Diamonds for 3rd and 4th Generation X-ray Sources

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Abstract

The 3rd and 4th generation X-ray sources are characterised by their high brilliance. This may induce high heat loads and high local power densities on the beamline optical elements such as monochromators, filters, phase plates, beam splitters, lenses, vacuum windows and on beam position monitors. Optical components are often made of silicon (available in large dimensions, grown with high crystal perfection and with very good surface quality). Instead of silicon we can use diamond, a material that has excellent thermal characteristics and thus considerable advantages compared to silicon. Nevertheless, up to now, the diamond material available had small dimensions and many defects in the bulk and often an insufficient surface quality. Nowadays, the diamond industry is developing an improved High Pressure High Temperature growth process for highly pure type IIa single crystal diamond. This results in a considerable reduction of the number of crystallographic defects within the material. The key parameters of a diamond crystal for the majority of X-ray applications are crystalline perfection of its bulk and also of its surface. In the most advanced applications it should conserve the coherence of the X-ray beam. Industry efforts must be focused on these directions as well as on increasing the crystal dimensions. In a successful collaboration project between the authors, many diamond samples have been studied over the past few years. At the ESRF, X-ray topography is the most important and effective experimental method used to characterise the defects structure in diamond crystals. Some of the topographs are presented below. It appears that for most of the future practical diamond applications the efficiency of crystal cooling methods has to be improved; this will reduce the thermo-mechanical deformation of the crystal. We are working at the ESRF on two complementary approaches. The first is to increase the surface of thermal exchange with the cooled support. The size of available single crystal diamond plates is about 7x7 mm^2 (with a perfect central region of about 4x4 mm^2, (100)-orientation). Such single crystal diamonds can be brazed on larger CVD diamond plates. Brazing tests have been initiated in order to qualify the different brazing techniques and to measure the stress induced within the single crystal material by this process. The second approach is to increase the efficiency of the cooling support structure. The design and manufacture of dedicated supports are in progress.

1. Introduction

The ESRF is a third generation high energy light source that has been in operation since 1994. Component upgrade and optimisation are key issues for the future of this source. Among the present R&D programmes, the characterisation of diamonds and their development are of prime importance at ESRF.

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At present, many of the optical elements (in particular the monochromators), located on the synchrotron beam path, are made of silicon. This material was selected due to the high crystalline perfection and the ease of its processing to obtain large optical surfaces of good quality. The third, and furthermore the fourth, generation light sources are optimised for high brilliance. Thanks to technological advances of insertion devices (e.g. in-vacuum undulators), optimisation of the vacuum vessels, and machine parameters (e.g. increase of the machine current intensity, emittance reduction), the brilliance of the beam delivered to the samples on the beamlines is still increasing. This may induce higher heat loads and high local power densities on the beam optical elements, often beyond that for which they were initially designed. The present power density is already in the order of hundreds of watts per square millimetre. Components which are exposed to the highest thermal loads are those located upstream of the beamline sample station where a considerable amount of the beam thermal load is absorbed.

Due to the thermal constraints listed above, silicon based devices might need to be replaced by another material in the future. Diamond appears to be a serious candidate for this. Components which might benefit from the outstanding characteristics of diamond are: monochromators, filters, phase plates, beam splitters, lenses, and other 'optical' elements such as in-line beam position monitors. At the ESRF, the original beryllium 'front end' vacuum windows of undulator beamlines were replaced by diamond over six years ago: diamond is the only material capable of withstanding the heat load generated by the beam absorption.

2. Types of Diamonds

Diamonds are classified according to their optical properties which are related to the impurity content, mainly that of nitrogen, a common impurity found in both natural and synthetic diamond crystals, as being of type I (high nitrogen concentration) or II (very low nitrogen concentration). This classification is then subdivided into a or b, according to the specific forms in which impurities are arranged [1].

