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# CVD diamond handbook

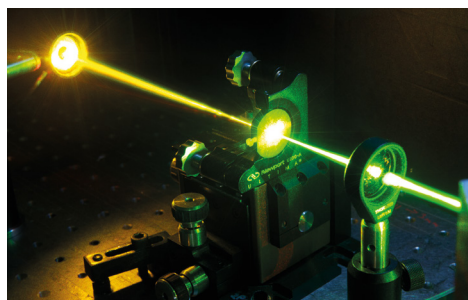
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Advances in the synthesis and processing technology for CVD diamond has resulted in materials with exceptional diamond properties in practical components. Engineered single crystal CVD diamond, with ultra low absorption and birefringence combined with long optical path lengths, has made **monolithic diamond Raman lasers** a practical reality.

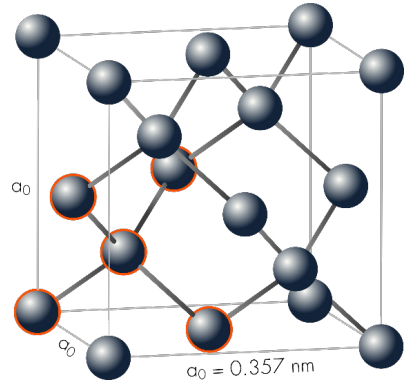
## Further reading

1. Monolithic Diamond Raman Lasers

Diamond is characterised by its exceptional hardness, robustness and its optical and thermal properties; pre-eminent as a gemstone and an industrial tool.

Natural diamond has an inherent variability and scarcity that limit its use in engineering applications. Developments in synthesis processes have enabled the production of consistently engineered synthetic diamond; firstly in the 1950s using high pressure and high temperature and later in the 1980s using chemical vapour deposition to produce the exceptional covalent crystal diamond.

The modern industrial world consumes approximately 800 tonnes of synthetic diamond, around 150 times the amount of natural diamond mined as gemstones.



## It is all in the structure

Diamond's properties derive from its structure; tetrahedral covalent bonds between an atom and its four nearest neighbours, linked in a cubic lattice. This strongly bonded, tightly packed, dense and rigid structure gives rise to its outstanding properties. Manipulating the impact of defects and the synthesis conditions means that material scientists have been able to optimise and tailor the remarkable properties of diamond for a wide range of applications.

5 B 10.811	6 C 12.011	7 N 14.007
aluminium	silicon	phosphorus
13 Al 26.981	14 Si 28.085	15 P 30.973

Carbon's position as a group IV element above silicon in the periodic table.



High-pressure, high-temperature synthetic diamond is usually nitrogen doped, giving it a distinctive yellow hue.

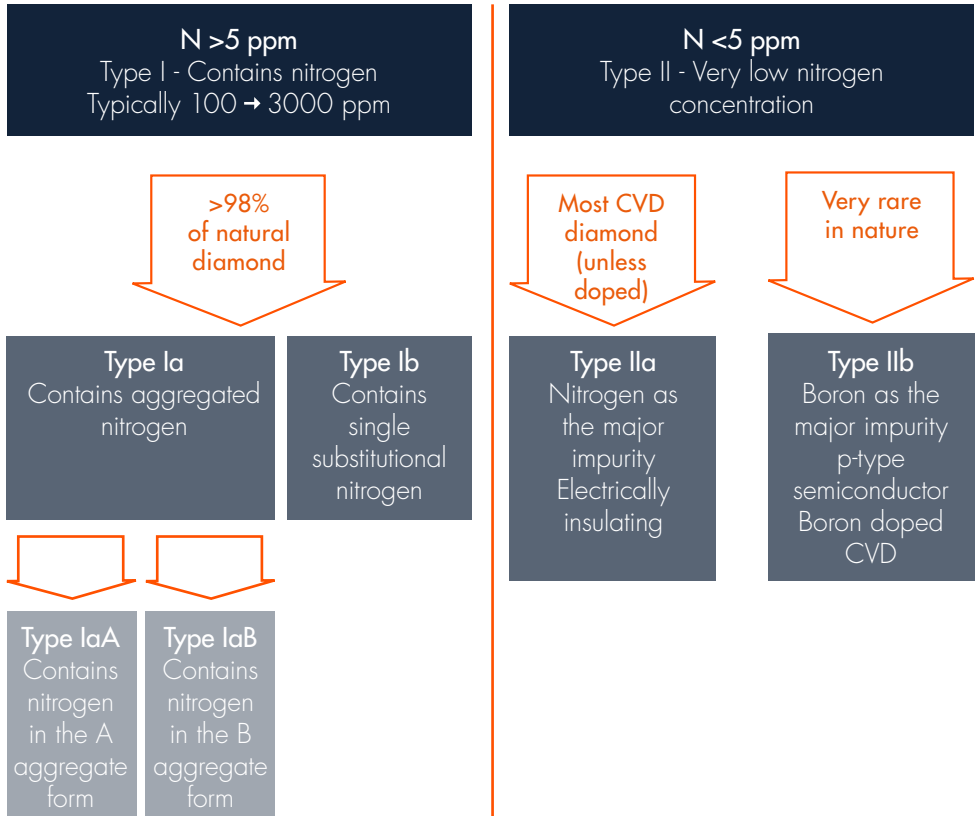
## Further reading

2. Science's Gem

Property	Value
Density	$3.51524 \times 10^3 \text{ kg m}^{-3}$
Number density	$1.77 \times 10^{23} \text{ cm}^{-3}$
Lattice type	Cubic $\text{Fd}\overline{3}\text{m-O}_h^7$
Lattice spacing	Lattice constant between $0.356683 \pm 0.000001$ and $0.356725 \pm 0.000003 \text{ nm}$ at 298 K
Fracture toughness $K_{Ic}$	$5 \text{ MPa m}^{0.5}$ single crystal
	$8.5 \text{ MPa m}^{0.5}$ polycrystalline
Poisson's ratio	0.1
Young's modulus	1050 GPa
Fracture strength	2.5 to 3 GPa single crystal (surface finish dependent)
	200 to 1100 MPa polycrystalline (grain size and grain dependent)
Fatigue life	>95% strength after $>10^7$ cycles to 70% of FS
Fracture plane	$\{111\}$ and occasionally $\{110\}$
Weibull modulus	2.5 single crystal
	20 Growth surface Polycrystalline
	10 Nucleation surface Polycrystalline
Hardness	70 to 120 GPa single crystal (plane and direction of indent dependent)
	$\sim 81 \pm 18 \text{ GPa}$ polycrystalline (grain orientation dependent)
Friction coefficient ( $\mu$ )	0.05 to 0.15 (orientation dependent) In air (requires surface termination)

### Further reading

#### 3. Mechanical Properties of Diamond



Natural diamonds were first classified according to their optical properties. The majority, being type I, has an absorption edge of around 330 nm, and a small group, being type II, has an absorption edge of about 220 nm. Over the years this natural classification scheme has been extended and further linked to different predominant defects, such as nitrogen and nitrogen clusters. In its broadest

sense, this classification scheme remains relevant to synthetic diamond, in that most HPHT-grown diamond falls into the type Ib classification and most CVD into type IIa, due to their different nitrogen levels. However, within this there are now multiple polycrystalline and single crystal grades, developed with specific tailored properties that this simple classification system does not distinguish between.

### Further reading

#### 4. The "Type" Classification

### Chemical vapour deposition (CVD)

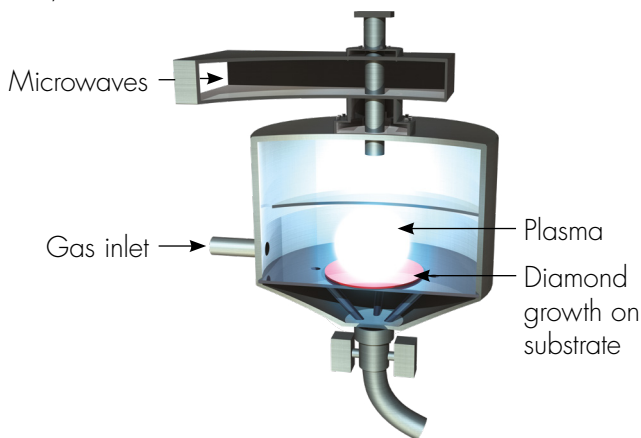
CVD diamond exploits the relatively small difference in stability between the two allotropes ( $sp^2$  &  $sp^3$ ) of carbon. Create the right surface conditions, the presence of atomic hydrogen and surface temperatures above  $\sim 600^\circ\text{C}$ , and the formation of diamond depends on having a faster nucleation and growth rate than graphite.

