments to explore inhomogeneity of thermal conduction related to variations of the sample structure in different parts of the specimen and highly resolved measurements for the detection of local variations of thermal conductivity inside single diamond grains. For data interpretation it has to be kept in mind that the material is not only inhomogeneous but also anisotropic; i.e., the lateral extension of grains is usually smaller than their extension into the depth.⁵ Therefore, the

thermally active volume is not strictly a hemisphere but certainly influenced by the local grain structure if the thermally active volume encloses a few grains only. Some implications of the grain structure on averaging thermal measurements are demonstrated in this letter. For simplicity, we refer to the three-dimensional heat flow present in our measurements as *hemispherical heat flow* even in cases where this is a rough approximation. This term is used for discrimination from *planar heat flow*, e.g., in the form of lateral flow with a thermal gradient that is always parallel to the sample surface. In the last section an attempt is made to relate local thermal conductivity to information about impurities obtained from micro-Raman measurements performed at the same locations.

Local and effective thermal conductivities are determined with the same method and on the same sample used in previous measurements.¹ Contrary to these earlier investigations, where measurements were performed in the center of the sample, here we take high-resolution data at selected areas of the surface located between the center and one edge of the sample. Care was taken to collect data in large diamond grains so that results obtained in the high-frequency limit represent thermal properties of the respective grains and are not affected by grain boundaries. Also, in low-frequency effective conductivity measurements we analyze thermal profiles in a region of a few micrometers around the heated spot centered in a grain, and thus measure effects due to adjacent grains and boundaries indirectly by their influence on the heat flow inside the grain.

In a first set of experiments the effective conductivity in several areas of the surface is measured as a function of the thermally active volume, which can conveniently be controlled by the modulation frequency in our photothermal experiment.⁶ The frequency is varied from 10 to 100 kHz translating into a range of averaging volumes from

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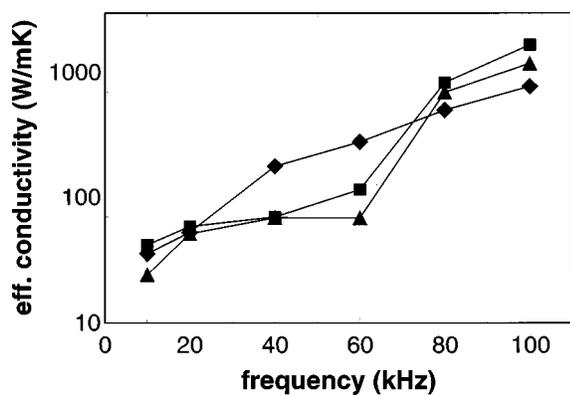


FIG. 1. Effective thermal conductivity extracted from photothermal measurements performed in the center of large diamond grains (typical diameter some ten μm) as a function of modulation frequency. The three curves represent data sampled at grains that are about 2 mm apart from each other.

(8 to 0.2) $\times 10^6 \mu\text{m}^3$, assuming hemispherical heat flow from the point source into a half-sphere with a radius equal to one thermal diffusion length. A conservative estimate of experimental errors including scatter in data, reproducibility of results, and measurements on reference samples shows that the method allows the determination of conductivity with an uncertainty less than $\pm 15\%$. Although our experimental method is not very sensitive to local disturbances of the surface optical quality⁷ care was taken to avoid defective regions when selecting measurement points.

Representative examples, i.e., the frequency dependence in three different areas several millimeters apart from each other are displayed in Fig. 1. The most striking result of such measurements is the strong decrease in effective conductivity when the frequency is lowered from the 100 kHz starting value that will be discussed in detail in a forthcoming paper. The important feature to be reported here, however, is the deviation between the curves shown in Fig. 1. Two of these curves are rather close to each other while the third one shows a distinctly different frequency behavior. We attribute this difference to variations in the crystalline composition of the diamond sample. At 100 kHz modulation frequency the thermal diffusion length is slightly larger than the linear dimensions of the grains selected for the measurements¹ and we probe thermal properties of the respective grain and the adjacent grain boundaries, while at 10 kHz the measurement covers several grains next to the sampling point. The behavior for intermediate frequencies depends on the number of grain boundaries present in the thermally active volume and the height of the thermal barriers associated with the boundaries. Both quantities are not uniform over the sample. The number of grain boundaries is determined by the size and shape of the grains and their thermal resistance is strongly dependent on the local structure and may vary considerably,² while both factors determine the effective conductivity. In the intermediate frequency range effective conductivities differ by a factor of 2 for the measurements shown in Fig. 1. The exact reasons for the difference cannot be revealed by the photothermal analysis, however, we speculate that the curve with square and triangle symbols corresponds to locations with a predominantly columnar grain structure while the curve with diamond symbols represents a structure of grains limited in depth. For a columnar structure the