The majority of natural diamond single crystals are of type Ia, with a concentration of nitrogen of a few tens to a few hundreds of part per million (ppm), while type IIa single crystal diamond has little nitrogen (less than ten ppm). Type IIa diamond single crystal is extremely rare in the nature; it represents probably less than 2 % of the existing natural diamond [1]. It appears nowadays that in quality the synthetic materials exceed the best natural material by several orders of magnitude [3]. Recently, a new category type IIIa has been introduced for an ultra pure grade of single crystal diamond that is grown homoepitaxially by Chemical Vapour Deposition (CVD) and produced with chemical impurity levels $<10^{15}$atom.cm^{-3}. Although it is at present of relatively poor crystallographic quality, the absorption of the X-ray beam in this ultra pure diamond creates photocurrents that can be accurately measured, making it of interest for the fabrication of near-transparent X-ray beam monitoring devices [12].

Nitrogen is a substitutional impurity atom which takes the place of a carbon atom in the lattice. There is a correlation between nitrogen concentration and the mesoscopic defect structure of diamond. Those defects that should be avoided in diamond plates for X-ray optical applications are inclusions, precipitates, stacking faults and dislocations [2]. The impurities are harmful when they develop considerable macroscopic strain fields. This may be the case e.g. for inhomogeneities of highly concentrated nitrogen. They appear as strain fields created by growth sector boundaries due to concentration differences between growth sectors, and as growth striations due to concentration changes within a growth sector.

3. Diamond Properties

Diamond based optical elements are attractive in many respects. Diamond has very low absorption at X-ray energies and it has a small thermal expansion coefficient, α, and a high heat conductivity, κ. These particular thermal properties are the key parameters for any optical device which will be placed into the intense beam path of a third, and furthermore of a fourth, generation X-ray source.

The thermal conductivity coefficient, κ, of type Ib single crystal diamond is smaller than for type IIa. For single crystal diamond, the linear coefficient of thermal expansion, α, is less than 10^{-6} K^{-1} at room temperature. If we compare these values of κ and α with silicon, currently the favourite material for Bragg diffracting elements, we clearly notice the superiority of single crystal diamond (see Table 1).

By comparing the absorption coefficient, μ, of both diamond and silicon, it is obvious that with an order of magnitude of difference, diamond will absorb much less radiation. The low absorption might still be better with beryllium, but this material can not be grown with high monocrystalline quality.

The amount of thermal deformation of a crystal is proportional to the quantity: $P_a.(\alpha / \kappa)$. For the symmetrical Bragg case, the absorbed X-ray power (P_a) is given by: $P_a = P_o.\exp(-\mu.t/\sin\theta_B)$ where P_o is the incident power and t is the crystal thickness. A figure of merit can therefore be deduced as being $\kappa /(\alpha.\mu)$, which is listed in Table 1 for different materials. At room temperature, this figure of merit for diamond is two orders of magnitude higher than for silicon.

Additional favourable properties of diamond are both its high elastic modulus and fracture strength. The average value of the diamond elastic modulus is 1035 GPa, to be compared with the silicon value of 191 GPa. With an anisotropy coefficient of 1.21, the Young's modulus of diamond is fairly constant in all directions (for silicon the anisotropy coefficient is 1.44).

For the purpose of producing optical elements, such as monochromators, a relevant parameter in comparing the thermal resistance of a material is the ratio of its compressive strength (8.6 GPa for diamond) to the product of its Young's modulus and thermal expansion. At room temperature this ratio is two orders of magnitude higher for diamond than for silicon [1].

Even with such attractive properties, most of the X-ray optical elements built up to now have mainly used silicon instead of diamond. In the past years, single crystal diamond was not the preferred material for this type of elements due to its low quality and small dimensions.