The growth conditions are created by thermal dissociation of hydrogen, and a gaseous source of carbon in plasma, with a gas temperature above  $2000^\circ\text{C}$ .

The plasma can be heated by microwaves, radio frequency, lasers, direct current,

hot filament and chemical reactions. The nucleation and growth of continuous diamond requires a substrate with refractory characteristics, stable carbide formation and a low thermal expansion coefficient.

After nearly four decades of stop-start research into CVD diamond growth, microwave plasma-enhanced CVD diamond synthesis emerged as a commercial synthesis method in the 1990s. The growth rates and control over purity of this method lend themselves to manufacturing high quality, free-standing, polycrystalline and single crystal CVD diamond.



### High pressure, high temperature (HPHT)

The vast majority of synthetic diamond is made using high pressure, high temperature methods. HPHT aims to mimic the thermodynamic conditions that diamond naturally forms in, but with the addition of a molten metal solvent, or catalyst, to reduce the large kinetic barrier

and act as transport medium for dissolved carbon. Material grown this way typically has a yellow hue, as a consequence of nitrogen incorporation into the diamond lattice from the atmosphere and growth materials.

### Further reading

5. CVD: The Early Years
6. Synthesis Methods

Technical ceramic

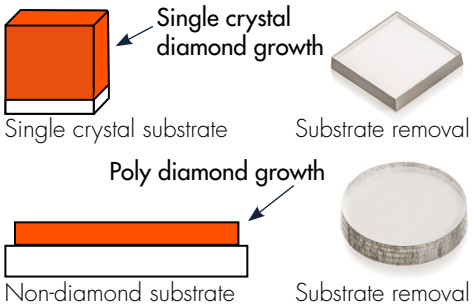
CVD diamond is sometimes classified by its grain size: ultra nano crystalline (< 10 nm), nano crystalline (< 50 nm) micro crystalline (< 500 μm) and single crystal diamond. The grain size depends on the synthesis conditions, substrate and layer thickness. Layers above ~50 μm can be removed from the carrier substrates, leaving free-standing bulk CVD diamond materials.

Polycrystalline CVD diamond

By controlling the impurities and the grain boundaries, free-standing polycrystalline diamond wafers can be fabricated 120 mm in diameter, with thermal and infrared optical properties that approach the highest quality perfect diamond. Free-standing polycrystalline diamond wafers 140 mm in diameter that are more durable, with finer grains and thermal conductivities still more than 2.5 times that of copper are also manufactured.

Single crystal CVD diamond

Single crystal diamond materials, with uniformly exceptional type IIa optical, thermal and mechanical properties, are routinely grown via homoepitaxy. Samples up to 8 x 8 x 2 mm are available.



Single crystal CVD diamond grades

Single crystal MCC	Engineering replacement for natural type IIa diamond
Optical grades	Controlled absorption and birefringence diamond
Electronic grade	Ultra-high purity for quantum optics and electronics

Polycrystalline CVD diamond

Optical grade	Engineered for far infrared laser optical applications
Electronic grade	Ultra-high purity material for large area passive electronics
Thermal grades	High thermal conductivity diamond heat spreading
Mechanical grades	High strength diamond for precision machining
Electrochemistry grade	Boron doped diamond for electrochemical applications

Further reading

7. Technology and Applications

Diamond structure

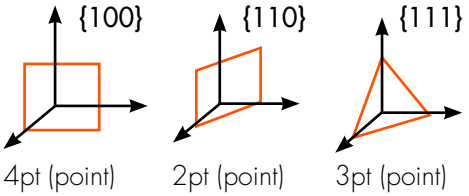
Each carbon atom in diamond is bonded to its four nearest neighbours in a regular tetrahedron. These are arranged in a variation of the face-centred cubic structure  $Fd3m-O_h$ <sup>7</sup>.

The three primary planes to consider for the octahedral diamond crystal are {111}, {100} and {110}. The nomenclature, more commonly used within the diamond industry, describes these as 3 point, 4 point and 2 point respectively.

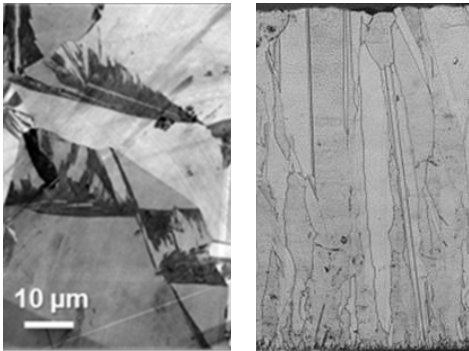
The majority of CVD single crystal diamond is available with {100} orientated surfaces, with {110} edges, while the {111} is the cleavage plane. All of these surfaces can be presented in CVD diamond engineered products.

Polycrystalline diamond

The grain structure of polycrystalline CVD diamond has a non-uniform composition, due to the growth process. Small, randomly orientated grains form during the nucleation process, then grains with facets favoured by the growth conditions rapidly form large grains, that are ~10% of the film thickness in diameter, elongated in the direction of growth. When processed it still presents an inhomogeneous surface of many orientations.



Face plane	4pt (100)	2pt (110)	3pt (111)
4pt {100}	0° 90°	45° 90°	54°44'
2pt {110}	45° 90°	0° 60° 90°	35°16' 90°
3pt {111}	54°44'	35°16' 90°	0° 72°32'



SEM image of the polished surface of boron doped diamond, highlighting the different orientations. A polished cross section, illustrating the elongated structure originating from the nucleation surface along the direction of growth.

Further reading

8. Structure of Diamond



## Strength of diamond

The covalent carbon to carbon bonds make diamond a very high strength material. The extreme rigidity of the diamond lattice also makes it a very stiff material, thus diamond is the ultimate high strength ceramic. The stress to fracture diamond is related to the size of the critical flaws in the material.

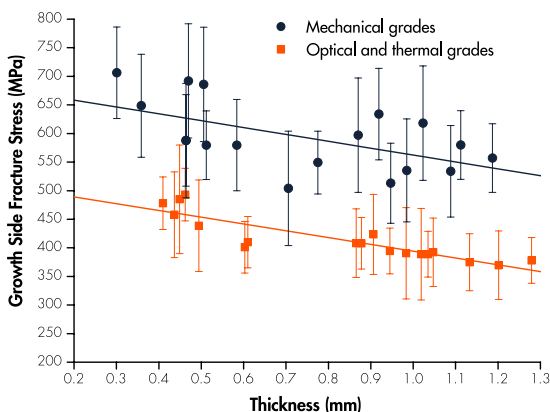
## Strength of single crystal

Tensile fracture testing of single crystal diamond finds the critical flaw size to be  $\sim 100$  nm. In mechanical testing the fracture strength is dependent on the surface finish and volume under test. With careful surface preparation,  $3 \times 5 \times 0.2$  mm samples achieve fracture stresses in the region of 2.5 - 3.0 GPa.

## Strength of polycrystalline diamond

Bulk polycrystalline diamond (PCD) is in the range 200 to 1100 MPa. It is significantly weaker due to the critical flaw found to be proportional to the grain size. Since the critical flaw/grain size is large at  $\sim 50$  to  $300$   $\mu\text{m}$ , PCD strength is relatively independent of surface finish, with a Weibull modulus of  $\sim 20$  when grain size is above  $\sim 100$   $\mu\text{m}$ .

With grain size increasing with layer thickness, strength is also dependent on thickness. Grain size is also dependent on the growth conditions and the orientation of the layer; with the nucleation surface in tension, the fracture stress is higher and the differences between grades less pronounced. In use, consideration should be given to which side is under tension. After  $10^7$  cycles to 70% of fracture stress, there has been found to be no degradation expected in fracture strength.



The strength of polycrystalline diamond is dependent on the grain size. Finer grained mechanical recipes are stronger, whilst material from all recipes exhibits a dependency with thickness. This effect is most pronounced on the growth surface.

