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Andrew M. Bennett
Element Six Limited

Benjamin J. Wickham
Element Six Limited

Harpreet K. Dhillon
Element Six Limited

Ying Chen
University of Central Florida

Scott Webster
University of Central Florida

See next page for additional authors

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Authors

Andrew M. Bennett, Benjamin J. Wickham, Harpreet K. Dhillon, Ying Chen, Scott Webster, Giorgio Turri, and Michael Bass

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Development of High Purity, Optical Grade Single Crystal CVD Diamond for Intra-Cavity Cooling

Andrew M Bennett^{*a}; Benjamin J Wickham^a; Harpreet K Dhillon^a; Ying Chen^b, Scott Webster^b, Giorgio Turri^{b*} and Michael Bass^b

^aElement Six Limited, Global Innovation Centre, Fermi Avenue, Harwell Oxford, Oxfordshire, OX11 0QR

^bCREOL, The College of Optics and Photonics, University of Central Florida, Orlando, FL 32816

ABSTRACT

Microwave assisted chemical vapour deposited bulk diamond products have been used in a range of high power laser systems, due to low absorption across a range of wavelengths and exceptional thermal properties. However the application of polycrystalline products has frequently been limited to applications at longer wavelengths or thermal uses outside of the optical path due to the birefringence and scatter that are intrinsic properties of the polycrystalline materials. However, there are some solid state structures, including thin disc gain modules and amplifiers, that will gain significantly in terms of potential output powers if diamond could be used as a heat spreader in the optical path as well as a heat spreader on the rear surface of the disk.

Therefore single crystal grades of diamond have been developed that overcome the limitations of the polycrystalline material, with low absorption, low scatter and low birefringence grades for demanding optical applications. We will present new data, characterising the performance of these materials across infra-red and visible wavelengths with absorption coefficient measured by laser calorimetry at a range of wavelengths from 1064 nm to 452 nm.

Keywords: Diamond, High power applications, Materials processing, Low Absorption, Single Crystal, Synthesis, Processing,

1. INTRODUCTION

It has long been accepted that high quality diamond grown by chemical vapour deposition (CVD) makes a valuable material for a range of optical applications due to its extremely wide transparency window, ranging from the ultraviolet (UV) cut-off at 226 nm¹ to beyond 500 μm through the far infra-red (FIR)² and into terahertz, with one region of weak absorption between approximately 3 and 6 μm related to the excitation of multiple phonons in the diamond. This low absorption coefficient is complemented by the highest thermal conductivity of any bulk material³, high laser induced damage threshold (LIDT)⁴, high resistance to thermal shock, low coefficient of thermal expansion, high hardness, high fracture strength and chemical inertness⁵.

Optical grades of synthetic polycrystalline diamond have been available for use in IR applications since the 1990s, when CVD growth technology became established⁶. Since then, polycrystalline diamond has been implemented into a wide range of optical applications with engineered defect densities resulting in optimised properties. For use in the optical path of lasers, polished windows of high purity, optical grade, polycrystalline diamond are available in diameters up to 135 mm and up to 2.0 mm thick and are routinely used in IR applications, for example as output couplers for high power (>2kW) carbon dioxide (10.6 μm) lasers⁷.

However some performance parameters of polycrystalline grades in shorter wavelength applications (including the wide range of doped solid state systems operating around 1 μm) have suffered due to scatter, intrinsic to the non-uniform structure and resulting largely from grain boundaries and intragranular strain-induced birefringence⁸. The development of single crystal diamond has taken the optical, thermal and mechanical advantages of polycrystalline diamond to lower

wavelengths and new applications⁹. By the elimination of grain boundaries and total control of crystal orientation with respect to its use, deficiencies such as scatter and birefringence, which would be prohibitive to the use of polycrystalline diamond, can be controlled. Single crystal parts are available in smaller sizes than the polycrystalline components, however careful management of both growth conditions and processing techniques can achieve a regime of control within which, impurity and defect levels are substantially and reproducibly better than for polycrystalline products and are optimized for a variety of high power, high precision uses in future laser applications.

