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Thermal and Optical Applications of Thin Film Diamond

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Thermal and optical applications of thin film diamond

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Virtually all recent reviews of the market potential for chemical vapour deposited (cvd) diamond have featured the thermal management of electronic semiconductor devices as an imminent application for this new material. There is an existing market for natural diamond substrates ('heat sinks') in sub-millimetre sizes, and their thermal performance has been extensively studied. cvd diamond heat sinks in millimetre and larger sizes are already in use, but there are constraints to their applicability arising from thermal and mechanical factors. Their advantages and limitations are discussed.

The first 'optical' applications of cvd diamond films were as X-ray transmissive components (lithography masks and windows for soft X-ray detectors), but with improvements in the technology of cvd diamond growth a larger market for wide-band infrared transmissive windows is now developing. This results from the availability of large area (greater than 1000 mm^2) cvd diamond plates of adequate thickness and with transparency achieved through control of diamond grain size and orientation.

1. Introduction

Diamond has many extreme properties. They include hardness, strength, elastic moduli, gram atom number density (Angus 1986), thermal conductivity at room temperature, and spectral range of light transmission. This paper is concerned with the last two of these, and with the applications of thin film diamond that are based on them and likely to become important in the near to mid-term future. Those that depend directly on the thermal and optical properties of thin film diamond will most probably be, in the first place, extensions of similar applications of natural diamond.

Of the many uses of natural diamond where its high thermal conductivity plays a role, as abrasives, turning tools, or wire drawing dies for example, the use as a thermally conducting substrate (or 'heat sink') is probably the one which depends most directly on this property. It is one which has attracted the attention of virtually all analysts of the new market for chemical vapour deposited (cvd) diamond, perhaps because the much larger plate areas now becoming available in thin film diamond offer intriguing possibilities of extending an established market. The technical basis of these possibilities is discussed below.

The major use of diamond with relevance to the optical properties is of course the use as a gem. Its attractiveness in jewellery depends on the high refractive index and the high optical dispersion which yields a play of colour, plus the purity of its whiteness in the non-internally reflecting condition (or in some cases the subtlety of a fancy colour). However, gem diamonds are by their nature non-thin. They thus fall by definition outside the scope of this paper and it seems in any case highly unlikely

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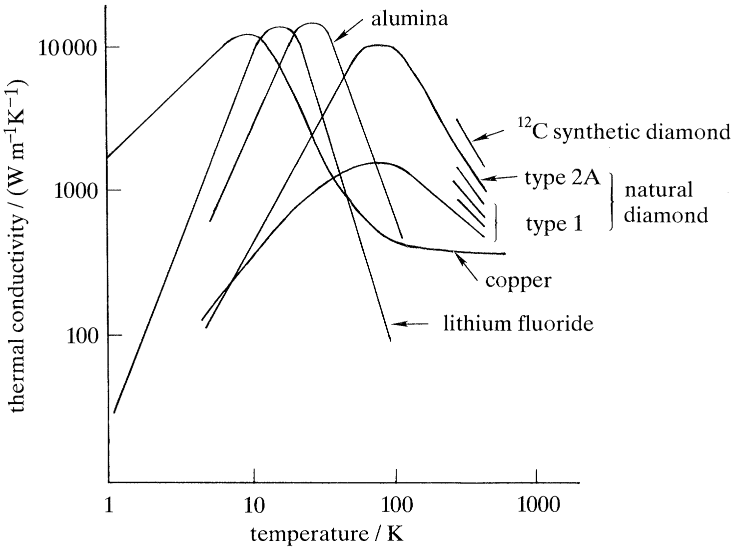

Figure 1. Thermal conductivities of various materials. Data from Berman (1965, 1973), Burgemeister (1978), Onn *et al.* (1992).

that growth of sufficiently thick, sufficiently pure plates of single crystal CVD diamond for gem application will be feasible and economic in the foreseeable future.

