

The Quest for Diamond Crystal Perfection to Meet the Needs of Physics: Unrealistic Dream or Attainable Target?

J. P. F. SELLSCHOP¹) (a), A. FREUND (b), J. HOSZOWSKA (b), S. H. CONNELL²) (a),
M. REBAK (a, c), and R. C. BURNS (c)

(a) *Schonland Research Institute for Nuclear Sciences, University of the Witwatersrand,
P.O. WITS, 2050 Johannesburg, South Africa*

(b) *European Synchrotron Radiation Facility, Grenoble, France*

(c) *De Beers Industrial Diamonds (Pty) Ltd., PO Box 12093, Selcourt, 1567 South Africa*

(Received March 13, 2002; accepted June 3, 2002)

PACS: 61.10.Eq; 61.66.Bi

The ongoing need for single crystal diamond of high quality in physics research and application, has been amply demonstrated. This need cannot be satisfied by access to natural diamonds. In recent years much progress has been made in the synthesis of diamond at high temperature and high pressure. Several interrogation methods were deployed to ascertain the crystal quality attainable for HPHT diamond. It is shown that the best of such materials can approximate in quantitative terms closely to the theoretical predictions for perfect diamond.

1. Introduction The unique physical properties of diamond are well known and remain impressive. By way of example, a subset of these reflecting relevance to electrical properties is presented in Table 1. Other subsets can be presented bearing on different properties. It is not surprising therefore that many ideas for exploiting these properties have been current for some time.

One important application, which serves also as a stringent testbed for diamond crystal quality, is as monochromators for X-rays. Diamond excels in terms of the widely accepted figure of merit, based on the very weak absorption of X-rays, the very high heat conductivity, and the small thermal expansion:

$$\text{FOM} = 100\kappa/\mu\alpha,$$

where κ is the heat conductivity in W/cm/K; μ is the linear absorption coefficient at 8 keV, in cm⁻¹, and α is the expansion coefficient, in units of 10⁻⁶ K⁻¹. The simple ratio α/κ should be as small as possible, so as to minimize thermal strain and thermal deformation. Values of α/κ are 0.04 for diamond, 1.4 for silicon and 8.0 for germanium.

Some further comparative figures reflecting on the attractiveness of diamond in this application, are

at 300 K: FOM (diamond) = 333; FOM (silicon) = 0.47; FOM (germanium) = 0.028;

at 77 K: FOM (diamond) = 1200; FOM (silicon) = 20; FOM (germanium) = 0.66.

¹) Deceased.

²) Corresponding author; e-mail: connell@inkosi.src.wits.ac.za

Table 1

band gap	5.45 eV
thermal coefficient of expansion (linear)	$(0.8 \pm 0.1) \times 10^{-6} \text{ K}^{-1}$ at 293 K
thermal conductivity	
– at 293 K	type Ia: 600–1000 $\text{W m}^{-1} \text{K}^{-1}$ type II: 2000–2100 $\text{W m}^{-1} \text{K}^{-1}$
– max at $\sim 80 \text{ K}$	type Ia: 2000–4000 $\text{W m}^{-1} \text{K}^{-1}$ type IIa: up to $1.5 \times 10^4 \text{ W m}^{-1} \text{K}^{-1}$
hole mobility	1200–2010 cm^2/Vs (natural type IIb)
breakdown field	$\sim 10^7 \text{ V cm}^{-1}$
resistivity	$\sim 10^{18} \Omega\text{m}$ (natural types Ia and IIa) $10^3\text{--}10^5 \Omega\text{m}$ (natural type IIb)
doping can change	
resistivity to	$10^2\text{--}10^8 \Omega\text{m}$
saturated carrier velocity	electrons $\sim 1.6 \times 10^7 \text{ cm/s}$ holes $\sim 1.1 \times 10^7 \text{ cm/s}$
hole effective mass	$m^* = \sim 0.5m_0$ m_0 is the free electron mass
Hall mobility and coefficient	0.16 m^2/Vs (typical value at 293 K) 2200 cm^2/Vs (n-type RT) 1600 cm^2/Vs (p-type RT)
dielectric constant	5.5 at 300 K
low or negative electron affinity,	
very resistive to chemical corrosion,	
biological compatible/equivalent	

In the case of diamond, all interaction processes other than Bragg scattering are very weak, hence the monochromatized beams are “clean”. That is, the background intensity due to Compton and thermal diffuse scattering is small.

