THERMAL CONDUCTIVITY OF NATURAL TYPE IIA DIAMOND BETWEEN 500K AND 1250K

J.W. Vandersande, C.B. Vining and A. Zoltan
Jet Propulsion Laboratory/California Institute of Technology
Pasadena, CA 91109

ABSTRACT

The thermal conductivity of a natural type IIa diamond was measured between 500K and 1250K using the flash diffusivity method. This is the first time that the thermal conductivity of natural diamond has been measured above 450K. The results provide a baseline for comparison to the recently obtained results on isotopically pure diamond. Also, it provides a goal for the thermal conductivity of diamond films which are now routinely being fabricated and have numerous possible high temperature applications.

INTRODUCTION

The thermal conductivity of diamond has taken on increased significance with the high value very recently obtained on isotopically pure diamond (1). Also, the discovery of the synthesis of diamond films by means of chemical vapor deposition (CVD) at low pressures (2) has made numerous high temperature applications for diamond films now possible. A good baseline is thus needed to determine the improvement in conductivity of the isotopically pure diamond compared to the best natural diamonds (type IIa) and to be able to compare the thermal conductivity of the films with that of the best natural diamonds to assess their quality. However, the thermal conductivity of diamond has been measured only up to 450K and then on different samples, over a variety of temperature ranges, using different measurement techniques. There is scatter in these data and some disagreement between different measurement techniques. The accurate measurement of the thermal conductivity of a natural type IIa diamond (the best heat conducting type natural diamond) over a wide temperature range is thus badly needed to provide the needed baseline. Data above 450K would then provide, at least initially, an upper limit or goal for the thermal conductivity of diamond films at high temperatures. The values could be used to calculate the potential benefit of the use of diamond films at high temperatures for numerous applications.

The thermal conductivity of isotopically pure diamond at room temperature (the only sample measured to date) was found to be 33 W/cm-K(1) compared to 22-25W/cm-K found for three single crystal type IIa diamonds (3, 4). This increase in thermal conductivity appears to be around 50 percent, which would indeed be a significant improvement. There appears to be uncertainty as to the exact cause of this improvement. Whereas Anthony et al. (1) suggested it was the removal of the one percent ^{13}C from their sample, standard thermal conductivity theory predicts less than a 5 percent improvement as a result of eliminating the one percent ^{13}C

isotope (5). The cause of the improvement could be due to different mechanisms. Natural type IIa diamonds, although generally whitish, do have numerous impurities and defects (especially dislocations). A reduction in the concentration of these impurities and defects could easily result in a natural diamond with a considerably higher thermal conductivity. The Anthony et. al. (1) result was compared to the Berman et al. (3, 4) results. The latter, very likely, were samples that came from brownish rather than white type IIa stones (6) since the diamond supplier (DeBeers Corp.) usually kept, and still keeps, the large pure whites for jewelry purposes.

The thermal conductivity of several diamond films have been measured up to 300K (7, 8). At that temperature, the thermal conductivities of three films were found to be between 5 and 10 W/cm-K which compares to between 22 and 25 W/cm-K for natural type IIa diamond. These lower values are most likely due to the polycrystalline nature (very small grains) of the films.

The thermal conductivity of diamond has up until now not been measured above 450K due to the lack of a proper measuring technique and lack of sufficiently large samples. Both these obstacles were overcome by obtaining a large type IIa stone and by using the flash diffusivity method on diamond for the first time. The results are presented here.

EXPERIMENTAL

The natural diamond measured was determined to be a type IIa based on the UV absorption spectrum. The color was white but according to the supplier (DeBeers Corp.) it came from a slightly brownish stone (not quite good enough for gem stone purposes). The dimensions of the sample were 8.04mm by 8.84mm by 2.35mm thick.

The thermal diffusivity was determined by the flash method in an apparatus described elsewhere (9, 10). Briefly, a xenon flash lamp applies a heat pulse to one side of the sample, by means of a sapphire light pipe, while an InSb infrared detector measures the temperature rise of the rear surface of the sample. The output of the detector is fed through a Textronic differential amplifier into a Nicolet digital storage scope which displays the rear-face sample temperature rise (in mV) versus time (in ms). A flash lamp has several advantages over a laser. The main ones are that it is inexpensive, is capable of higher power levels, and has a very reproducible flash intensity. The main disadvantage is a larger finite pulse time but corrections to that have been developed (11).

The sample was coated (sputtered) all over with a few micrometer thick layer of tantalum on top of which was sputtered a few micrometer thick layer of graphite, to ensure that no light from the flashlamp would pass directly through the sample. The double layer was needed to prevent light being transmitted through the sample. The tantalum layer by itself reflected too much light while the graphite by itself allowed some transmission. The diffusivity was measured both through the short

direction (2.35mm) and the long direction (8.04 cm) of the sample. The latter required minor redesign of the sample holder and fixtures to minimize the amount of flash lamp light entering the detector.