1.1 Power scaling in disc lasers

Since the invention of the thin disc laser in the 1990s it has become a favored tool for cutting and welding applications. Disc lasers combine reliability and high efficiency with excellent beam quality at high average and peak powers. These excellent beam qualities are possible at high power due to the axial heat flux enabled by the thin disk structure where heat sinking is via the large back face of the disc. This axial heat flux means that thermal lensing is minimized even at significant laser power since radial temperature gradients are low when compared to other systems¹⁰. In addition to this the disc structure enables power scaling of both average and peak powers simply by increasing the beam cross section, and by scaling in this way all internal intensities as well as pump source brightness can be kept constant¹¹. Recently 8kW with a beam quality of 3 mm mrad from a single disk has been reported¹², and 30kW output beams are reported for multiple disk resonators.

Separately, thin disc structures made from semiconductors have developed rapidly over the last few years and are now replacing incumbent technologies in a range of wavelengths¹³, due to a similar range of benefits as for the solid state YAG-based systems, albeit at lower average powers ref-VECSEL. Hopkins et al. have reported improvements in power output of over two orders of magnitude on using an intracavity diamond heat sink¹⁴.

However as power is pushed higher even the thin disk structure starts to lose beam quality. Some improved thermal management is possible by using diamond as a heat spreader on the reverse side of the gain disc, however one of the issues for these systems is that the heat spreaders are invariably applied to the back face of the disc laser, and there can be significant thermal resistance between where heat is being produced and this heat sink. For further power scaling a low absorption, low birefringence, higher area diamond product is required with extremely high thermal conductivity that can be placed on the thin disk, inside the cavity.

2. SYNTHESIS

Single-crystal diamond samples used in these experiment were synthesized with a microwave plasma-assisted chemical vapour deposition reactor. Sample were produced from homoepitaxial layer grown on a <100>-orientated diamond surface that had been prepared using high quality polishing techniques to minimise Ra (< 20 nm) and therefore reduce the nucleation of dislocations in the epitaxial layer.

For high purity products with low absorption, the key requirement is to minimise the impurities in the system. This is achieved by designing a synthesis system with minimal leakage of impurities into the chamber, as well as controlling the impurities in the synthesis gases through the sourcing of high purity feedstocks. Using these techniques the diamond utilised in this experiment has approximately 20 parts per billion (ppb) of nitrogen impurities in the solid, as measured by electron paramagnetic resonance spectroscopy⁹.

3. OPTICAL PROPERTIES

3.1 Absorption

The absorption spectrum of intrinsic diamond, from the UV to far IR, is illustrated in Fig 1. The absorption edge at 225 nm corresponds to the indirect band gap of diamond, and results from absorption as electrons are excited from the valance to the conduction band of the material. The complex set of IR absorptions between 2.5 and 6.5 μm are due to the multi-phonon absorption². Single phonon absorptions are not allowed in this symmetric material, which notably is a reason there is no IR cut-off for the material.

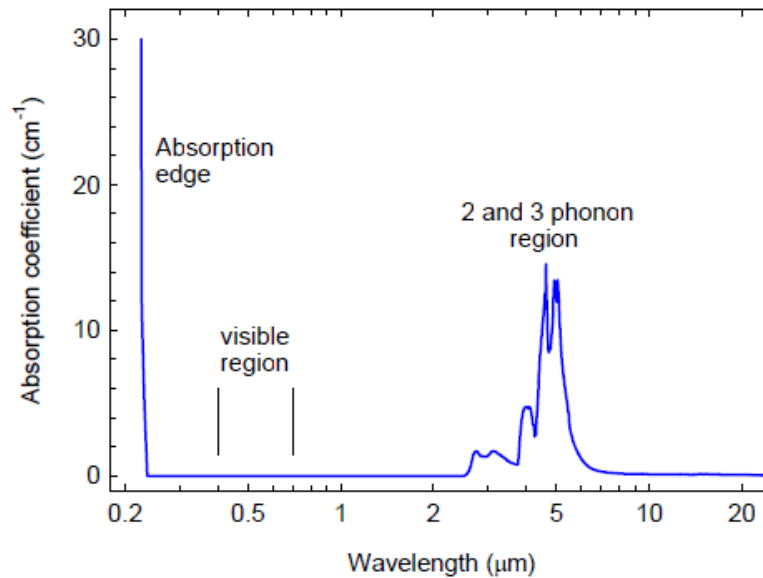


Figure 1: Absorption spectrum of intrinsic diamond.