## Further reading

3. Mechanical Properties of Diamond

Processing the hardest bulk material is not trivial. To date most methods still rely on diamond to process diamond. The {111} plane of diamond is substantially harder and more wear resistant than the others.

### Lapping

Rough processing of diamond is achieved using lapidary processes with a diamond grit slurry to remove material quickly. The physical wear mechanism is brittle fracture, leaving a rough surface with significant sub-surface damage.

### Scaife polishing

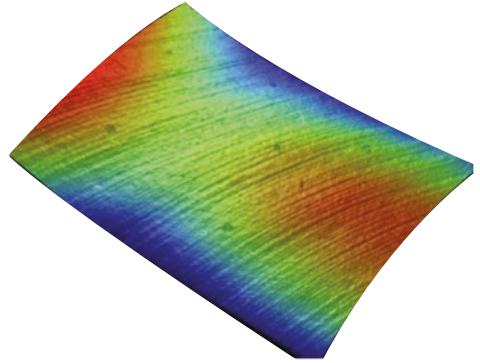
For single crystal diamond, by confining the direction of the wear fracture plane, low damage and low surface roughness can be achieved. The diamond is pressed onto a high speed rotating cast iron plate, a scaife, which has diamond particles embedded. It can achieve high surface finish  $R_a < 1$  nm with low damage.

### Resin bonded wheel polishing

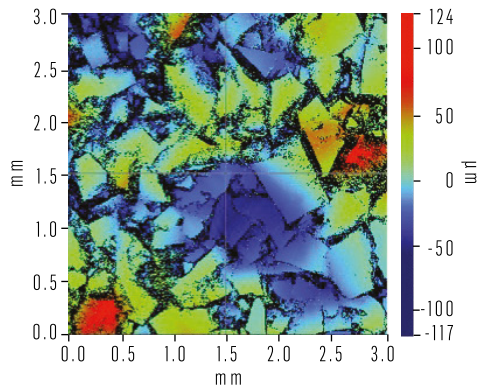
This can be used to process both single crystal and polycrystalline diamond. Large areas and higher flatness can be achieved, however the subsurface processing damage is more severe than with scaife polishing.

### Etching diamond

CVD diamond can be etched in high pH chemical mechanical polishing (CMP) slurries and in reactive ion-etching plasma based processes.



High quality, low damage surfaces prepared on single crystal diamond by traditional scaife polishing. The shallow polishing grooves,  $< 5$  nm are  $> 20$  nm wide.



Polycrystalline diamond, polished with a fixed grit diamond wheel. The grain relief is due to the different grain orientations, which polish at different rates.

### Further reading

9. Diamond Polishing

### Surface termination

The diamond lattice terminates with dangling carbon bonds and typically O and OH groups covalently bond to them. The surface can also be terminated with hydrogen via a plasma treatment process. Exposed diamond surfaces have an inherent affinity for oils and dust particulates.

### Cleaning diamond

Residual surface contamination can be removed from diamond using aggressive high temperature, > 150 °C, oxidising solutions, such as a combination of acid, e.g.  $\text{H}_2\text{SO}_4$  and an oxidising agent, e.g.  $\text{KNO}_3$ . These types of cleaning steps are used in the manufacturing processes of bulk CVD diamond and leave the diamond surface with an oxygen termination. Cleaning diamond, and/or care to avoid surface contamination, are required immediately prior to processes such as bonding and metallisation.

### Oxidation and graphitisation

The thermal oxidation in the air starts at above 600 °C. In a reducing atmosphere, e.g.  $\text{H}_2$ , the onset of graphitisation is above 1300 °C. Surface graphitisation can also occur under ion bombardment, such as with low pressure plasma cleaning processes.

### Carbide formation

Two distinct groups of metals react with diamond. The first group form their stable carbides, such as Si, W & Ti. The second group, including Fe, Co, Cr & Ni are solvents for carbon and exhibit poor/no adhesion via graphitised interfaces.

### Metallisation and optical coatings

Ohmic metal carbide contacts can be formed using thin film, multi-layer metal coatings, with a carbide former as the basis for adhesion, followed by a stable inert metal such as Au, Pt. Stable to ~400 °C, these coatings are used for the indirect attachment of contacts or heat sinks. Dielectric optical coatings can also be employed using extremely thin carbide adhesion layers.



Mounted ATR prisms for spectroscopy.

### Brazing

CVD diamond can be attached using active brazes, formulated to form a stable carbide interface, in high temperature vacuum processes, at ~800 °C. Interface shear strengths > 200 MPa can be achieved. The stresses generated by the thermal expansion mismatch between diamond and most mount materials require careful consideration.

### Further reading

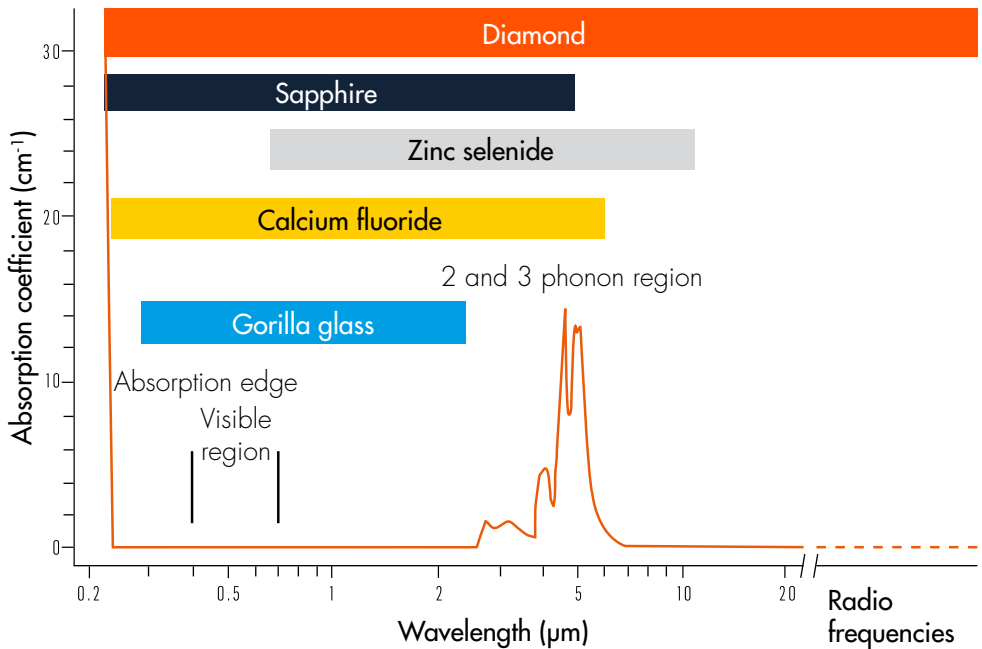
10. Cleaning Diamond

11. Brazing Parameters

### Transmission spectrum

The exceptional properties of synthetic CVD diamond place it at the pinnacle of modern optical materials, from ultraviolet (UV) to radio frequency transmission. The intrinsic optical properties are governed by its band gap in the deep UV, with a

cut off at 225 nm (5.47 eV). It is then transparent in the ultraviolet, visible near infrared regions, far infrared and radio frequencies, with only weak phonon band absorption, in the  $\sim 2.5$  to  $7\ \mu\text{m}$  region peaking at  $14\ \text{cm}^{-1}$  at  $4.63\ \mu\text{m}$ .



Absorption coefficient for ultra high purity CVD diamond from the UV cut-off 225 nm to far infrared region. Diamond has a relatively low dielectric constant making it highly suitable as a window for radio frequency applications.