The high thermal diffusivity of diamond means that the heat pulse can propagate through the sample in only a few milliseconds around room temperature. Since the flash lamp pulse itself lasts about 4.61 msec, proper account must be taken for this effect. Both the exact solution to the heat pulse problem as well as an approximate solution have been given previously (11). The approximate solution is quite accurate for usual purposes, but the very short pulse times of this sample raised a question about the reliability of the approximate method in this case.

This concern was addressed in two ways. First, the full solution of the equations for the temperature of the backface was performed numerically to calculate the thermal diffusivity and heat loss from the time to half maximum ($t_{1/2}$) and the time to maximum (t_{max}). Results calculated in this way were lower than calculated using the approximate expressions given previously. The difference between the two calculations is negligible (less then 1%) for the 'long' data, as expected since the half-times are long enough in this case to make the approximate solution quite reliable.

For the 'short' data, the approximate solution was about 3% high at 1000 C, 12% high at 500 C, 23% high at 400 C and rapidly getting worse as the temperature decreases further. Because of this the exact solution was used in the 'short' data case. Data below 400 C were rejected because the corrections were too large to be reliable.

The second check on the heat pulse corrections was done by recording the full temperature vs. time history of the backface for several data points, rather than simply $t_{1/2}$ and t_{max}. There are still only two adjustable parameters, the diffusivity and the heat loss, so it is a good test of the theory to see how well the full time dependence of the backface temperature can be accounted for by the theory. The diffusivity calculated using the fit of the full curve agrees with the diffusivity calculated using only $t_{1/2}$ and t_{max} to better than 1%. This indicates that the theory works.

The analysis used assumes the heat pulse travels down the sample in one direction only and also assumes that heat is lost only from the front and back faces. In the usual case, and for the diamond in the short direction, this appears to be an excellent assumption. Unfortunately, for the diamond in the long orientation, heat losses from the edges are no longer small compared to heat loss from the front and back faces, simply because most of the sample surface is now edge. From the analysis of the $t_{1/2}$ and t_{max} data for the long direction it is estimated that the total heat loss correction is very small up to about 1000 C. Above this temperature, heat loss corrections are no longer negligible. Unfortunately, the analysis neglects edge heat loss from the edges. In this case, the problem becomes a strongly two-dimensional heat flow problem with a non-trivial geometry. Thus, the long results

above about 1000 K are probably somewhat higher than the actual diffusivity of diamond.

The thermal conductivity was calculated from the measured diffusivity, measured density (3.5 gm/cm^3) and the published specific heat (12).

RESULTS AND DISCUSSION

The experimental results (both "short" and "long" direction data) are shown in figure 1. The Berman et al. (3, 4) data on three type IIa diamonds and the Burgermeister data (13) on one type IIa diamond are also shown. Several aspects are worth noting. First, the data reported here is a reasonable extension to high temperatures of the previously published data. However, upon closer examination there is an interesting difference. Figure 2 shows both the "short" direction and "long" direction data expanded. The best fit lines through each one is drawn and extended down to 300K. There clearly is a difference in slope (T$^{1.13}$ for the "long" direction and T$^{1.54}$ for the "short" direction). Also, the slope through the "long" data extends back up to Berman et. al. data at 300K while the slope through the "short" data extends back to around where the Anthony et. al. data point is for the isotopically pure diamond. As was discussed in the experimental section, the "long" data above 1000 K is probably slightly high due to the heat losses associated with the more complex geometry. At lower temperatures(below 600 K), "long" data was noisy due to the lower sensitivity of the detector at these lower temperatures. There is thus a larger error bar on that data but it is definitely systematically lower (possibly due to the operator systematically reading the noisier data). Based on these two considerations it would be tempting to consider the "short" data to be more accurate and, hence, the correct thermal conductivity. If it is, then it would appear that the Anthony et. al. data on isotopically pure diamond is about the same as the thermal conductivity of a purer (white or less brownish) type IIa diamond.

The thermal conductivity should vary as T^{-1} at the highest temperatures (above the Debye Temperature of around 2000K) since phonon-phonon interactions dominate the phonon scattering at these temperatures. The "long" data with a slope of -1.13 is closer to this -1 value than the "short" data with a slope of -1.54. No compelling case can thus be made for either the "short" or the "long" data. To resolve this impasse, the sample has been sent to Cornell University where the thermal conductivity will be measured between 200K and 400K. Those results will be reported shortly.

Figure 3 shows the results reported here, the Berman et. al. data on the best type IIa diamond as well as published data on two diamond films (7, 8). This high temperature data will be an upper limit for diamond films until high purity single crystal films can be synthesized. The data also indicates that thermal conductivity of the films shown in figure 3 probably peaks at around 300K and then would probably drop sharply with increasing temperature in order to stay below the high temperature data reported here. The data reported here can be used to calculate the

best current performance of the numerous possible high temperature applications of diamond films.