In a perfect diamond crystal, these would be the only regions of absorption, however point and extended defects in the lattice result in electronic and vibrational transitions which cause deviation from this. Typically CVD grown single crystal diamond contains two major absorptions which encroach on the visible and UV regions of the spectrum; the single-substitutional nitrogen, N_s^0 (270 nm)¹⁵ and its associated tail in addition to broad absorption which are believed to be related to extended vacancy clusters in the bulk material which can induce a brown colouration in the material¹⁶. There is a very wide range of well characterized point and extended defects in diamond, each of which lends a particular character to the material. These can be taken advantage of, such as the paramagnetic nature of the NV (nitrogen-vacancy defect), with application in quantum information processing and sensing, however development of the low absorption grade single crystal has concerned itself with the removal of as many of these defects as possible, seeking to approach the ideal model of intrinsic diamond.

3.2 UV/Vis and Laser Calorimetry

CVD processes, including gas chemistries and growth temperatures can be modified with consideration of factors such as cost and performance to yield well-defined and controlled grades of material. The optical absorption coefficient of CVD low absorption grade single crystal diamond was measured with a Perkin Elmer Cary Model 500 Spectrophotometer to obtain room temperature absorption spectra from 3600 to 200 nm, and also by laser calorimetry. For comparison, UV/Vis spectra for standard grades of material are presented alongside, see figure 2. All samples were laser cut and mechanically processed to the same surface finishes using the same polishing techniques.

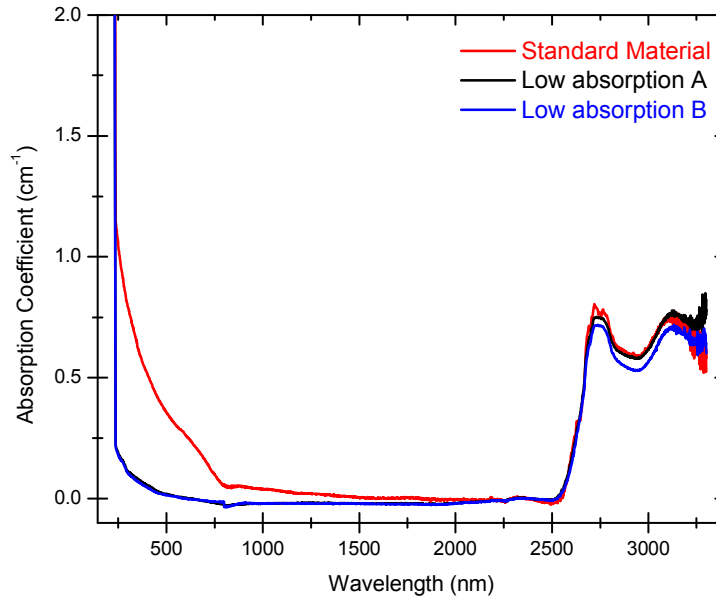


Figure 2: Room temperature UV/Vis spectra plotting absorption coefficient material against wavelength. Low absorption grade material (black and blue lines) compared directly with typical standard material (red line). A correction for reflectivity has been applied. Low absorption samples A and B refer to two plates synthesised and processed under equivalent conditions.

UV/Vis spectroscopy clearly demonstrates improved performance from low absorption grade material, compared to standard material, especially evident at wavelengths below 1500 nm. The extended brown defect (typically characterized as a ramped absorption across the visible region, increasing at lower wavelength, associated with N and extended vacancy-type defects) is evident in all spectra, but is significantly reduced in the low absorption grade material, compared to standard. The disadvantage of this analytical technique is that all losses to transmission are classed as contribution to absorption, not accounting for any reflection or scatter from the material, and while theoretical correction can be applied they are not ideal. Furthermore, the absorbances being measured are very low, approaching the limits of capability of the instrument and the final spectra can contain artifacts originating from the instrumentation rather than the material, (such as the Wood's anomaly) and errors relating to lamp and detector changes across a wide spectrum. From this analysis, classical UV/Vis spectroscopy was determined to be useful for comparison but not sufficiently sensitive to accurately calculate the absorption coefficients of single crystal diamond at any particular wavelength, such is the scale of the real values. However, despite this lack of accuracy, it is still clear that absorption coefficient around the key wavelength of 1064nm is very low indeed.