A more imminent optical application is the use as infrared transmissive windows. Diamond has a uniquely wide range of transparency, ranging in the case of high purity type 2A diamonds from the ultraviolet cut-off near 230 nm wavelength in the ultraviolet to beyond 100 μm in the far infrared, interrupted only by a relatively weak multi-phonon absorption system in the 2–6 μm region. Large flat CVD diamond plates are now available. They are polycrystalline, but their optical quality is improving rapidly with continued industrial development and they are by now effectively transparent through most of the infrared.

2. Thermal conductivity

It is probably still not generally realized that diamond is the best conductor of heat known at ambient temperatures. A good (type 2A) natural diamond conducts heat some five times better than copper at 300 K with a conductivity about 2000 W m^{-1}K^{-1}. As was pointed out by Berman *et al.* (1953) and Berman (1965, 1973) there is nothing surprising in this. It is a consequence of the tightly packed atoms and strong bonds of the diamond lattice, generally interpreted as resulting in easy phonon flow, coupled with a high Debye temperature. The functional dependence of conductivity on temperature is normal (figure 1), but with the curve shifted towards higher temperatures as compared with other dielectric crystals. Because impurity atoms scatter phonons, the thermal conductivity of diamond depends on its purity. Correlations have been established between conductivity and infrared spectral absorption features attributed to nitrogen in diamond (Schorr 1969; Martinez 1976; Burgemeister 1978). These are some of the spectral features used in assigning diamonds to type 1 or type 2 according to the physical classification first put forward by Robertson *et al.* (1934) and later sub-divided. Extreme type 1 (nitrogen-containing) diamonds are little better thermally than copper (Burgemeister 1978).

Above these there are all gradations in thermal conductivity up to the high values of the pure type 2A (figure 1).

Synthetic diamonds produced at high pressures and temperatures also show variation in thermal conductivity. At best they are comparable with natural type 2A (Slack 1973). The curves are similar in shape with absolute values reflecting the nitrogen content. However, the nitrogen is normally in non-aggregated (substitutional) form which has a smaller effect on thermal conductivity due to less effective phonon scattering (proportional to the product of nitrogen concentration and aggregate size). Also the amounts of nitrogen are lower, normally a few hundred parts per million (p.p.m.), as compared with the quantities of 1000 p.p.m. upwards which are common in natural diamond. There is also the possibility of removing the nitrogen from synthetic diamond by gettering the metal solvent during growth. The result is a diamond thermal conductivity which is normally in the range 1200–2000 W m^{-1} K^{-1} at 300 K and for gettered samples near 2000 W m^{-1} K^{-1}. One may also increase the thermal conductivity of synthetic diamond by making it from isotopically purer carbon, as compared with carbon of the natural isotopic abundance (1.1% ^{13}C). Anthony *et al.* (1990) grew diamond by a two-stage CVD/high pressure process from carbon containing only 0.1% ^{13}C and obtained a thermal conductivity (deduced from the diffusivity) of 3300 W $m^{-1}K^{-1}$.

Thermally CVD diamond has the advantage that it can be grown reasonably pure chemically, though some processes are more prone to give contamination than others. The hot filament method is, for instance, likely to introduce the filament metal as an impurity in the sample. Also the carbon is not always incorporated with sp^3 bonding. Regions with sp^2 bonding do occur. However, the main problem thermally is the polycrystalline nature of all the CVD diamond films that have so far been considered for thermal applications. The grain size increases as the film grows thicker and this results in a variation of thermal conductivity through the layer (Graebner *et al.* 1992). These authors reported a thermal conductivity of at least 2100 W $m^{-1}K^{-1}$ at the growth surface of a 350 μm diamond film, but only about 7 W $m^{-1}K^{-1}$ near the substrate interface.

Polycrystalline CVD diamond films show an anisotropy of thermal conductivity between directions parallel to and perpendicular to the film plane (Graebner *et al.* 1992). That perpendicular to the plane was found to be at least 50% higher than that parallel to the plane. There is variation with growth conditions and for a sub-set of these the conductivity has been found to vary inversely with the growth rate and Raman line width (Graebner *et al.* 1992). Overall variation over at least a range 200–2100 W $m^{-1}K^{-1}$ at 300 K has been reported in the literature for a range of CVD diamond samples. Values for currently available commercial films seem to be about 1100 W $m^{-1}K^{-1}$ or possibly somewhat higher (Visser *et al.* 1992).