It might appear as evident that the best crystal quality for X-ray optics applications would be diamonds of type II, being low in nitrogen. However, from a crystallographic standpoint the single diamond crystals of type I may be more perfect in the sense that even though they contain higher amounts of impurities, they generally have a smaller number of extended defects such as dislocations or stacking faults. These extended defects give rise to a broadening of the diffraction profile and thus affect the energy resolution when used as monochromators, whereas impurities that are isolated point defects or arranged in small clusters would tend to decrease rather than increase the reflection profiles (static Debye–Waller effect).

The question is whether actual diamond samples, both of natural and of synthetic origin, measure up sufficiently closely to theoretical values. The major technique deployed in this quest is the measurement of rocking curves using the optics beamline BM-5 of the ESRF.

2. Natural Diamonds Since diamonds of high quality are recovered in mining operations, the question arises as to whether such sources cannot provide for the needs of science and technology. In principle, no doubt many of the needs could be satisfied from such natural sources. However, it would be impossible to achieve any regularisation of the characteristics of the material: it has been truly averred that no two natural diamonds are the same. An additional aspect is that of size: dimensions of $10 \times 10 \text{ mm}^2$ are justified in many cases and this takes one into competition with the gem market.

The solution to this problem is to turn to the provision of raw materials as produced synthetically at high pressures and high temperatures (HPHT). There has been considerable progress in the HPHT field [1] and we will concentrate on the examination and evaluation of this source of diamond.

3. HPHT Synthetic Diamonds – Simpler Measurements Generally type Ib diamonds are grown under synthesis conditions. This category is distinguished by the feature that it has a reasonable amount of nitrogen present as an impurity, located in single substitutional sites. Special efforts can be made to exclude nitrogen from the growth capsule, producing type IIa diamond.

For some years now an active collaboration between the European Synchrotron Radiation Facility at Grenoble and the Schonland Research Institute for Nuclear Sciences at the University of Witwatersrand in Johannesburg has examined both type Ib and IIa material as produced by Messrs. De Beers Industrial Diamonds (Pty) Ltd. Using X-ray rocking curve measurements and topography [2] a consistent picture has emerged – the best quality HPHT diamond crystals, for the (111) orientation, can be near-perfect as implied by the measured mosaic spread of 1 arcsec or less. For 12.4 keV X-rays the measured (111) reflectivity, when convoluted with Si (220) reflection and with another diamond in (111) reflection, was 60% and 50%, respectively. The theoretical perfect-crystal value was 82% for both cases. Another example, again for a type Ib HPHT specimen, at an X-ray energy of 10 keV, for the (111) orientation, gave a rocking curve width of 6.8 arcsec for measurements with the X-ray beam collimated so as to illuminate only selected areas of the diamond. Since the value for a theoretically perfect diamond is 5.5 arcsec, this indicates that the extent of the mosaic spread is limited to 1.3 arcsec. In this case the peak reflectivity was measured to be $(84 \pm 3)\%$, the highest value yet in our experience, which should be compared with the theoretical value for the full crystal face of 82%. (For the full crystal face exposure to the interrogating X-ray beam, the measured rocking curve width increased to 8.6 arcsec.) Other workers have obtained similar results with similar material [3].

That measured values so close to those of the theoretically perfect crystal, should be found, is at first glance surprising. One might have expected substantially greater mosaic spreads judging from the evidence from, for example, X-ray white beam topographs. Typically such topographs show a variation in defect density throughout the diamond, often from very low to quite high. Observed are growth bands, dislocations, stacking faults, cleavage traces, inclusions and surface scratches. Nevertheless, this apparently far-from-perfect diamond shows only a very small increase in the rocking curve width. However, the beam intensity distribution is nonuniform and the local reflectivity is weak, due to these defects.

Still considering the (111) reflection, we have also investigated type IIa HPHT synthetic diamonds. Again the results for the rocking curve widths are very close to the theoretical values, particularly if the X-ray beam is collimated so that measurements are confined to restricted areas of the diamond surface.