### Further reading

12. Single Crystal Optics

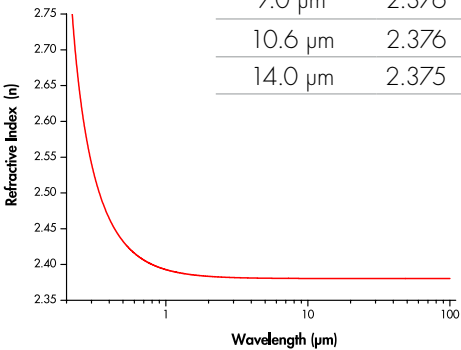
Refractive index

Diamond has a refractive index in the range of 2.7, at 220 nm, to 2.38 at 10.6 μm. The incident reflectivity is in the range 21.3% to 16.7%. The Turri equation approximates the dispersion curve for 300 to 1650 nm, where λ is in nm.

$$n^2(\lambda) = 1 + \frac{4.658\lambda^2}{\lambda^2 - 112.5}$$

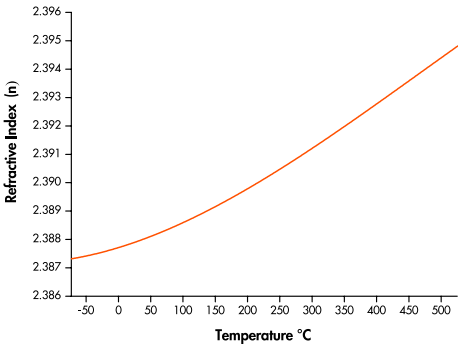
Beyond 2 μm diamond has almost no dispersion and the above equation can be used to 25 μm with reasonable accuracy (± 0.004). The alternative Hertzberger expression, fitted to experimental data in the range 2.5 to 25 μm is shown below.

Wavelength	n
300 nm	2.534
400 nm	2.461
500 nm	2.430
600 nm	2.414
700 nm	2.404
1064 nm	2.390
7.0 μm	2.376
10.6 μm	2.376
14.0 μm	2.375



$$n(\lambda) = 2.37837 + \frac{1.18897}{\frac{\lambda}{1000} - 0.028} - \frac{1.0083 \times 10^{-4}}{(\frac{\lambda}{1000} - 0.028)^2} - 2.3676 \times 10^{-5}\lambda^2 + 3.24263 \times 10^{-8}\lambda^4$$

The thermo-optic coefficient of refractive index (1/n)×(dn/dT) is in the range 3.2 to 6.7 × 10<sup>-6</sup> K<sup>-1</sup> IR region, 2.0 to 4.0 × 10<sup>-6</sup> K<sup>-1</sup> in the UV to NIR region.



Further reading

- 13. Refractive Index
- 14. Thermo Optic Properties

Raman spectroscopy

The Raman frequency of diamond, at RT, is  $\omega = 1332.3\text{ cm}^{-1}$ , line width  $1.5\text{ cm}^{-1}$ . The peak shape, position and luminescence in the Raman spectroscopy can be used by material scientists to assess diamond film quality, including phase purity, crystalline perfection and stresses.

In applications, the Raman shift can be used as a sensor itself. Temperature dependency is given by the semi-empirical expression:

$$T = \frac{Dhc\omega_0}{k\ln\{1 + c/[\omega_0 - \omega(T)]\}}$$

where  $\omega_0 = 1333 \pm 0.6\text{ cm}^{-1}$ ,  $C = 61.14 \pm 5$  and  $D = 0.787 \pm 0.03$ .  $C$  &  $D$  are fitted constants and  $\omega_0$  is the Raman frequency at  $T = 0\text{ K}$ .

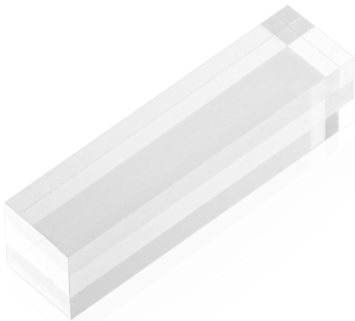
The approximate relationship of peak shift with hydrostatic pressure is given by:

$$\Delta\omega(P) = 3.2\text{ cm}^{-1}\text{ GPa}^{-1}$$

Raman laser

CVD synthesis enables intra-cavity laser optics, including Raman frequency converters. In comparison with other high gain Raman crystals, synthetic diamond has a larger frequency shift at much higher brightness.

$$\text{Raman FOM} = \frac{kgL}{(dn/dT)\Delta\lambda}$$



A CVD diamond 6 x 2 x 2 mm Raman laser crystal, which combine a large frequency shift and high gain with the inherent extreme mechanical properties of diamond making it much less sensitive to its environment.

	SC CVD diamond	KGW KGD(WO <sub>4</sub> ) <sub>2</sub>	YVO <sub>4</sub>	Ba(NO <sub>3</sub> ) <sub>2</sub>
Raman gain (g)	15	4	5	11
Raman shift $\Delta\lambda\text{ cm}^{-1}$	1332	901	892	1047
Crystal length (L) mm	8	25	25	25
Thermal conductivity (k) $\text{W m}^{-1}\text{K}^{-1}$	> 2000	5	5.2	1.2
Raman figure of merit	1440	3	20	1

Further reading

- 15. Raman Thermometers
- 16. Raman Spectroscopy
- 17. Raman Laser

### UV to NIR optical properties

Large area, up to  $\sim 60 \text{ mm}^2$  high purity single crystal CVD diamond is available and it enables many applications in the UV, visible and near infrared bands.

### Scatter

Scatter from CVD single crystal diamond is very low, as the macroscopic defects and surface finish giving rise to scatter are highly controlled. Total forward scatter can be as low as 0.02% at 1064 nm.

### Single crystal CVD diamond

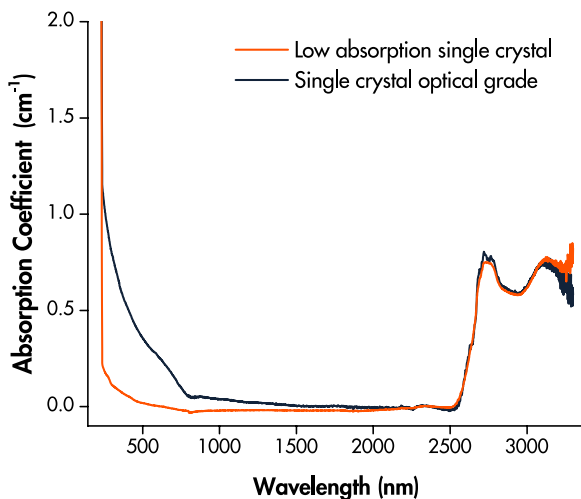
Absorption in the range 220 to  $\sim 2.5 \mu\text{m}$  is mainly attributable to nitrogen. When nitrogen is less than 5 ppm, single crystal optical grade diamond has Type IIa optical properties. Broad spectral range and low absorption  $n$  below  $\sim 1 \mu\text{m}$ .

### Optical plus low absorption

When nitrogen is less than 20 ppb, single crystal diamond has the lowest possible absorption. Suitable for the most demanding optical applications, this is a new class of synthetic optical material.

### Optical plus low birefringence

Due to its cubic lattice symmetry, diamond is an optically isotropic material; the refractive index should be independent of the polarisation of light. However, the presence of strain, typically from grown-in defects, leads to birefringence. With careful engineering, the defect density and orientation of the diamond optical component result in samples with isotropic refractive properties with no significant loss of polarisation of light. The birefringence loss of polarisation ( $\Delta n$ ) can be  $< 2 \times 10^{-5}$  in the visible and NIR bands.



### Further reading

18. Low Birefringence

### Polycrystalline optical grade diamond

With low absorption across the UV, VIS and IR bands, polycrystalline diamond is also an excellent optical material. Combined with its thermal and mechanical properties, it offers up to 100 times power handling capability compared to conventional IR laser optics.

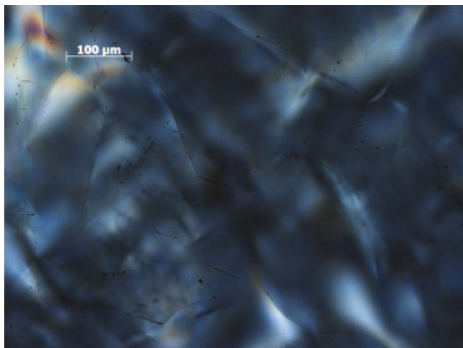
Competitive grain growth and a high density of defects, such as stacking faults, result in relatively high strain. Consequently it is less suitable for low birefringence, or UV to NIR applications where scatter is more of consideration. Diamond has a refractive index of 2.38 at 10.6  $\mu\text{m}$  and thin film AR coatings can be used to achieve > 99% transmittance.

### Scatter

Scatter losses are insignificant below 2  $\mu\text{m}$ ; polycrystalline diamond has excellent infrared optical properties. High incident angle scatter is correlated with micro-features in the diamond, while low angle scatter is attributed to strain induced birefringence. The residual extinction coefficient of diamond is 0.04 to 0.07  $\text{cm}^{-1}$  at 10.6  $\mu\text{m}$ .