3. Heat sinks

(*a*) *Type 2A diamond*

The optimum dimensions and proportions of natural diamond heat sinks have been extensively investigated both experimentally and theoretically. The experimental investigations have been complicated by thermal resistances in the semiconductor chip materials, in solder layers, and at interfaces, but appear in all cases to be consistent with theory. The definitive theoretical study is probably that of Molenaar & Staarink (1985), extended later by Doting & Molenaar (1988). These

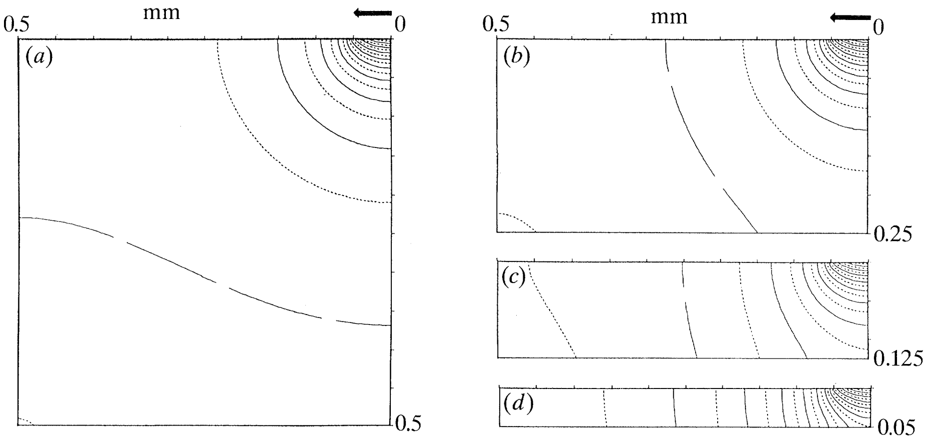

Figure 2. Isotherms in half-sections of diamond heat sinks. See text for details. Courtesy Drukker International B.V.

authors based their calculations on Burgemeister's (1978) result for type 2A diamond that the thermal conductivity (in MW $m^{-1}K^{-1}$) over a temperature range 300–450 K can be represented by

$$k(T) = 2.75T^{-1.26}. \tag{3.1}$$

They considered various geometries including diamond heat sinks mounted on copper (mesa mounting) and embedded in copper (flush mounting). The semiconductor chip was assumed centrally mounted on the diamond and both square and circular axial symmetries were treated for the mesa-mounted case (cylindrical only for flush mounting). These geometries represent those used in the mounting of microwave diode chips. The copper mount was assumed plane-bounded semi-infinite. In practical cases it is generally large enough that this assumption will not introduce excessive error. The copper was taken to have a thermal conductivity of 387 W $m^{-1}K^{-1}$, not varying with temperature. A geometry approximating that used for mounting semiconductor diode laser chips was also studied. This has an elongated rectangular 'stripe-geometry' chip edge-mounted on an assumed quarter-infinite copper block (defined by two perpendicular plane surfaces). The stripe is mounted on one surface with its length perpendicular to the edge.

The mathematical treatment proceeded from the heat flow equation (conservation of energy in an elemental volume) directly to a Laplace equation in the copper and via a derived function in the diamond. After definition of boundary heat fluxes a computer iterative method yielded a converging solution for the distribution of isotherms in the diamond heat sink. This method started with an arbitrarily assumed homogeneous heat flux across the diamond–copper boundary, calculated from the copper side the temperature distribution over this boundary, computed the derived function of temperature everywhere in the diamond including all boundary conditions, and calculated a new temperature distribution over the diamond–copper boundary. Combination of new and old distributions with a weighting factor for rapid convergence yielded after appropriate iteration a self-consistent solution.