Low absorption grade material and standard material were measured using laser calorimetry at a series of wavelength throughout the visible, near-IR and near-UV regions. Laser calorimetry was carried out by researchers at CREOL using lasers operating at 1064, 640, 532, 445, 405 and 325 nm. The 1064 nm laser was a side pumped, diode pumped CW laser assembled at CREOL. The 532 nm laser was a frequency doubled, diode pumped, CW Nd:YAG made by Visible Diode Lasers LLC, the 445 and 405 nm diode lasers were also purchased from Visible Diode Lasers LLC, and the 325 nm laser was a HeCd gas laser. Two (three if the sample were large enough) thermocouples were attached to each sample, suspended by monofilament fishing line from a holder in an insulating chamber. The insulating chamber was necessary to minimize effects of air currents and room temperature drift. The holder was attached to a mount that allowed for fine positioning the sample in two axes and two angles to properly place the sample. To avoid striking the

thermocouples directly the laser beams were focused into the central region of the samples which were up to 2 mm thick and had other dimensions ranging from 4 x 6 to 7 x 7 mm. The absorption coefficient data is recorded in Figure 2.

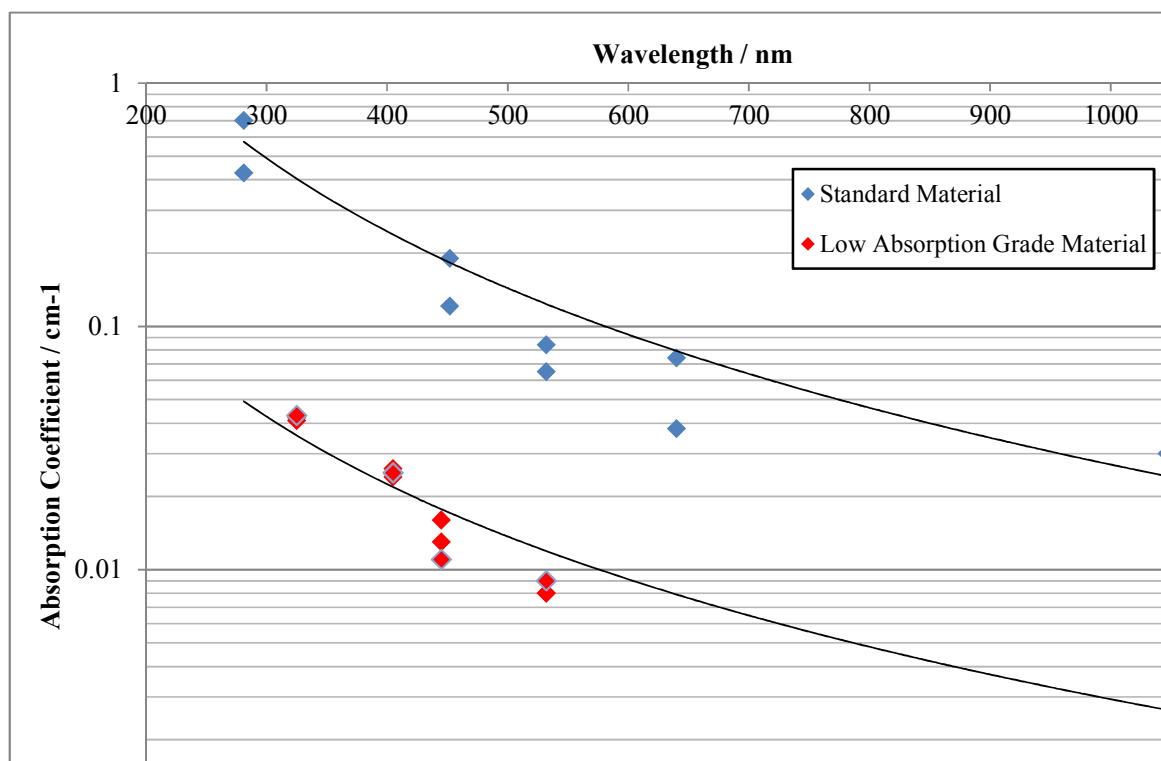


Figure 3 – Graph of absorption coefficient with wavelength (taken at room temperature) for low absorption grade single crystal at a variety of wavelengths from 1064 nm to 281 nm. Absorption coefficient is plotted on a logarithmic scale. Two samples of standard material and three of low absorption grade material were measured and all individual results are plotted. Curve fitted for guidance only.

Figure 3 shows the measured absorption coefficients of a series of standard material and low absorption grade material, at a range of wavelengths from IR to UV. All stones were measured at room temperature and repeated measurements of samples grown under the same conditions confirmed that the low absorption grade material routinely achieved the target absorption coefficient $<0.005 \text{ cm}^{-1}$ for 1064nm radiation, an order of magnitude lower than standard material. Moreover, the prominent increase in absorption coefficient with decreasing wavelength, consistent with observations from the UV/Vis spectra in Figure 2, commonly seen in CVD single crystal diamond and dependent on the brown defect, is significantly reduced. This data confirms the suitability of low absorption grade single crystal for use in high power laser applications such as intra-cavity coolers and for use in the wider optical market.

3.3 Birefringence