### Micro crack features

Cracks at the grain boundaries are a characteristic of polycrystalline CVD diamond growth. These macroscopic cracks are formed during synthesis and are a mechanism of intra and transgranular stress relief.



The strain induced birefringence results in the colour in this cross polar transmitted light optical micrograph of polycrystalline transparent grade CVD diamond.



For industrial lasers large area polycrystalline CVD diamond optics are more robust and reliable than the ZnSe optics they typically replace.

### Further reading

19. Polycrystalline Optics



Emissivity in the infrared band

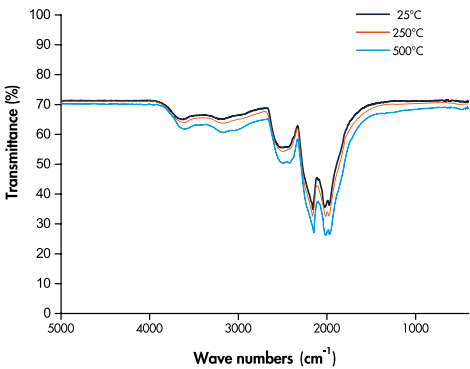
The residual absorption in the far infrared is due to the tail of the multi-phonon vibrational absorption processes. These are temperature dependent and diamond is emissive. However, these processes are only significant above ~100 °C and the absorption is successfully described by a phonon recombination and destruction model.

Dielectric properties

Diamond has a nearly constant dielectric constant from the terahertz region down to radio frequencies and beyond. The dielectric constant for diamond is at 35 GHz  $\epsilon = 5.68 \pm 0.15$  with a loss tangent of  $< 1 \times 10^{-4}$ .



Polycrystalline diamond optics > 100 mm diameter are used in high power window applications.



The temperature dependent infrared spectra of optical grade polycrystalline CVD diamond.

Temperature (°C)	10.6 μm Abs. cm <sup>-1</sup>
25	0.035
100	0.063
150	0.082
200	0.102
250	0.123
300	0.145
350	0.168
400	0.191
450	0.216
500	0.241

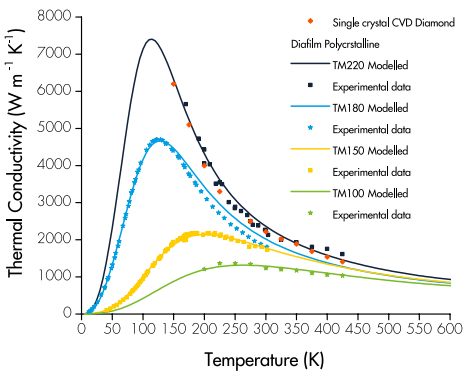
Approximate absorption coefficient as a function of temperature. See reference.

$$\epsilon(T) = 5.700111 - 5.35167 \times 10^{-5}T + 1.6603 \times 10^{-7}T^2$$



Thermal conduction

Unlike metals, heat conduction in diamond is dominated by lattice vibrations (phonons). The thermal conductivity is then determined by how these are scattered. In diamond, at room temperature, this is related to phonon-phonon scattering (Umklapp processes) and defect/impurity scattering. With grain size above ~50  $\mu\text{m}$  and high phase purity, polycrystalline CVD diamond has been found to have a through-plane conductivity varying by less than 10% of its in-plane value.



The thermal conductivity of diamond versus temperature. In single crystal and high phase purity polycrystalline diamond, phonon scattering dominates. While finer grained materials exhibit lower but less temperature dependent characteristics. Room temperature thermal conductivity of polycrystalline optical grade CVD diamond exceeds  $2200\text{ Wm}^{-1}\text{K}^{-1}$ .

Thermal expansion

Diamond has an extremely low coefficient of thermal expansion, attributed to the very high bond energy. In general the expansion of materials is related to the phonon characteristics as a function of temperature and generally varies with temperature. Diamond has a low coefficient of thermal expansion at room temperature, rising steadily with temperature, as shown in the table below.

Temp. (K)	Linear coefficient (a) ppm	Mean expansion referenced from 300 K
200	0.37	-
300	1.07	-
400	1.81	1.45
500	2.46	1.80
600	3.02	2.11
800	3.86	2.65
1000	4.45	3.09

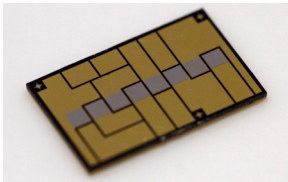


Polycrystalline thermal grades are used in heat spreading applications.

Further reading

- 21. Thermal Conductivity
- 22. Thermal Expansion

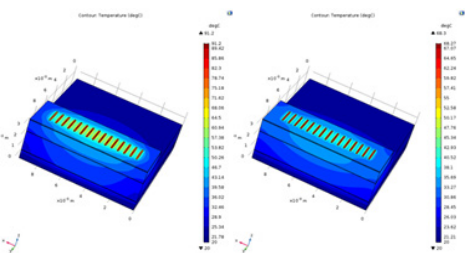
With its extremely high thermal conductivity CVD diamond is an ideal heat spreader material. Typical copper-based heat spreaders are 380 to 450 W m<sup>-1</sup> K<sup>-1</sup> while insulators e.g. AlN, BeO are between 200 to 300 W m<sup>-1</sup> K<sup>-1</sup>.



A patterned gold terminated metallisation, enables the high quality Diafilm TM100 heat spreader function to be integrated with device contacting and packaging requirements.

Modelling heat flow

High power density devices are complex structures with critical interfaces between the semiconductor, heat spreader and the heat sink. To design and evaluate the performance of packaged devices finite element modelling is used to compare different heat spreader and packaging options.



A FE model of a multichannel ASIC chip on a CMC heat spreader (left) and ASIC on CVD diamond heat spreader on CMC (right). The performance of this device is determined by the peak temperature in the channel.

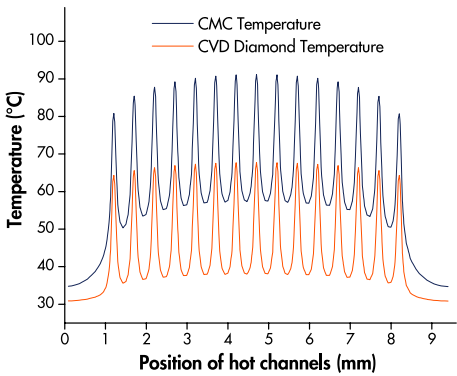
Further reading

- 27. Thermal Management
- 33. Thermal Modelling

Material options

With a FE modelled system the impact of different thermal conductivity, attachment and sizes can be assessed. Thermal grades of CVD diamond can be engineered to be from 700 to 2200 W m<sup>-1</sup> K<sup>-1</sup> with an electrically conductive grade made for RF resistive applications.

Lowering junction temperatures



Modelling predicts the insertion of a 1 mm TM220 diamond heat spreader between an ASIC and the 350 W m<sup>-1</sup> K<sup>-1</sup> CMC heat sink, reduce the peak temperature of the active amplifier area of 25% from 92°C to 68°C.

Applications

CVD diamond heat spreaders are used to enhance the performance, reliability and of ASICs, RF power amplifiers, semiconductor and solid state lasers and is found in a diverse range of industries from materials processing, telecommunications, aerospace and space.

## Type IIa single crystal diamond

Single crystal diamonds have been critical to the development of ultra-precision machining over the last decades. In some applications higher purity type IIa diamond ( $N < 1$  ppm), has an advantage over Type Ib diamond ( $N > 100$  ppm), synthesised in the HPHT process due to its superior hardness.



Since the introduction of CVD type IIa single crystal, the availability of larger areas, regular shapes and more consistent properties has seen it replace naturally sourced type IIa diamonds in ultra-precision machining applications.

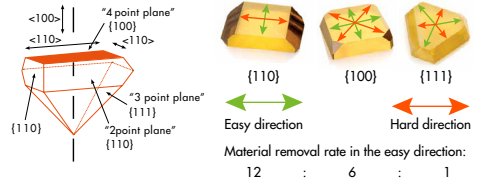
## HPHT type Ib single crystal diamond

In all high hardness materials there is an inverse relationship in the hardness and toughness. In ultra-precision applications, there is a trade-off between wear resistance and fracture toughness. With more crystal defects type Ib can exhibit higher toughness than type IIa diamond.