SUMMARY

The thermal conductivity of a natural type IIa diamond was measured between 500 and 1250K. This is the first time that the thermal conductivity of natural diamond has been measured above 450K. The measurement was performed through both the "short" and "long" direction of the sample. Although the data from these two measurements agree well between 700 and 1000K, there were two distinct slopes through the two sets of data points. An extension of the lower slope ($T^{1.13}$) data down to 300K agreed with the Berman et. al. data while an extension of the higher slope ($T^{1.54}$) data agreed well with the Anthony et. al. data on isotopically pure diamond. The thermal conductivity of the diamond will be measured at Cornell University using the 3Ω method between 200 and 400K in order to resolve the difference. That data will be published shortly. The reported thermal conductivity can be used as a goal value for the thermal conductivity of diamond films and hence be used to calculate performance of devices using diamond films at high temperatures.

ACKNOWLEDGEMENTS

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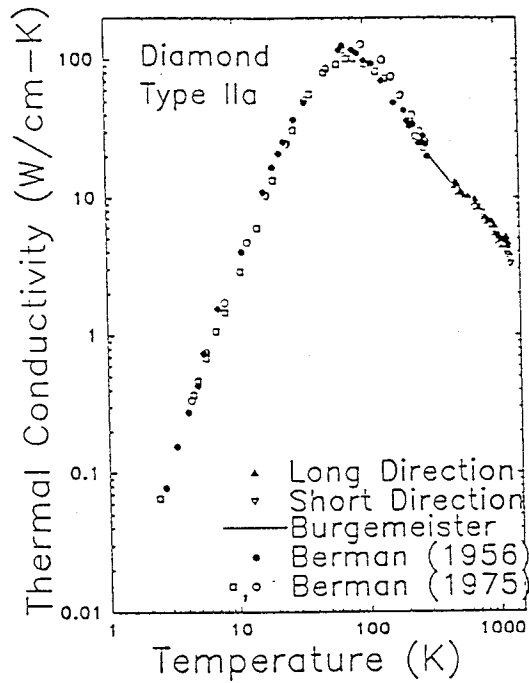13) E.A. Burgemeister, Physica 93B, 165-79 (1978)

Figure 1: Thermal conductivity of a natural type IIa diamond between 500 and 1250K measured in two directions. The Berman and Burgemeister data is shown for comparison.
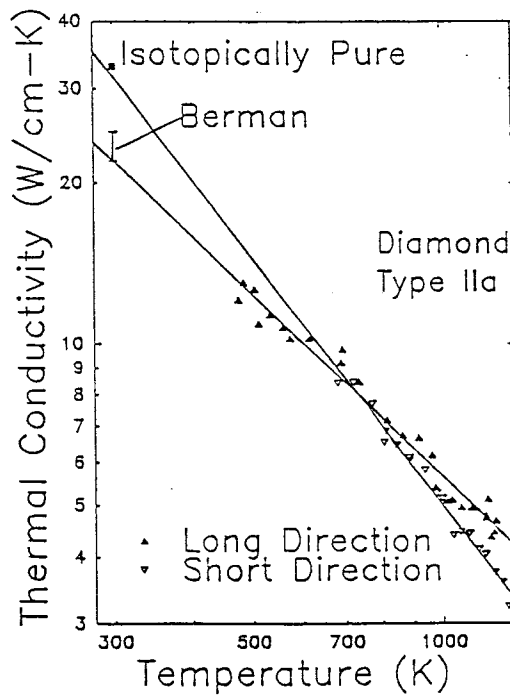

Figure 2: The "long" and "short" direction thermal conductivity data shown expanded. The two slopes are 1.13 and 1.54 respectively. The Berman 300K data range and the isotopically pure 300K data point are shown for comparison.
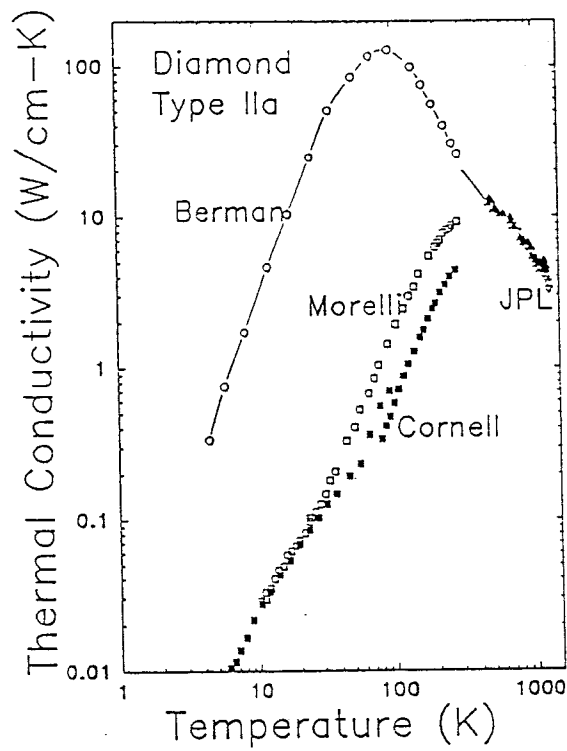
Figure 3: The thermal conductivity of a natural type IIa diamond between 500 and 1250K. The Morelli and Cornell data on diamond films is shown for comparison.