SINTERED DIAMOND: ITS POSSIBLE USE AS A HIGH THERMAL CONDUCTIVITY SEMICONDUCTION DEVICE SUBSTRATE

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Natural single-crystal diamond has the highest thermal conductivity of any known material. It has high electrical resistance, low dielectric constant and low loss tangent at microwave frequencies. These properties have been exploited in preparing by high pressure, high temperature sintering of diamond particles, molded substrates for semi-conductor devices possessing thermal conductivity at least one and one-half times greater than that of copper and with the excellent dielectric properties of diamond.

More than 140 substrate samples were prepared by the Megadiamond process using various types of additives, sintering pressures in the region of 65 kilobars and temperatures in the region of 2200° C. This paper discusses the experimental program for achieving high thermal conductivity in the substrate samples. The results indicate that sintered diamond substrates of pre-determined dimensions and with properties suitable for semi-conductor substrates may be made economically.

The use of single crystal diamond as a heat sink for semi-conductor devices has been investigated for the past decade. Swan,[1,2] one of the earliest workers in the filed, showed that the performance of avalanche (IMPATT) diode oscillators improved significantly when a single crystal Type IIa diamond was used as a heat sink to lower the junction temperature below the temperature possible with a conventional copper heat sink. Both the scarcity of Type IIa diamond and the difficulty of shaping heat sinks inhibit greater use of single crystal Type IIa diamond.

This paper will describe the possible use of sintered diamond as a high thermal conductivity substrate for semi-conductor devices.

Table I. Thermal Conductivity of Diamond and Other Substrate Materials- Nominal Values at 25°C

Material	Thermal Conductivity Watts/Cm°C
Type I Diamond	9
Type IIa Diamond	24
OFHC Copper	4
Beryllia (sintered)	1.9
Alumina	0.4
Silicon Carbide (pure)	4

Thermal Properties of Substrate Materials

Single crystal natural diamond has a higher thermal conductivity at 300° K than any other known material. From Table I its thermal conductivity may be seen to be 2 to 6 times of that of oxygen-free, high conductivity (OFHC) copper, the common material for heat sinks. The comparison with beryllia and alumina is even more favorable.

Process of Sintering Diamonds

In 1958 Hall[3] disclosed the possibility of a corbonado-like polycrystalline diamond made by high pressure, high temperature sintering of diamond powder. Experiments were continued with both pure diamond powder and with additives of refractory oxides, refractory metals, transition metals, and other materials. Evolution of the process has resulted in a sintered diamond product, called Megadiamond, which has found extensive use in cutting tools, wear parts, and is being tested in drilling, wire drawing, burnishing, and many other operations.

The sintering process, which is discussed elsewhere in greater detail by Hall, Pope and Horton,[4,5]consists in placing properly-selected and prepared diamond powder into a mold, which usually also functions as a resistance heater. The mold is placed inside of a pyrophyllite form, the shape of which depends on the type of high pressure press used. Suitable

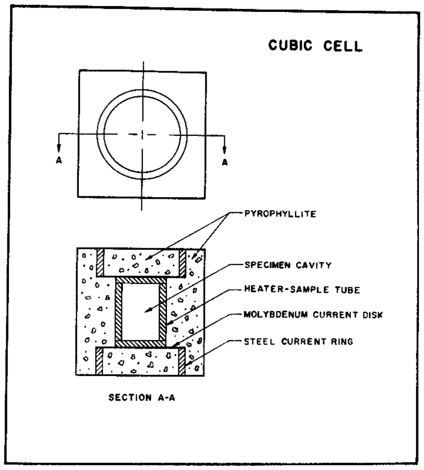

Figure 1. Typical mold used to make a sintered diamond.

current rings are located in the sample to carry electrical current from the anvils of the press through the sample. Figure 1 shows the mold configuration for making a cylindrical sintered diamond in a cubic press.

The sample is placed in the press and the hydraulic pressure driving the anvil rams is increased to the region of 65 kilobars. The electrical current is then passed through the sample at the proper temperature level for sufficient time to accomplish sintering. A temperature of 2200° C would be somewhat typical. The sample is cooled, the pressure released and the sintered diamond sample is recovered from the mold.

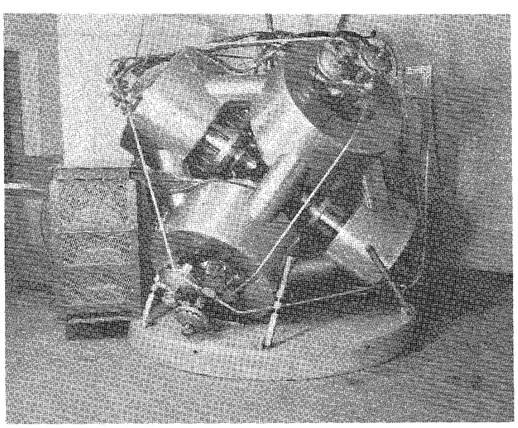

Figure 2 shows a cubic press suitable for sintering diamond.