Table 1: Properties of materials used in X-ray applications (values given at 297 K) [2]

	Beryllium	***Diamond***	***Silicon***	***Germanium***
Z *Atomic Number*	*4*	*6*	*14*	*32*
κ *Thermal Conductivity* *[$W.cm^{-1}.K^{-1}$]*	*2*	*Type Ib: 5-18* *Type IIa: 20-25* *Isotopically pure: 35* *Polycrystalline CVD: 4-18*	*1.5*	*0.64*
α *Thermal Expansion Coefficient* *[10^{-6} K^{-1}]*	*11*	*1*	*2.4*	*5.6*
μ *Absorption Coefficient at 8 keV* *[cm^{-1}]*	*1.7*	*14*	*143*	*350*
100. κ /(α.μ) *Figure of Merit* *[10^6 W]*	*11*	*36-178* *(for Type Ib – IIa)*	*0.44*	*0.03*

4. Collaborative Work

For many years, the ESRF, the University of Witwatersrand Physics Department and Element Six (formerly De Beers Industrial Division Ltd) have worked together on an R&D collaborative programme to improve the quality and size of diamond crystals for synchrotron applications. The first tests of diamonds took place at the ESRF in 1992, which was the starting point of this collaboration [4] [5].

The work covers three areas; synthesis, processing and X-ray characterisation of the resulting single crystal diamonds. The ultimate goal of this program is to make highly pure IIa single crystal diamond, suitable for the most demanding optical elements, available for all of the synchrotron community.

Over the past years, growth and surface preparation parameters have been adjusted in response to feedback provided by the ESRF to Elements Six and University of Witwatersrand on the basis of the X-ray characterisation at the ESRF.

5. Current Status

The High Pressure High Temperature (HPHT) growth technique is complicated and time consuming: to obtain useful crystal sizes, growth runs may take several hundreds of hours. The allowable temperature range in which high-quality crystal grow is very narrow (30° C tolerance at 1350° C), and the pressure must be kept stable in the 5 to 6 GPa range (i.e. in the region of diamond stability) during the whole growth cycle. The crystal growth mechanism is based on re-crystallisation under a temperature gradient [6].

Until two years ago, HPHT grown diamond was mainly of type Ib. The Ib diamond plates produced at Element Six had nitrogen contents of a few hundred ppm, and were available in sizes of typically 4 to in exceptional cases 8 mm. Many experiments took place at the ESRF to characterize these. It was definitely concluded in 2004 [2] [7] that this material was suitable only for applications which do not make great demands on the crystallographic quality (e.g. phase plate). Type Ib crystals had too many defects and only IIa diamond would satisfy the stringent requirements of monochromators and other beamline optical elements for applications involving imaging and phase contrast. Recently, Element Six has started an R&D programme to improve the HPHT synthesis process and to produce IIa single crystals diamonds of size comparable to the earlier Ib type.

The crystalline quality obtained, assessed by the topographic methods used on the ESRF ID19 beamline, has shown a great improvement since the beginning of the collaborative program. X-ray diffraction topography, an X-ray diffraction imaging technique, was systematically used to investigate the quality of all the samples. The technique is very strain sensitive and has a rather high spatial resolution in the order of micrometers, well adapted to the characterisation of the crucial defects [2]. The white beam and monochromatic beam topography techniques are well suited to detect strains and defects in the crystal bulk as well as in regions close to its surfaces [3].

In addition to X-ray topography, other techniques were also used to characterise the quality of the single crystal diamond, such as measurement of the rocking curve broadening. This technique gives an integral measurement, but with lower spatial resolution, and is generally less sensitive to strain. As an example, a broadening of the rocking curve due to the presence of dislocations may be only detected if their density starts to be superior to about 10^3 cm^{-2} [2]; whereas X-ray topography allows us to detect a single lattice dislocation. For the best samples produced by Element Six, no broadening of the rocking curves was observed, implying that the crystal reflectivity was determined by the intrinsic response of a perfect crystal. Figure 1 shows the progressive improvement over the years in the measured rocking curve broadening of diamond single crystals at the ESRF.