Though differing in detail, the solutions for the different mesa-mounted geometries showed many similarities. The proportions, and in particular the aspect ratios of diamond thickness to lateral dimensions, are extremely important. Figure 2 shows isotherms for a representative series of geometries. The plots each represent a half

Table 1.

diamond thickness/µm	maximum temperature rise/°C
500	121
250	117
125	119
50	141

section of a mesa-mounted cylindrical heat sink with the axis at the right. The chip is mounted centrally at the top right, the arrow indicating its radius. The lower surface is mounted on copper, which extends to a large distance on either side. The cylinder diameter is 1 mm and the chip diameter 0.1 mm. The chip is assumed to dissipate 20 W uniformly over its lower surface. The isotherm interval is 5 °C. The effect of progressive reduction in diamond thickness is shown in the series figure 2*a*–*d* (0.5–0.05 mm). Table 1 lists the corresponding maximum temperature rises centrally under the chip. If one starts from the best geometry (*b*) it is clear that doubling the thickness of diamond from 250 µm to 500 µm has resulted in a slight worsening of performance, a disappointing result for a substantially more expensive heat sink, whereas reducing the thickness by a factor of 2 gives only marginal worsening. Reduction by a factor 5 gives substantial worsening.

The reasons are clear from figure 2. The top half of (*a*) shows roughly hemispherical isotherms, i.e. good heat spreading. The lower half shows something like linear heat flow through a bar. It is an unnecessary thermal resistance not contributing significantly to the spreading. At the other extreme (*d*) there is little spreading and a high temperature rise (about 85 °C) at the centre of the diamond–copper interface. In case (*a*) there is a major heat flux through the outer part of the diamond–copper interface (particularly near the outside edge where the cooling effect is enhanced by that of the copper outside the diamond edge). In case (*d*) most of the heat flow is through the central part of the diamond–copper interface and the spreading resistance of the copper from that central part becomes dominant. The isotherms in the outer part of the diamond in (*d*) show some lateral heat transport in the diamond layer, but the flux is low because of the small cross section.

Clearly the diamond can be too thick or too thin. Experience has led to a rule of thumb that ideally the thickness should be about one-third of the lateral dimensions with a range from about one-quarter to one-half acceptable. Down to one-tenth may sometimes be acceptable. In turn the lateral dimensions should be related to the chip dimensions. The ratio of ten used in figure 2 is larger than normal. It was chosen to illustrate the effects better. A ratio of five would be more normal. Similar considerations apply in the case of the edge-mounted, stripe-geometry, laser diode chip. The diamond square size should be at least a factor of 2 larger than the stripe length and preferably a factor of 3. The thickness should be about equal to the stripe length, though thicknesses down to about one-quarter of the stripe length may be acceptable with loss of efficiency. There is a wider range of acceptable thicknesses on the high thickness side, but little point in using this. In summary for mesa-mounted chips, the diamond heat sink lateral dimensions should be about 5 times the chip dimension for centrally mounted chips and $2\frac{1}{2}$ times for edge mounted chips corresponding to the lower solid angle of heat flow. The diamond thickness should be about one-third of the lateral dimensions in either case, though with more flexibility in the case of the edge-mounted chip (because of the thinness of the stripe).

Embedded diamond heat sinks behave quite differently, however. Since diamond replaces copper, a larger diamond is always better than a smaller, though the gain in advantage factor becomes very small beyond diamond diameters about 10 times the chip diameter or diamond thicknesses twice the diamond diameter. On the low thickness side there is never likely to be much point in using diamonds thinner than about one-tenth of properly chosen lateral dimensions.