There is a wide latitude of configuration for the shape and size of the sintered diamond. Table II shows ranges of size of various samples produced.

Table II. Pressure Sintered Diamond, Ranges of Sample Size

	Diameter or Width mm	Length mm
Circular	0.3- 12.7	0.5- 12.7
Square	0.6- 9.5	0.5- 2
Triangle	0.5- 9.5	0.5- 2
Hemisphere	0.2- 9.5	-

The possibility of sintered diamond heat sinks had been discussed earlier and research on the thermal and electrical properties of Megadiamond by Wheeler[6] showed that some samples had thermal conductivity equal to that of commercial conductor copper (2.3 Watts/Cm°C). Work since that time (sponsored by US Army Electronics Command Contract DAAB07-73-C-0829, Ft. Monmouth, N. J.) has improved thermal conductivity of sintered diamond substrate materials to more than one and one-half times that of OFHC copper.

Experimental

The general approach to achieving a target thermal conductivity of 6 Watts/Cm°C or more for the model substrate has been experimental, though a semi-theoretical model was developed.[7]

Table III. High Thermal Conductivity Sintered Diamond, Experimental Values

Variables	Number of Levels Tested
Diamond	
Type	4
Size	10
Shape	2
Additive	9
Cubic Boron Nitride (BN)	
Silicon (S)	
Alumina (Al_2O_3)	
Beryllia (BeO)	
Beryllia (BeO), Titania (TiO_2)	
Silica(SiO_2)	
Glass	
Aluminum Nitride (ALN)	
OFHC Copper (Cu)	
Press Condition	
Pressure	5
Temperature	6
Time	6

Experience has shown that sintered diamond properties are strongly influenced by composition, particle size, and run conditions. Variables considered in the experimental design are summarized in Table III.

Obviously all combinations of variables were not tested. Judicious selection of conditions based on earlier experiments reduced the number of required experiments. At this writing 140 experimental samples have been run and work is continuing. Table IV shows the results for the 3 most promising substrate samples.

Thermal conductivity of the sintered diamond samples was measured by the comparative method described by Schorr.[8] In this method the sample is placed between a heat source and a heat sink (thermodes) both of known thermal conductivity and of the same cross-section as the sample. Sample and thermodes are coated with lamp-black or velvet black paint to give the same surface radiation properties. A temperature gradient is established through the source thermode. At steady-state conditions the thermal gradient of the source, sample and sink are determined by measuring temperature versus position with a model RM2B Barnes Engineering infrared radiometric microscope. The ratio of the thermal conductivities is inversely proportional to the ratio of temperature gradient of the thermodes and the unknown sample. Since the thermal conductivity of the thermodes is known the unknown thermal conductivity of the sample can be calculated.

Table IV. Thermal Properties of Pressure-Sintered Diamond Substrates

Sample Components	Thermal Conductivity Watts/Cm°C
1. Type I 1-5 micron plus, selected flats	5.7- 7.9
2. Synthetic Blocky, gap-filled	5.0- 9.2
3. Type IIa 40/400 mesh Infiltrated with OFHC Cu	5.8

The thermal conductivity of all samples was tested and promising candidates were checked for electrical and mechanical properties.

Discussion

In general any factor which disrupts the crystalline structure of a material will also affect the mean free path of phonons and hence the thermal conductivity of a material. Some of the disrupting factors are grain boundaries, point defects, stacking faults, impurites and even isotopes. The presence of any of these factors tends to lower the peak thermal conductivity. According to Berman[9] nitrogen impurity in Type I diamond is the principle cause of peak thermal conductivity lowering. The peak thermal conductivity of Type IIa diamond is 120 Watts/Cm°C (70°K) and the peak thermal conductivity for Type I diamond at that temperature is about 24 Watts/Cm°C. Type IIa is relatively nitrogen-free as compared to Type I. At room temperature the relative difference in thermal conductivity is less, 24 for Type IIa as compared to 9 Watts/Cm°C for Type I diamond.

In polycrystalline and amorphous materials the crystallites are randomly oriented, the mean free path is extremely short and the thermal conductivity is proportional to the heat capacity of the material. The smaller the crystallite the more nearly the mean free path approaches the dimension of the unit cell and the smaller the effect of temperature change on the thermal conductivity. Figure 3 illustrates the behavior of thermal conductivity of crystalline and amorphous solids as a function of temperature.