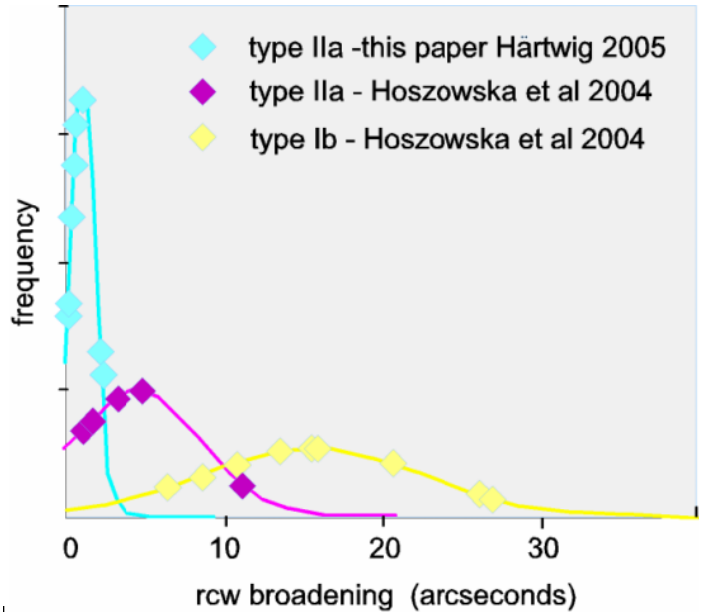

Figure 1. Improvement of typical rocking curve broadening [2]

The IIa single crystal diamonds studied over the last years at the ESRF were plates of dimension up to 7x7 mm^2 with thickness ranging from 0.5 to 1 mm. They were obtained by sawing the crystal into parallel plates, as shown in Figure 2.A, followed by careful polishing. It was noticed that on many occasions the plates having the lowest defect concentrations were those located farthest away from the original growth seed. Figure 2. C shows a white beam topograph, in transmission geometry, of a 7x7 mm^2 plate cut from the upper part of the diamond. On this topograph a central region of 4x4 mm^2 is seen, which is free of crystallographic defects such as dislocations or stacking faults. Only some surface scratches could be observed in this area. This highly pure IIa single crystal, (100)-oriented, was the best sample ever measured at the ESRF in terms of absence of defects in its central zone. The goal for industry is to develop a process to reproduce this crystalline quality on a routine basis.