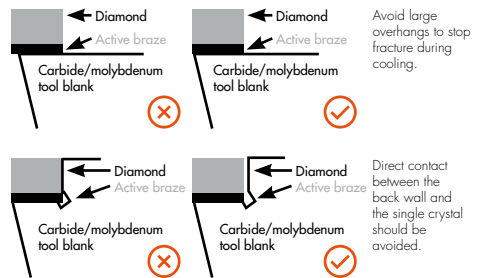
## Ultra-precision tool preparation

Understanding crystallographic planes and directions is a key factor for successful sizing and finishing of the cutting edge. The planes of atoms will impart different degrees of abrasiveness or ease of polishing depending on which orientation is presented to the workpiece.

In practical terms, the “easy and hard” directions in the planar symmetry of the diamond determine the material removal rate during tool preparation.



The softest polishing directions in a {100} plane are parallel to the  $\langle 100 \rangle$  directions lying in the plane. The hardest polishing directions are the  $\langle 110 \rangle$  directions lying in a {111} plane.



Tools are actively brazed, see page 11, to hard metal carriers and tool holders and positioning is critical for avoiding fracture due to differences in thermal expansion.

## Polycrystalline mechanical cutting tools

With excellent balance of wear resistance, fracture toughness and thermal stability, polycrystalline CVD diamond provides an outstanding cutting performance, in some applications. Due to its polycrystalline nature, the tool cutting ability is also unaffected by the crystal orientation. To facilitate tool fabrication, metal-like conductivity (boron doped) polycrystalline CVD diamond is also available.

## Further reading

### 34. Diamond Turning

Semiconducting properties

Diamond is a wide bandgap semiconductor, with an indirect gap of 5.47 eV. Experiments on high purity CVD diamond have reported high mobility values and long lifetimes for electrons and holes. Combined with the high breakdown field and thermal conductivity, this makes diamond the preferred material for a number of demanding electronic applications.

Diamond’s radiation hardness arises from its high atomic displacement energy (42 eV/atom) and low atomic number. Thus it can demonstrate stable high sensitivity to radiation in comparison to other solid state detector materials.

Doping diamond

All known dopants for diamond are deep, but with  $B > 1 \times 10^{20}$  atoms  $\text{cm}^{-3}$ , the acceptor levels overlap with the valence band as the diamond undergoes the Mott transition to demonstrate metal-like p-type conductivity.

Due to the activation energy, n-type doping in diamond has only been considered for high temperature and UV applications, with limited success.

Further reading

- 23. Diamond Detectors
- 24. Boron Doping
- 35. Electronic Diamond

	Poly-crystalline	Single crystal
Band gap (eV)	5.47	5.47
[N] <sub>s</sub> <sup>0</sup> (ppb) EPR	< 50	< 5
B (ppb) SIMS	< 0.5	< 0.5
Dopants	Activation energy	Achievable levels
Boron	0.37 eV	10 <sup>21</sup>
Phosphorus	0.6 eV	10 <sup>20</sup>
Nitrogen	1.7 eV	10 <sup>19</sup> (111)



High purity electronic grade single crystal diamond is used in high energy particle detection.

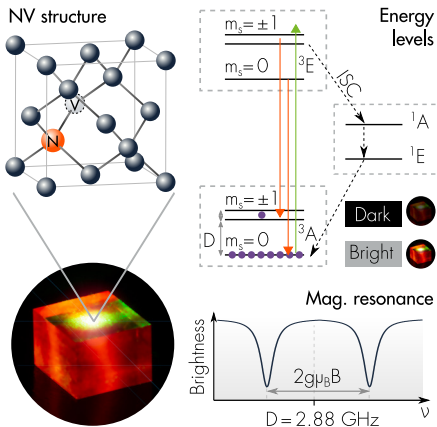
Electronic single crystal diamond

CVD synthesis enables synthetic diamond with unintentional defect density around or below the parts per billion level ( $\sim 10^{14} \text{ cm}^{-3}$ ) to be manufactured. These diamonds have exceptional wide band gap electronic properties. As an extremely low point defect material these are a platform for engineering defects at low or single point concentrations.

Defects in a material may possess a quantum property called “spin”. With diamond’s strong C-C bonds comes a high Debye temperature (~2200 K). This has the result that spin states can be long-lived, even at room temperature (RT).

### The NV centre in diamond

The negatively charged nitrogen-vacancy (NV) in diamond possesses such a spin and has a collection of unique properties.



The NV centre, its energy-level structure, and its use in measuring a magnetic field.

A green light source (often a laser) can be used to generate red light from NV defects, as shown in the figure above. During illumination, NV is initialised into a particular spin state. This can then be coherently controlled by the application of microwaves and the state read out by monitoring the amount of red light emitted. NV can be engineered into CVD diamond at the desired concentration.

### Further reading

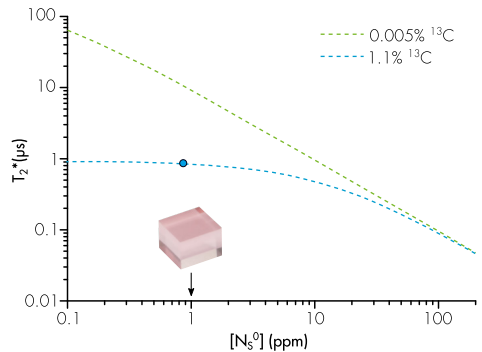
36. Quantum Revolution
37. Coherence Times
38. Magnetic-field Sensing

In the case of single NV defects in EL-grade samples where  ${}^{13}\text{C}$  has been depleted the coherence time (time the quantum-state is retained) can extend to seconds at RT. There has therefore been great interest in utilising NV centres in the following areas:

- Secure communication
- Quantum computation/simulation
- Next generation of sensors

### B-field sensing and NV coherence time

The spin-levels of the NV centre are also affected by a magnetic (B) field, via the Zeeman effect. With multiple NV centres, the strength and direction of B can be measured, forming a vector sensor that has high sensitivity and dynamic range.



Dependence of NV coherence time ( $T_2^*$ ) with concentration of N and  ${}^{13}\text{C}$  in diamond.

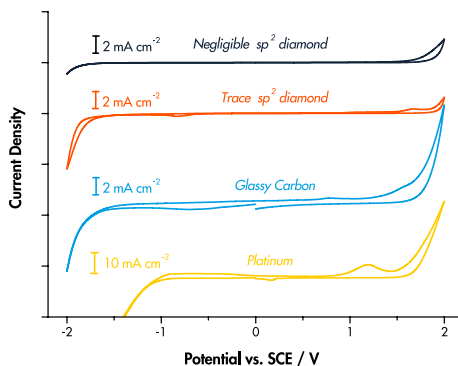
The sensitivity ( $\eta$ ) can be estimated by:

$$\eta \sim \frac{1}{g_e \mu_B} \frac{1}{C \sqrt{\beta}} \frac{1}{\sqrt{N_{\text{NV}} T_2^*}}$$

The number of NV centres ( $N_{\text{NV}}$ ) and coherence time ( $T_2^*$ ) are the key material properties. These are linked, as increasing the concentration of nitrogen decreases  $T_2^*$ . Hence the concentration of NV and  ${}^{13}\text{C}$  may be tailed, depending on the size and sensitivity requirements of the device.

## Boron doped diamond

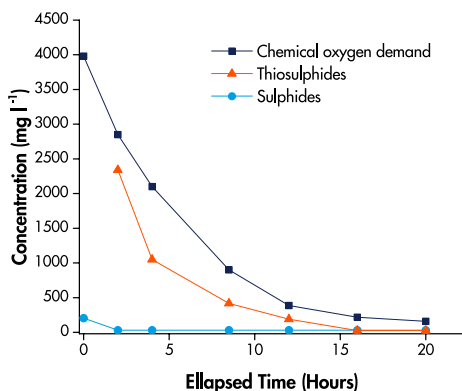
Conducting, polycrystalline boron doped diamond (BDD) has the widest solvent window of all electrode materials in aqueous solution. It also has very low background and capacitive currents, and reduced fouling, compared to other electrodes along with the ability to withstand extreme potentials and harsh environments. However, these properties are highly dependent on the diamond quality, with the properties improving as the non-diamond-carbon (NDC) content decreases. Free-standing, solid BDD electrodes can be grown with both trace and negligible NDC content.