(*b*) CVD *diamond*

As indicated in §2 above, the thermal conductivity of CVD diamond differs from that of natural in that it may vary through the thickness of a sample and be anisotropic. Absolute values may vary over a wide range depending on the manufacturing process and the exponent in equation (3.1) may vary. The Molenaar–Staarink treatment of §3*a* is thus not directly applicable, though changes of uniform conductivity values and exponent should be trivial. A tensor treatment for the anisotropic case might be possible, but is certainly far from trivial. However, some general conclusions look possible. Since the diamond layers are heat spreaders it is the lateral conductivity which is limiting. In an extreme case of diamond film having columnar crystallites of excellent conductivity isolated thermally from each other, the crystallites would simply channel the heat downwards. There would be no heat spreading and the diamond layer would be useless thermally. Fortunately it is the limiting lateral thermal conductivity that is usually measured and materials with high values of this are obtainable.

The most obvious advantage of CVD diamond films is that they can be of relatively large area, an order of magnitude larger in linear dimensions than is normally possible with single crystal diamond. This brings two principal claimed advantages. One is that wafer processing of small components should be possible, provided the problems of polishing and dicing diamond wafers can be solved. The other is that larger diamond components should become economic and thus open up new thermal management applications in electronics for diamond. In the wafer processing case the products, if made from the highest conductivity CVD material, should be capable of directly replacing natural diamond heat sinks. The advantages will be in price and ease of applying metallization patterns by photolithographic means. The second is much more problematic.

If the 'one-third lateral dimensions' rule of §3*a* holds, or even a one-tenth lateral dimensions rule, available thicknesses of CVD diamond are going to need to increase as component sizes increase. The differences between natural and CVD diamond are likely to increase the critical thickness. One may thus assume that CVD diamond heat sinks for 3 mm square transistor chips, which would need to be 15 mm square and 1.5–5 mm thick, are not yet near commercial reality. Perhaps they will become so as people learn to make thicker diamond films more cheaply, but at the moment such thicknesses look to be prohibitively expensive.

There is, however, a possibility for use of larger area CVD diamond heat sinks in the thermal management of devices having multiple small heat sources on a larger chip. An example would be a laser diode array chip having perhaps 10 well-separated, light-emitting stripes on a single chip. The small size of the individual stripes determines the critical thickness of the substrate, whereas a larger area of substrate is necessary to accommodate the rather large chip. Large area CVD diamond heat sinks may also be appropriate in cases where a hard, mechanically stable substrate is needed simply to conduct heat rather than spread it. This might be the case where

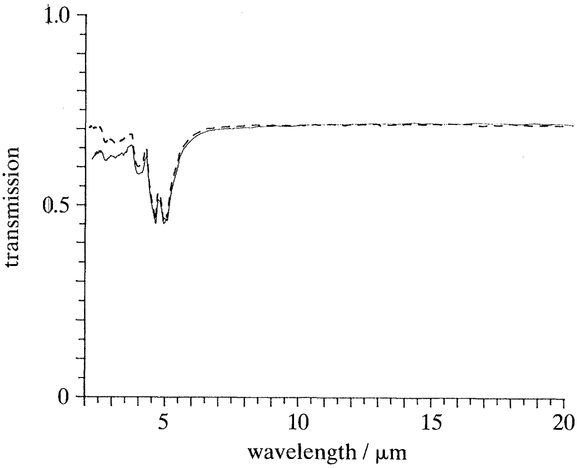

Figure 3. Infrared transmission spectra of a natural type 2A diamond and a CVD diamond film. Courtesy Norton Company. ——, TD826A; ––––, natural.

active cooling is involved (micro-channel fluid cooling, heat pipes, Peltier cooling elements).

4. Optical applications

(*a*) *Infrared windows*

Optical applications obviously depend on the availability of optical quality CVD diamond. For the foreseeable future this is likely to have to be polycrystalline material and there is the problem of light scattering at grain boundaries rendering the material translucent or opaque. The present situation seems to be that the best material is only translucent in the visible, but effectively transparent in the infrared because of the longer wavelength. Figure 3 shows an infrared transmission spectrum of a sample of currently commercially available material. The transmission is equivalent to that of natural type 2A diamond at the longer wavelengths and starts to fall off towards shorter wavelengths. It is limited to slightly over 70% because of Fresnel reflection losses at the high refractive index diamond–air interfaces.