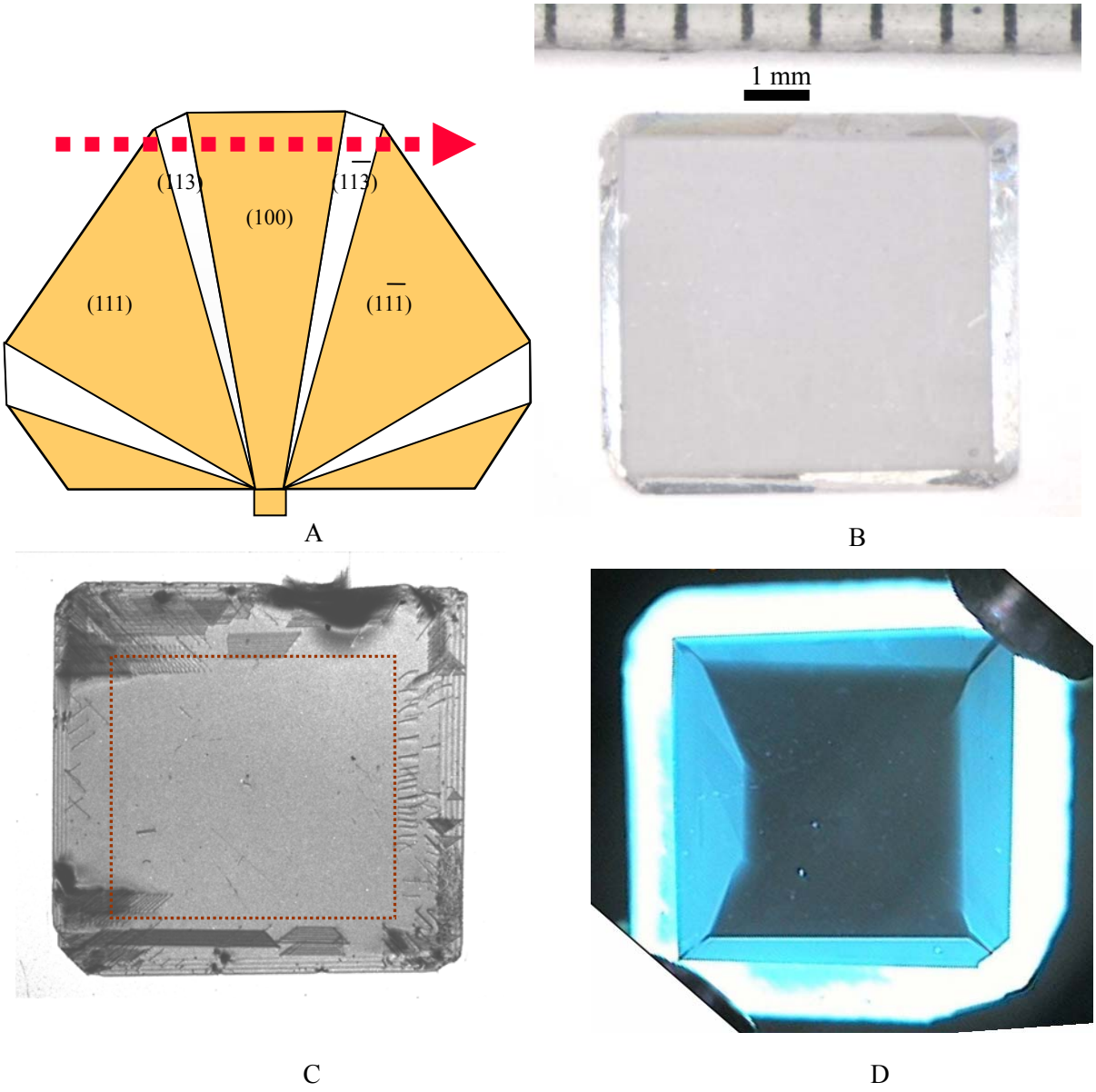

Figure 2. A. Growth sectors in type IIa diamond single crystals; the dotted arrow indicates where sawing took place. B. Optical microscope view of a 7x7 mm^2 plate. C. White beam topograph of the plate in transmission geometry (the dotted square indicates the 4x4 mm^2 central region which is free of defects). D. Ultraviolet luminescence image of the growth sectors [2].

6. Future Needs

At present, from the many single crystal HPHT diamonds plates that we have measured, we have identified samples which could be used in 'counting' applications or for phase plates. For imaging applications, we have found small regions, in several crystals, with sufficient perfection. For the future, we need larger crystals. The currently available size limitation of 7x7 mm^2 (with a perfect central region of about 4x4 mm^2, in (100)-orientation) is not yet sufficient for most applications. Also the surface quality has to be improved, as this strongly influences the X-ray beam coherence preservation.

For many applications, a (111) or (110)-orientation is desirable, instead of the more usual (100)-orientation. The development of high quality (111) and (110) plates will require further R&D work.

7. Increase of the Crystal Cooling Efficiency

As stated in the previous paragraph, the available diamond sizes are a bottleneck for diamond-based applications, for several reasons:

1. Once the diamond plate is inclined at the Bragg angle, the beam footprint might be larger than the diamond dimension.
2. On some beamlines, the useful beam dimension might be larger than the actual size of available diamond single crystal plates, even in conditions of normal beam incidence.
3. To accommodate a cooling device and efficiently cool the diamond plate, the fraction of the diamond 'lost' to contact surfaces must be as large as possible.