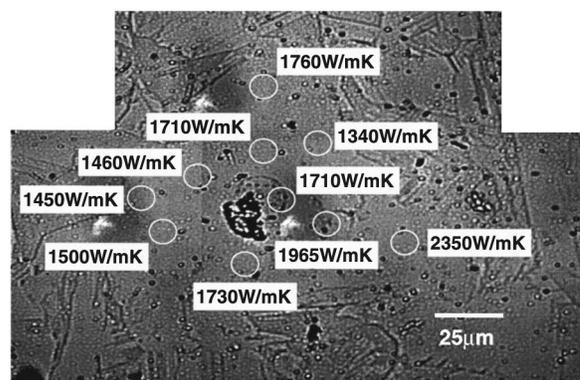


FIG. 2. Map of local conductivities measured inside a large diamond grain. Data were sampled in the center of the circles while their radius is equal to the thermal diffusion length and thus indicates the spatial resolution of the photothermal measurement.

frequency-dependent curve is expected to rise more steeply when the thermally active volume approaches the limit of a single grain since in this case there is a transition from hemispherical heat flow limited by the vertical boundaries of the grain to planar vertical flow inside the grain.

In the discussion so far we tacitly assumed that the effective conductivity is determined mostly by the presence of thermal barriers and thermal conductivity inside grains exhibiting only minor variations. To verify this assumption we determined the local conductivity κ_{loc} for various grains and at various locations inside large grains. These measurements were performed at 12 MHz modulation frequency yielding a thermal diffusion length smaller than $5 \mu\text{m}$, and thus, a spatial resolution allowing measurements that are not influenced by grain boundaries. As a typical result, an optical micrograph of the specimen with the position of sites of measurement of local conductivity indicated by circles is shown in Fig. 2. There, we find conductivities ranging from 1340 to 2350 W/mK with a mean value of 1700 W/mK. Since measurement uncertainty is less than $\pm 15\%$ the observed scatter is not only due to experimental uncertainty but reveals some significant local variations. These variations, however, are much smaller than those found in measurements of the effective conductivity averaged over several grains.

In a final set of experiments we tried to elucidate the origin of the variations in local conductivity by relating them to data obtained by micro-Raman analysis. Micro-Raman analysis is capable of detecting variations in crystalline quality, the predominant type of bonding and trace impurities,⁸ and it has been demonstrated that results from a Raman analysis can be correlated with macroscopic one-dimensional thermal conductivity data.⁹ In our experiments the laser beam was focused so tightly ($1 \mu\text{m}$ diam) that the sampled area was somewhat smaller than that for a local thermal conductivity measurement. A typical emission spectrum obtained from the center of a large grain excited with 488 nm laser light is shown in Fig. 3. This spectrum is a testament of the high quality of the sample under investigation. The width of the diamond line at 1332 cm^{-1} representing sp^3 bonding is 4 cm^{-1} , and thus, close to the best values obtained for perfect crystalline quality but above the instrument resolution of 2 cm^{-1} . Comparing measurements at different locations we found a variation in broadening of the sp^3 Raman

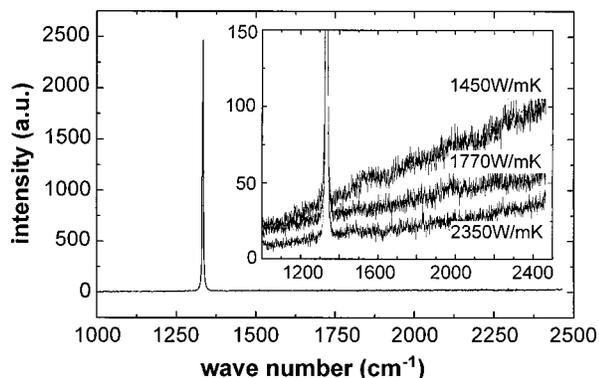


FIG. 3. Raman and luminescence spectrum measured in the center of a large diamond grain. The inset shows parts of three spectra on an expanded intensity scale to visualize differences in background luminescence. These spectra were recorded inside the grain shown in Fig. 2 and are labeled by the values of local conductivity measured at the respective locations.