Optical grades of polycrystalline diamond have always suffered from one major flaw, prohibiting its use in some highly specialized optical applications; the lack of birefringence control. The random nature of grain orientations and low control over inter- and intra-granular stress build-up during both production and use, give a distribution of refractive indices in the direction of use and no real control over polarisation of extant light from the part. The development of CVD grown single crystal diamond has eliminated only part of the problem contributing to birefringence; the presence of multiple grain orientations and the inter-granular stresses associated with that, despite the optical isotropy of the perfect crystal structure. The remaining birefringence is typically due to dislocations that propagate from the seed crystal into

the bulk of the diamond during synthesis. These dislocations cause a strain in surrounding diamond that can lead to birefringence, however light only experiences any significant birefringence if the path length is substantially parallel to the dislocation direction, therefore parts can be produced using careful processing which minimize birefringence.

CVD single crystal diamond is now routinely used for in-beam applications where polarisation of the extant beam is crucial to the performance of the entire system, such as Raman frequency shifting, by carefully aligning the beam path perpendicular to the growth direction.

A qualitative measure of birefringence is available using cross-polarised microscopy; under transmitted light conditions, with crossed polarizing filters installed behind and in front of the sample. This technique is excellent for detecting contrasting regions of high and low birefringence in single crystal diamond however it is not powerful enough to apply numerical values to such. The Metripol system is routinely used to give quantitative measures of $\sin(\delta)$ the absolute measure of rotation of transmitted light, from which can be calculated birefringence in single crystal diamond parts and has been instrumental in the development of low strain, ultra-low birefringence single crystal material. Comprising a microscope, monochromatic light source, rotating polariser and circular analyser, Metripol is sufficiently powerful to measure values of birefringence as low as $\Delta n = 10^{-8}$.

The highly anisotropic nature of strain and therefore birefringence in CVD-grown single crystal diamond is such that careful design and processing of parts with respect to not only a particular crystal plane but also the direction of growth can give extremely low levels of birefringence in the direction of use, enabling low absorption grade single crystal diamond to compete with values observed for some optical glasses, see Figure 3.