Solvent windows in 0.1 M  $\text{KNO}_3$ , pH 6.5. For diamond electrodes the solvent window is heavily influenced by the non diamond carbon content of the BDD electrode.

## BDD applications

The very wide solvent window of diamond in aqueous solution pushes out gas evolution to very high cathodic/anodic potentials and enables the generation of highly oxidising hydroxyl radical, with very high current efficiency. This phenomenon can be exploited in advanced oxidation processes. The inert characteristics of the BDD electrode make it an ideal platform for electrochemical sensing applications.



Removal of recalcitrant dissolved contaminants from spent caustic industrial waste water. Chemical oxygen demand (COD) is a measure of how polluted an effluent is and BDD enabled electrochemical advanced oxidation is one of only a handful of techniques capable of removing contaminants to below safe discharge limits.

## Electrochemical properties of BDD

Polished bulk, free standing polycrystalline BDD, with  $B > 1 \times 10^{20}$  atoms  $\text{cm}^{-3}$  and negligible NDC, with oxygen terminated surfaces, exhibits the following electrochemical properties:

- Resistivity  $\sim 0.5 \times 10^{-3}$  Ohm m
- Diamond solvent window  $> 3.0$  V
- Reversibility  $< 70$  mV ( $\text{Ru}(\text{NH}_3)_6^{3+}$ )
- Capacitance  $< 10$   $\mu\text{F cm}^{-1}$

## Further reading

25. BDD Electrochemistry
26. BDD Water Treatment



		Polycrystalline		Single crystal	
Properties		Optical grade	RF grade	Optical grade	Optical plus
Hardness (GPa)		81 ± 18 <sup>(30)</sup>	81 ± 18 <sup>(30)</sup>	70 - 120 <sup>(3)</sup>	70 - 120 <sup>(3)</sup>
Fracture toughness (MPam <sup>0.5</sup> )		8.5 <sup>(3)</sup>	8.5 <sup>(3)</sup>	5 - 7 <sup>(3)</sup>	5 - 7 <sup>(3)</sup>
Young's modulus (GPa)		1054 <sup>(3)</sup>	1054 <sup>(3)</sup>	1054 <sup>(3)</sup>	1054 <sup>(3)</sup>
Poisson's ratio		0.1 <sup>(3)</sup>	0.1 <sup>(3)</sup>	0.1 <sup>(3)</sup>	0.1 <sup>(3)</sup>
Fracture stress (MPa) [Weibull modulus]				3500 [2.5] <sup>(3)</sup>	3500 [2.5] <sup>(3)</sup>
Nucleation surface		800 [10]	800 [10]		
Growth surface		400 [15]	300 [15]		
Rain impact DTV (ms <sup>-1</sup> ) 2 mm drop size		525 <sup>(31)</sup>		457 - 533 <sup>(31)</sup>	-
Sand erosion (mg/kg) at 100 ms <sup>-1</sup> C300/600 sand		2.1 ± 0.6 <sup>(30)</sup>		-	-
Thermal conductivity at 300 K (Wm <sup>-1</sup> K <sup>-1</sup> )		1900 - 2200	1900 - 2200	1900 - 2200	> 2000
Thermal conductivity at 500 K (Wm <sup>-1</sup> K <sup>-1</sup> )		1100	1100	1100	1100
Thermal expansion coefficient (ppm K <sup>-1</sup> )		1.0 at 300 K	1.0 at 300 K	1.0 at 300 K <sup>(22)</sup>	1.0 at 300 K
		4.4 at 1000 K	4.4 at 1000 K	4.4 at 1000 K <sup>(22)</sup>	4.4 at 1000 K
Refractive index	(10.6 µm)	2.376 <sup>(30)</sup>		2.376 <sup>(30)</sup>	2.376 <sup>(30)</sup>
	(1550 nm)	2.386 <sup>(13)</sup>		2.386 <sup>(13)</sup>	2.386 <sup>(13)</sup>
	(1064 nm)	2.392 <sup>(13)</sup>		2.392 <sup>(13)</sup>	2.392 <sup>(13)</sup>
dn/dT (K <sup>-1</sup> )		9.6 x 10 <sup>-6</sup> <sup>(30)</sup>		9.6 x 10 <sup>-6</sup> <sup>(30)</sup>	9.6 x 10 <sup>-6</sup> <sup>(30)</sup>
Dielectric constant D (35 GHz)		5.68 ± 0.15 <sup>(30)</sup>	5.68 ± 0.15 <sup>(30)</sup>	-	-
Loss tangent 145 GHz (10 <sup>-6</sup> )		8 - 20 <sup>(32)</sup>	10 - 100 <sup>(32)</sup>	-	-
10.6 µm absorption coefficient (cm <sup>-1</sup> )		< 0.07		< 0.05 <sup>(12)</sup>	< 0.05
3-5 µm absorption coefficient (cm <sup>-1</sup> )		min 0.8 at 3.7 µm <sup>(30)</sup>		min 0.8 at 3.7 µm <sup>(30)</sup>	min 0.8 at 3.7 µm <sup>(30)</sup>
1.064 µm absorption coefficient (cm <sup>-1</sup> )		Typical 0.12 <sup>(12)</sup>		< 0.1 <sup>(12)</sup>	0.005 <sup>(12)</sup>
Emissivity at 10 µm (1 mm thick)		0.02 at 573 K		0.02 at 573 K	0.02 at 573 K
		0.3 at 773 K <sup>(19)</sup>		0.3 at 773 K <sup>(19)</sup>	0.3 at 773 K <sup>(19)</sup>
Integrated forward scatter 8 - 12 µm (%)		0.1 - 0.7% <sup>(19)</sup>		-	NA
Integrated forward scatter visible (%)		< 4% <sup>(19)</sup>		< 0.7% <sup>(12)</sup>	0.10%
Birefringence (n <sub>e</sub> - n <sub>o</sub> )				1 x 10 <sup>-4</sup> <sup>(18)</sup>	< 5 x 10 <sup>-5</sup> <sup>(18)</sup>
Specific heat capacity (J/Kg <sup>-1</sup> K <sup>-1</sup> ) 300 K		520 <sup>(21)</sup>	520 <sup>(21)</sup>	520 <sup>(21)</sup>	520 <sup>(21)</sup>
Transmission 8-200 µm (1 mm thick)		71.4% #	68 - 70% #	71.4% #	71.4% #
Transmission 633 nm (1 mm thick)		> 64% #		> 69% #	70.6% #

Property	TM 100	TM 150	1M 180	TM 200	TM 220	ETC 700
Thermal conductivity						
@ 300K (W m <sup>-1</sup> K <sup>-1</sup> )	>1000	>1500	>1800	>2000	>2200*	~700*
@ 425K (W m <sup>-1</sup> K <sup>-1</sup> )	>900	>1400	>1500	>1500	>1620	>500
Thermal expansion coefficient						
@ 300K (pmm K <sup>-1</sup> )	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1
@ 1000K (pmm K <sup>-1</sup> )	4.4 ± 0.1	4.4 ± 0.1	4.4 ± 0.1	4.4 ± 0.1	4.4 ± 0.1	4.4 ± 0.1
Thermal diffusivity						
300K (cm <sup>2</sup> s <sup>-1</sup> )	>5.5	>8.3	>10.0	>11.1	>12.2	>3.9
Specific heat capacity						
300K (J kg <sup>-1</sup> K <sup>-1</sup> )	520	520	520	520	520	520
Hardness						
GPa	81 ± 18	81 ± 18	81 ± 18	81 ± 18	81 ± 18	81 ± 18
Fracture toughness						
(MPa m <sup>0.5</sup> )	5.3 - 7.0	5.3 - 7.0	5.3 - 7.0	5.3 - 7.0	5.3 - 7.0	8.5
Young's modulus						
(GPa)	1050	1050	1050	1050	1050	1050
Poisson's ratio	0.1	0.1	0.1	0.1	0.1	0.1
Density						
(10 <sup>3</sup> kg m <sup>-3</sup> )	3.52	3.52	3.52	3.52	3.52	3.52
Resistivity						
Bulk R <sub>v</sub> (Ω m)	10 <sup>12</sup>	10 <sup>12</sup>	10 <sup>12</sup>	10 <sup>12</sup>	10 <sup>13</sup>	0.05 - 0.07
Surface R <sub>s</sub> (Ω m)	10 <sup>10</sup>	10 <sup>10</sup>	10 <sup>10</sup>	10 <sup>10</sup>	10 <sup>11</sup>	0.05 - 0.07