CVD diamond infrared transmissive windows have major potential military markets. The combination of strength, hardness, chemical inertness, and high thermal conductivity with good optical properties would make them for instance particularly suited for use as the outer windows on infrared missile seeker devices flying at high Mach numbers. In the civilian sphere there is increasing interest in infrared instrumentation for industrial process control. Kilham & Le Blon (1990), for instance, describe a flow cell using diamond windows for the on-line analysis by infrared spectroscopy of molten polymers in the plastics manufacturing industry. They give as an example the measurement of concentrations of carbonyl groups resulting from oxidative degradation upstream in the continuous flow production of polyethylene. Real time detection of such degradation can prevent the manufacture of tonnage quantities of defective product (which might result if off-line analyses only were used). The cost savings are obvious. Such techniques have been used with sapphire windows in the near infrared (e.g. for the detection of water) but diamond transmits in spectral regions in the mid infrared (where sapphire does not) and these are of importance for the detection of organic groups.

Natural diamond windows have also been used in research projects involving infrared spectroscopy. The most spectacular of these was an 18.2 mm diameter window used in the Pioneer Large Probe experiment to investigate radiation energy balance and spectral distribution from measurements inside the Venusian atmosphere (Boese *et al.* 1979). There have also been many more down-to-earth projects as well as routine applications in instrumentation. Some have been reviewed by Seal & van Enckevort (1988). Besides spectroscopic applications natural diamond windows have also been used as simple, light-transmissive elements separating for example body fluids from instrument space in medical endoscope or laser therapy applications, or as exit windows for CO_2 lasers (diamond being particularly appropriate for transmission of their 10.6 μm radiation).

The vast majority of optical applications require physical apertures greater than can be met from natural diamond. CVD diamond has the potential to remove this restriction. If optical transmission quality and finishes can be produced, there will be the potential for a very large business as diamond has some most attractive properties. It is hard and scratch resistant. It is inert to virtually all the chemical environments that a window is likely to meet. It is strong, a fault free diamond window of 0.25 mm thickness being adequate to withstand a 1 atm ($\approx 10^5$ Pa) pressure differential to quite large diameters (say 25–100 mm depending on the permissible central deflection, method of mounting, and safety factor required). The spectral transmission range is enormous. Even the C–C absorption systems between 2–6 μm are weak (figure 3) to negligible in thin windows below say 50 μm thickness. On the negative side there would be problems of chromatic aberration in refractive components and the reflection is high (about 17% at a single interface). Anti-reflection coatings may thus be required for some applications.

(*b*) *Other optical applications*

One of the original applications of CVD diamond films was as X-ray transmissive components. The low atomic number ensures good X-ray transmission. High optical transparency, high strength, high thermal conductivity, low thermal expansion, and excellent chemical inertness are processing aids or requirements for many X-ray applications. The chief of these were as X-ray lithography masks and transmissive windows for soft X-rays. Thicknesses are low – a few micrometres at most – and support is a problem. Support grids can be used in the soft X-ray window case, as for example in windows protecting light element detectors in X-ray analysis adjuncts to scanning electron microscopy such as EDAX. Supports in the lithography case clearly must not interfere with the pattern and tensioned films are needed. Most of the details are subject to industrial secrecy, but Löchel *et al.* (1992) have recently surveyed the rather fragmentary literature. Other earlier papers are by Cuomo *et al.* (1991) and Windischmann *et al.* (1991). Additional possibilities exist of active optoelectronic uses. These are considered to fall outside the scope of the present paper, but might include ultraviolet and other radiation detectors, light emitting diodes, and possibly short wavelength lasers based on radiation-induced H3 centres (Rand & DeShazer 1985).

5. Conclusions

The principal thermal and optical applications of CVD thin film diamond that are likely to be of substantial commercial importance in the short term are as heat spreading substrates in electronics (heat sinks) and as infrared transmissive windows.

Both are extensions of current markets for natural diamond, based on lower costs and larger areas. Diamond membranes for X-ray masks will also be important and thin diamond windows for soft X-ray detectors fill a needed niche.

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