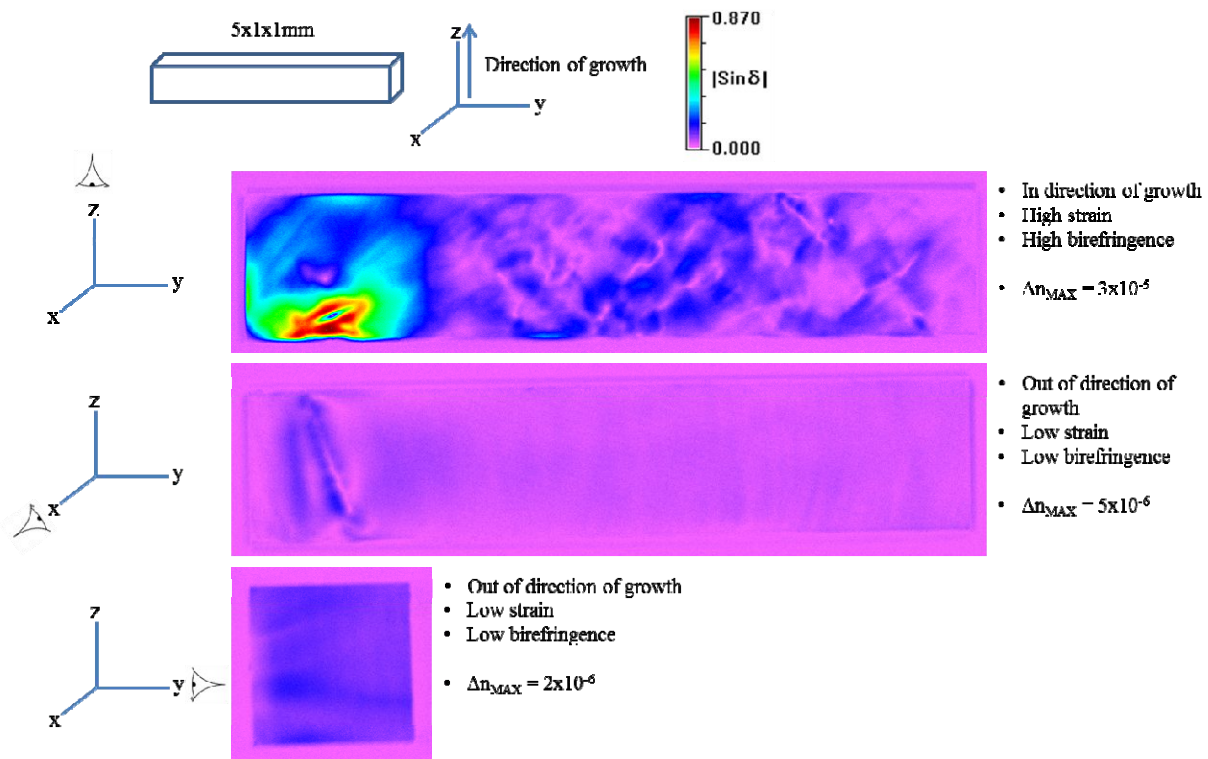


Figure 3 – The birefringence control in the cutting and processing of a 5x1x1 mm, CVD-grown single crystal diamond part for low birefringence applications. Samples were mounted for analysis on a microscope slide and background birefringence level has been subtracted. Images were captured using a 10 step polarizer rotation and regions of high colour indicate high $\sin(\delta)$, the absolute measure of rotation of transmitted light through length of the part.

4. CONCLUSIONS

Polycrystalline diamond has been a key technology in higher wavelength optical applications and while CVD single crystal diamond has found wide ranging mechanical applications, the development of low absorption grade single crystal diamond will be an enabling force in the future of laser technology and high power optics. By careful understanding and control of the CVD growth process, a range of diamond grades are possible with properties optimised for mechanical, thermal and now optical applications. Low absorption grade material performs around 10x better than standard material in terms of optical absorption and similarly better in terms of reducing scatter, with no forfeiture in potential sizes or obstacles to processing even the most challenging geometries and surface finishes. This performance is indicative of the control that can be wielded over defect uptake and uniformity during growth, through strict regulation of conditions and gas purities.

Diamond parts for advanced applications that include magnetic sensing and quantum information processing applications have been produced even with isotopic enrichment in thin layers with nitrogen impurities below 1 ppb¹⁷, and it can be foreseen that using the techniques exploited in the synthesis of these layers that in the future lower absorption bulk diamond products can be produced. Other future opportunities in single crystal development include growing thicker material with uniform strain and defect uptake, enabling the production of low absorption grade, low birefringence plates, and towards larger parts that can be utilized in full sized solid state disc laser systems.

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