To address the first two problems Element Six is working on an R&D program to increase the central region of type IIa single crystals [8]. For the third issue – efficient cooling of the optical element – we have considered a few options: as an alternative to increasing the size of the single crystal plate, the single crystal diamond could be brazed onto another large area diamond which itself is cooled. A second approach would be to increase the efficiency of the diamond cooling support; or thirdly combining these two techniques which are complementary towards an efficient cooling.

7.1. Increase Thermal Contact Area

A test program was recently initiated to braze a single crystal diamond to a polycrystalline diamond heat-sink [9]. Our initial concern was to observe the creation of defects in the single crystal as a result of the brazing process which, for an ultimate application like for an optical element, might cancel all the improvement in crystal growth technology. White beam topographs were taken before and after brazing. For this first trial, single crystal CVD diamond was used rather than HPHT IIa diamond. Diamond preparation and brazing were carried out by M. Rebak of Witwatersrand University. A circular single crystal of 4.98 mm diameter, 225 μm thick, was brazed onto a polycrystalline base plate 12x20 mm^2 and 230 μm thick. A hole 5.06 mm diameter was cut out to accommodate the single crystal diamond and a fine fillet of brazing material. The brazing material used was *Lucanex® 716* (alloy composition: Ag 71.5%, Cu 28%, Sn 0.5%) which had micron sized spheres of material. Brazing took place with flux at 750 °C and under vacuum.