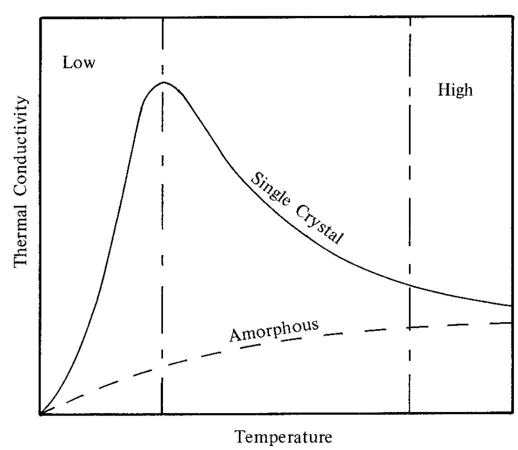

Figure 3 Typical Thermal Conductivity Versus Temperature for Single Crystal and Amorphous Materials

The behavior of a polycrystalline ceramic material would be expected to fall in an intermediate region. The larger proportion of volume filled with large particles the more nearly the behavior the polycrystalline material should approach the single crystal curve. This theory has not been tested for the sintered diamond substrates but work is continuing on a model to explain their behavior.

Increasing the average particle size has been found to give larger values of thermal conductivity in the pressure sintered diamond substrate. The highest thermal conductivity for a sintered Type I 1-5 micron diamond substrate was 1.8 Watts/Cm°C whereas a thermal conductivity of 5.3-7.9 Watts/Cm°C was found for a substrate made with a combination of 20 mesh Type I flats plus Type I 1-5 micron diamond powder. It was also found that a combination of larger blocky synthetic diamond particle with smaller sizes calculated to fill the gaps in a so-called gap-fill method yielded a substrate sample with a thermal conductivity of 5.0 to 9.2 Watts/Cm°C. The thermal conductivity of single crystal synthetic diamonds has been reported equal to that of Type IIa diamond.[10] This high value may also be true for good quality blocky synthetic diamonds in the mesh sizes, 30/400.

It is interesting that none of the substrate samples reflecting the highest thermal conductivity required the use of expensive Type IIa diamond and it appears that synthetic diamond is equally attractive as natural Type I diamond particles as a raw material for pressure sintered diamond heat sinks.

The production of high thermal conductivity sintered diamond substrates for use in solid-state semi-conductor heat sinks is a distinct possibility. The indications are that these can be produced economically with acceptable thermal electrical and mechanical properties.

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Questions and Answers

Q: A. Sawaoka----- Could you tell me the relation between thermal conductivity and mechanical strength of sintered diamond?

A: B. J. Pope----- For sintered diamond heat sinks of a particular composition as the mechanical strength of the material increases thermal conductivity also increases. The relationship is different for each composition such as particle size distribution, additions, etc. It is true that very high strength is not required for heat sink material; however, because high pressure is required for good thermal conductivity we obtain the good mechanical properties also. About the same pressures are required for heat sinks as are required for cutting tools.

Q: H. Vu----- I would like to know the transmission curve of sintered diamond in the IR region and the mechanical properties under high pressure of the material when it is used as a window for IR spectroscopy (compared to the natural diamond properties)

A: B. J. Pope----- The IR transmission curve for megadiamond has not been measured. The material is opaque to visible light and is probably transparent to IR similar to that the IR transmission of natural diamond. The mechanical properties are excellent with compression strengths equaling those of tungsten carbide. Transverse rupture strength is greater than 60000 psi. Knoop hardness exceeds 7800 kg/cm^2.

Q: M. Wakatsuki----- What material is best suited for filling spaces between particles?

A: B. J. Pope----- The sintered diamond heat sinks with the best thermal conductivity were those formed from pure diamond components. The sintered diamond infiltrated with OFHC copper increased in thermal conductivity from approximately 3.0 Watts/Cm°C to 5.8.

Q: E. G. Lundblad----- Is the surface smooth or porous? Will the thermal conductivity of the device be as good as measured using the indium spacer in your thermal conductivity apparatus?

A: B. J. Pope----- The surfaces of the high thermal conductivity sintered diamond is smooth, 2-3 micro inches with some porosity, which enhances metal bonding. Work we have done in metal coating with metals such as Ti, Pt, Au shows that the coating bonds well by standard procedures and that the bonding of the device to a sintered diamond heat sink may be less difficult than with bonding Type IIa diamond heat sinks.

Q: E. G. Lundblad----- Did I understand the size distribution in your sintered sample varied from 40 to 400 mesh? How is the surface conditions?

A: B. J. Pope----- Yes. Particle size may be even larger, 1/20 carats single crystal, and some of them as small as 0.1 micron.

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