\* Measured at 293K

Further reading

- 28. Thermal Applications
- 29. Metallized CVD Diamond

Property	Diafilm CDM	Diafilm CDE	MCC - Single Crystal	Mono
Thermal conductivity				
@ 300K (W m <sup>-1</sup> K <sup>-1</sup> )	1000	600	>1900	>800
@ 425K (W m <sup>-1</sup> K <sup>-1</sup> )	900	500	>1500	>700
Thermal expansion coefficient				
@ 300K (pmm K <sup>-1</sup> )	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1	1.0 ± 0.1
@ 1000K (pmm K <sup>-1</sup> )	4.4 ± 0.1	4.4 ± 0.1	4.4 ± 0.1	4.4 ± 0.1
Thermal diffusivity				
300K (cm <sup>2</sup> s <sup>-1</sup> )	>8.3	>10.0	11.1	
Specific heat capacity				
300K (J kg <sup>-1</sup> K <sup>-1</sup> )	520	520	520	520
Hardness				
GPa	80± 18	80± 18	70 - 120†	11 - 100†
Fracture stress				
	Growth - Nucleation	Growth - Nucleation	Surface finish dependent	
(MPa)	500 - 1100	500 - 1100	2000 - 3000	2000 - 3000
Fracture toughness				
(MPam <sup>0.5</sup> )	8.5	8.5	5	3.4
Young's modulus				
(GPa)	1050	1050	1050	1050
Poisson's ratio	0.1	0.1	0.1	0.1
Density				
(10 <sup>3</sup> kg m <sup>-3</sup> )	3.52	3.52	3.52	3.52
Resistivity				
Bulk Rv (Ω m)	1 x 10 <sup>12</sup>	0.05 - 0.07	1 x 10 <sup>12</sup>	1 x 10 <sup>10</sup>

† Orientation dependent

Properties	EP grade	Comments
<b>Electrochemical properties</b>		
Boron doping concentration (typical)	2 to 6 × 10 <sup>20</sup> atoms cm <sup>-3</sup>	Averaged over 0.16 mm <sup>2</sup>
Non diamond carbon	Trace	As measured by Raman spectroscopy
Resistivity (Ω m)	0.2 - 1.8 × 10 <sup>-3</sup>	± 0.25 × 10 <sup>-3</sup>
Contact resistivity (Ω m)	< 1 × 10 <sup>-3</sup>	For Ti:Pt:Au metallisation
Values quoted measured with ohmic contacted diamond with polished surfaces		
Solvent window* (V)	> 3.0	0.1 M KNO <sub>3</sub> versus SCE
Capacitance* (μF cm <sup>2</sup> )	< 20 μF	Derived from cyclic voltammetry at a scan rate of 0.1 Vs <sup>-1</sup>
Reversibility (ΔEp)* (mV)	< 100	Recorded at a 1 mm diameter disc electrode with 1 mM Ru(NH <sub>3</sub> ) <sub>6</sub> <sup>3+/2+</sup> at a scan rate of 100 mVs <sup>-1</sup> when an ohmic contact to diamond is made
Erosion rate (μg h <sup>-1</sup> m <sup>-2</sup> )	< 6	Measured at 10000 Am <sup>-2</sup>
Operating current density (A m <sup>-2</sup> )	> 20000	2 mm spacing 50 mScm <sup>-1</sup> electrolyte
<b>Mechanical properties</b>		
Nucleation side fracture stress (MPa)	> 800	
Growth side fracture stress (MPa)	> 450	
Young's modulus (GPa)	1050	
Fracture toughness (MPa m <sup>0.5</sup> )	8.5	
Weibull modulus	> 10	
Hardness (GPa)	81 ± 18	
<b>Thermal properties</b>		
Thermal conductivity (Wm <sup>-1</sup> K <sup>-1</sup> )	~700	Through plane at 300 K
<b>Dimensional tolerance un-processed</b>		
Thickness uniformity	± 25%	Typical values
Nucleation side roughness (μm)	Ra < 0.5	Typical values
Growth face roughness (μm)	Ra < 200	Typical values
Max. area available (round mm <sup>2</sup> )	12 270	Diameter 130 mm
Max. area available (rectangle mm <sup>2</sup> )	7150	Rectangle 110 x 65 mm
Lateral dimensional tolerance (mm)	± 0.2	All edges are laser cut
<b>Processed</b>		
Lapped face roughness (μm)	Ra < 0.25	Standard tolerance
Polished face roughness (μm)	Ra < 0.03	Standard tolerance
Thickness tolerance (mm)	± 0.05	Standard tolerance

\*Values quoted measured for ohmic contacted diamond with Ra < 0.03 μm surface finish

Properties	Single crystal	Polycrystalline	Comments
Electronic			
Hole mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	> 2000	1000	
Electronic mobility (cm <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	> 2000	1800	
Carrier lifetime (ns)	~2000	~1 - 10	
Charge collection distance	*Typically > 475 μm	†Typically >180 μm	*At 0.5 V μm <sup>-1</sup> applied field, for 500 μm plate †At 1V μm <sup>-1</sup> applied field, for 500 μm plate
Charge collection efficiency	Typically > 95%	Typically > 36%	for 500 μm plate
Bandgap (eV)	5.47	5.47	
Electron saturation velocity (cms <sup>-1</sup> )	20	20	
Radiation hardness cm <sup>2</sup> 24 GeV protons		> 10 <sup>15</sup>	With < 25% signal drop
Breakdown voltage (MV cm <sup>-1</sup> )	1 - 2		Experimental value. Threshold current 10μA 4 x 4 mm x 20 μm contact area 0.71 mm <sup>2</sup>
Impurities			
[N <sup>0</sup> <sub>S</sub> ] (ppb)	<5 (typically 0.1 -1)	< 50	Measured by EPR
[B] (ppb)	< 1	< 1	Measured by SIMS
Thermal properties			
Thermal conductivity (Wm <sup>-1</sup> K <sup>-1</sup> )	> 2000	> 1900	
Expansion coefficient (ppm K <sup>-1</sup> ) at 300 K	1.0 ± 0.1	1.0 ± 0.1	
Expansion coefficient (ppm K <sup>-1</sup> ) at 1000 K	4.4 ± 0.1	4.4 ± 0.1	
Dimensions			
Standard sizes (mm)	2 x 2, 4 x 4, 4.5 x 4.5	5 x 5, 10 x 10, 20 x20	Tolerance ± 0.05 mm Polycrystalline available up to Ø 110 mm
Standard thickness (mm)	0.3 & 0.5	0.3 & 0.5	Tolerance ± 0.05 mm
Laser kerf	3°	3°	
Edge features (mm)	<0.2	<0.2	
Crystallographic orientation (face/edge)	{100} ± 3°<110>		
Processed			
Surface finish side 1 Ra (nm)	< 0.5	Ra < 20	Single crystal polished on {100}
Surface finish side 2 Ra (nm)	< 0.5	Ra < 20	Single crystal polished on {100}

Product line: DNV-B1™

Properties	Values	Comments
Quantum properties		
<sup>13</sup> C fraction	1.1%	
Typical [N <sub>s</sub> <sup>0</sup> ] (before treatment)	800 ppb	
Typical [NV]	300 ppb	
Typical spin coherence time T <sub>2</sub> <sup>*</sup>	1 μs	
Typical spin coherence time T <sub>2</sub>	200 μs	
Thermal properties		
@ 300K (Wm <sup>-1</sup> K <sup>-1</sup> )	>1900	
@ 425K (Wm <sup>-1</sup> K <sup>-1</sup> )	>1500	
Dimensions		
Standard sizes (mm)	3 x 3	Tolerance ± 0.05 mm
Standard thickness (mm)	0.5	Tolerance ± 0.05 mm
Edge features (mm)	<0.2	
Crystallographic orientation	{100}	
Miscut for main face orientation	<3°	
Processed		
Polished face roughness (μm)	Ra < 30 <sup>*</sup>	Single crystal polished on {100} <sup>*</sup> < 1nm achievable

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