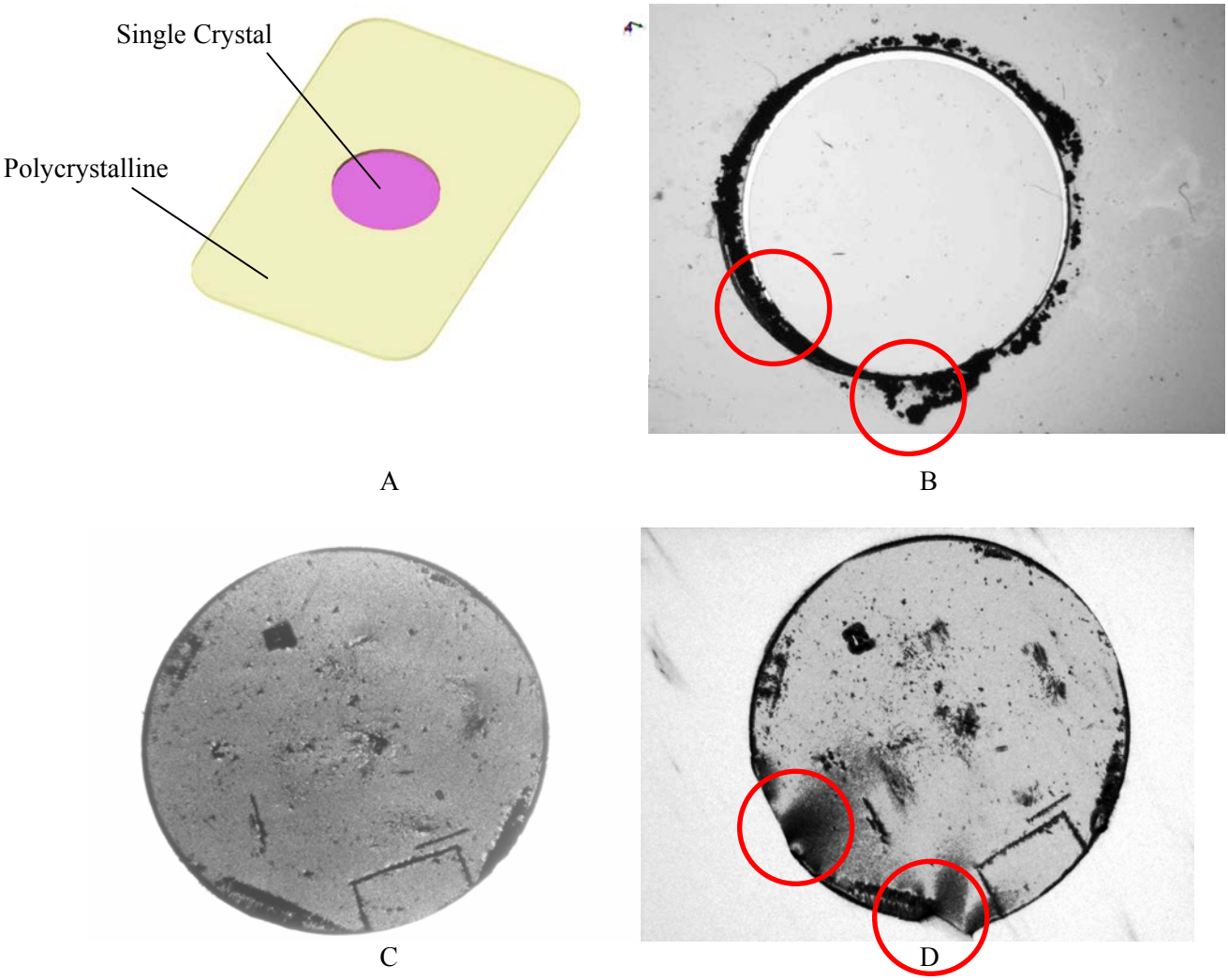

Figure 3. A. Drawing of the two CVD diamond plates. B. Close-up photograph of the brazed diamond. C. White beam topograph of the single crystal CVD before brazing (in transmission). D. White beam topograph after brazing

Comparing the pictures before and after brazing, we notice that no existing major crystallographic defects have been enhanced, nor have new defects appeared. On the other hand, we observe two areas of strain (marked with circles on pictures 3.B and 3.D) where the crystal was strongly distorted during brazing. This might be explained by a non-uniform brazing seam (lower circle) and/or an excess of brazing material (upper circle).

The thermal properties of this brazed assembly remain to be measured, in order to see the effect of the non-homogeneity of the brazing. In the future, other diamonds will be brazed to test different brazing techniques which might produce a more homogenous brazing seam and which will not distort the single crystal diamond.

7.2. High Efficiency Diamond Cooling Support

Different cooling schemes were modelled by finite-element-analysis (FEA) to improve the design and thus the efficiency of the water cooling support for diamond crystals used as X-ray monochromators. The immediate goal is to optimize the cooling support of the existing ESRF semi-transparent diamond monochromator design [10].

The parameters used in the thermal model were the following: the crystal size is 6 x 6 mm^2 with a thickness of 150 µm. The crystal is cooled on two lateral sides over a width of 1mm, i.e. the total cooling area is 12 mm^2. An In-Ga eutectic layer interfaces the diamond to the support without inducing stress. The total absorbed power from the X-ray beam is 20 W. The supports are made out of copper, coated with nickel. The reference temperature of the cooling water is T_{ref}= 295K. The heat transfer coefficient between water and copper is taken to be 10 000 $W/m^2.K$, but for the micro-channels cooling design below the value is estimated to rise to 30 000 $W/m^2.K$ [11]. The prototype support is designed to work in Bragg or Laue geometry. It might accept larger crystals (see Figure 4).