line and also its position shifted by a few cm^{-1} . The line shift can well be explained by residual stress in the sample. Our observations are well in accordance with results from recently published experiments where the distribution of stress inside a grain has been investigated by confocal Raman microscopy.¹⁰ In this high-resolution study it was demonstrated that stress results in a peak shift but not in a broadening. In our spectra there are virtually no contributions at 1350 and 1550 cm^{-1} where the Raman lines of disordered sp^2 -like carbon would be expected. Also, a sharp line at 1582 cm^{-1} that is typical for crystalline graphite is completely absent. A display of data on an expanded scale, as shown in the inset of Fig. 3, reveals that there is a weak fluorescence background monotonically rising with wave number. This background signal is attributed to impurities; however, since it does not exhibit a clear spectral characteristic, it cannot be assigned to a specific defect type. The intensity of the Raman peak was determined by integration of the spectrum over 80 cm^{-1} centered around the line. As a measure for the broadening, we took the full width at half maximum of the line. Both measures were taken after the luminescence background had been subtracted. We also determined the total luminescence intensity by integrating the signal between 1400 and 2400 cm^{-1} . Such an analysis was performed for various spots marked in Fig. 2 to correlate luminescence data with the previously determined local thermal conductivity at the respective locations; data for three examples are shown in the inset of Fig. 3. For these three measurements, the local thermal conductivity indeed shows a negative correlation with the intensity of the luminescence signal. To investigate this in more detail we determined the width of the Raman line corresponding to diamond and the integrated luminescence intensity normalized to the intensity of the diamond Raman peak for several locations. The Raman linewidth as a measure for crystalline quality and the inverse of the normalized luminescence intensity as a measure for crystal purity plotted against thermal conductivity at each respective location is displayed in Fig. 4. There is some scatter in this data mainly due to the fact that variations in thermal conductivity and Raman linewidth are close to the experimental limits of resolution, and measurements have been performed in two different experimental setups with an

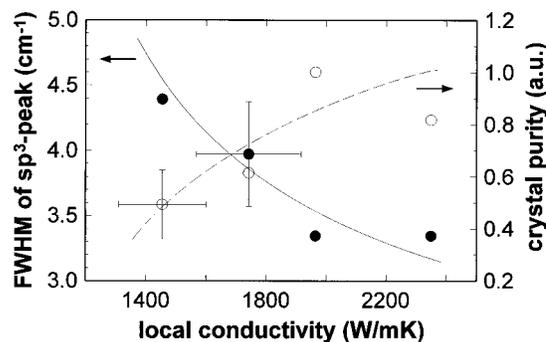


FIG. 4. Correlation of local thermal conductivity at various locations inside the diamond grain shown in Fig. 2 with the Raman peak width of diamond and crystal purity at the respective locations. Scatter in data was reduced by averaging measurements yielding the same local conductivity within the experimental error.

accuracy of repositioning the laser beam of a few micrometers. Nonetheless, the trend in the correlation of thermal and Raman data is found also in this graph; i.e., with increasing thermal conductivity a decreasing Raman linewidth and an increasing crystal purity is observed.

In conclusion, our measurements revealed that the local thermal conductivity in grains of high-quality polycrystalline diamond varies by $\pm 30\%$ and these variations are most probably due to impurities randomly distributed in the crystallites, which has been confirmed by a complementary Raman analysis. If, however, an effective conductivity is determined by measuring heat flow in the immediate vicinity of grains, such impurities are of minor importance since thermal transfer is dominated by the presence of thermal barriers at grain boundaries. These barriers may yield a reduction of the effective conductivity by one order of magnitude. Depending on the grain structure, the effective conductivity may vary by a factor of 2 when determined at different locations of the sample.

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³Note that our definition of *local conductivity* differs from others published in the literature. Here, the term local denotes averaging over a volume that is small compared to the grain size and the measurement is unaffected by grain boundaries.

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