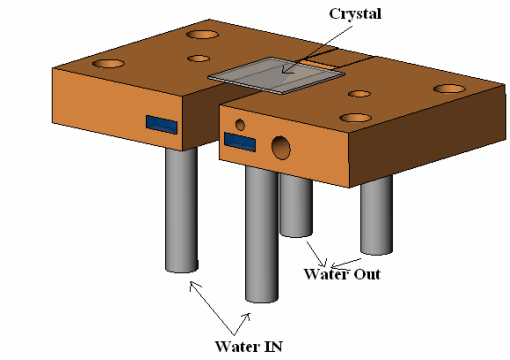

Figure 4. Prototype support

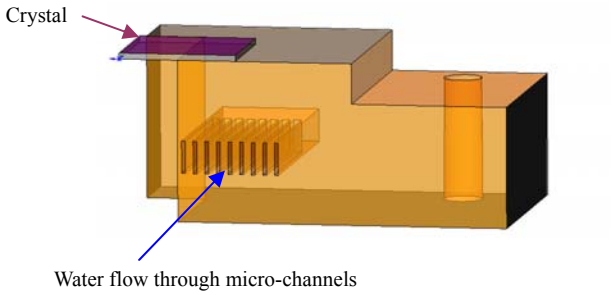

Figure 5. A quarter of a micro-channels support.

Five different schemes were considered: bottom cooling, pipe cooling, channel cooling with different geometries and micro-channels cooling (see Figure 5). For each design we report below the minimum and maximum temperatures in the support, the temperature gradient across the support itself and the difference between T_{min} and the water temperature. Table 2 compares the different cooling schemes.

Table 2: Results of the cooling scheme models

Type of cooling scheme	T_{max} ***[K]***	T_{min} ***[K]***	T_{max}-T_{min} ***[K]***	T_{min}-T_{ref} ***[K]***
1. Bottom cooling	*322*	*311*	*11*	*16*
2. Pipes Ø 2 mm cooling	*320*	*310*	*10*	*15*
3. Channel 0.4 x 0.8mm cooling	*315*	*306*	*9*	*11*
4. Micro-channels 0.1 x 0.8 mm cooling	*307*	*298*	*9*	*3*
5. Micro-channels 2x (0.1 x 0.8 mm) cooling	*304*	*296*	*8*	*1*

The temperature difference, $T_{max} - T_{min}$, over the support determines the extent of the internal deformation and bending of the support itself. T_{min}-T_{ref} expresses the temperature difference between the support and the environment. This temperature difference is important because it may introduce stresses and a parasitic deformation such as twist of the support.

The fifth scheme is clearly the best as regards the results from the model; however it would require advanced manufacturing techniques. Therefore, as a first step, we have ordered a cooling support of the

third type, with the wider cooling channels of 0.4 x 0.8 mm^2. After manufacturing, the following tests will be conducted at the ESRF with this prototype: topography of the diamond crystal fixed on its cooled support (at ESRF beamline ID19), and measurement of the Darwin width of the diamond crystal (at beamline ID10).

8. Conclusions

Over the last few years, spectacular improvement in diamond quality was obtained, as evidenced by low strain crystals, which are nearly defect-free. Nevertheless to meet our application requirements, diamonds must be produced with near-theoretical performance, corresponding to values calculated for a perfect diamond lattice.

Type IIa single crystal diamond, made by the HPHT method, is superior to type Ib crystals with respect to strain and defect structure. Therefore, type IIa is the best candidate to build optical elements for the third and fourth generation X-ray sources. At present, type IIa diamond plates of size 7 x 7 mm^2 in the (100)-orientation can be produced on an R&D basis where nearly no defects are present within a 4x4mm^2 region. Efforts must be focused to reproduce this sample quality on a production scale, and to increase the size of the defect free central region. Even larger sizes and higher quality crystals may still be needed for specific applications. Post growth processing must also be improved to obtain damage free surfaces. Once all this is achieved, type IIa single crystal diamond will be well adapted for the most demanding applications where beam coherence preservation is a key issue.

To increase the single crystal diamond's surface for cooling purposes, attachment to a larger polycrystalline diamond support by the brazing technique looks attractive. More tests are needed before the final choice of brazing method. According to the first topographs obtained, we may expect that if the brazing process is well mastered, no additional defects will be introduced in the central region of the brazed single crystal diamond. However, as this method is not yet proven, improvement in the efficiency of the diamond cooling support remains a priority.

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