In contrast, for (100) oriented diamonds, there is an apparent consistent difference between the types Ib and IIa, with the latter close to theoretical values but the type Ib's show much greater mosaic spread. However, this difference is starkly reduced if the X-ray beam is collimated so as to interrogate confined areas of the diamond surface and not the whole surface. In other words, the bulk rocking curve widths indicate that

the type IIa stones as a whole are of better crystal quality than the type Ib's. In local regions, however, both types Ib and IIa are near theoretical values.

The questions or issues that logically follow are the obvious need to analyse the whole interrogated surface of the diamond specimen, and to establish what the small measured mosaic spreads are due to. For small regions of interrogation where for all specimens we find close to theoretical values, the small values of the mosaic spread are due to defects and on the larger (whole crystal) scale crystal curvature can be an additional candidate. The defects could be lattice tilts, lattice strains, or d -spacing variations.

4. HPHT Synthetic Diamonds – More Sophisticated Measurements The traditional way in which the crystal quality was assessed (on the ESRF bending magnet Optics Beamline BM5) comprised monochromatization of the white beam to 10 keV by symmetric silicon (220) and (531) crystals. A set of slits upstream of this crystal permitted one to define the beam cross section. The diamond crystals were mounted in almost non-dispersive geometry so that the doubly reflected beam was nearly horizontal. A Si-PIN diode ($10 \times 10 \text{ mm}^2$) was used as a detector.

The whole set-up was checked with a second silicon (220) crystal instead of the diamond, and the theoretically perfect crystal values were found for both width and reflectivity.

When characterising single crystal properties, lattice tilts and d -spacing variations cannot be distinguished as an open detector is used which therefore integrates the scattering from the specimen over all angles within its aperture. Lattice tilts and d -spacing variations can be identified separately by restricting the angular acceptance of the detector. The tilt distribution is recorded with specimen-only rocking curves (ω -scans) whereas $\Delta d/d$ variations can be measured using a θ - 2θ scan. In the ω -scan, as the sample is rotated the 2θ angle is kept constant and the differently tilted regions will satisfy the conditions for diffraction. Thus, the scattered intensity is a measure of the distribution of the tilts.

Both tilts and $\Delta d/d$ variations can be determined separately by inserting an analyser crystal between the sample and the detector and performing either an ω - or a θ - 2θ scan. This is appropriately known as triple-axis diffractometry, and can be used to measure both lattice tilts and the range of lattice parameters present in the sample. However, we argue that the use of a third crystal can be avoided by replacing the Si-PIN diode with a 2D detector which should have a small enough pixel size so that good resolution can be obtained. At the ESRF such a 2D camera system has been developed, known as FReLoN (Fast Readout Low Noise), it has a CCD element with 1024×1024 pixels, and can be equipped with optics to achieve either $1 \mu\text{m}$ or $10 \mu\text{m}$ resolution. We chose $10 \mu\text{m}$ optics giving a field of $10 \times 10 \text{ mm}^2$ at a distance of 0.5 m from the diamond crystal.

The FReLoN camera was fixed during the recording of the rocking curves hence the scans were ω -scans and represented the distribution of lattice tilts, rather than lattice strains or d -spacing variations. As shown by Moore et al. [4] in triple-axis experiments, lattice tilts were much bigger than d -spacing variations. The latter were of the order of a few ppm and their contribution to the mosaic spread can safely be neglected. With this FReLoN camera rocking curves for fully illuminated diamond crystals were taken over 40 points. At each point of such scans the recorded image corresponded to a digital classical X-ray topograph. Software packages exist that can be used to calculate

three rocking curve parameters, namely width, peak reflectivity and peak position for each pixel and to present the results as contour maps.

The FReLoN output for a particular diamond specimen is shown in Fig. 1.

The three maps correspond to rocking curve width-FWHM (upper panel), peak reflectivity (middle panel), and peak position (lower panel). Even in a casual inspection, all these maps show the same general and even detailed structure, which correlates well with the main features as observed in X-ray white-beam topographs, as also in X-ray excited optical luminescence, and in optical interrogation. It is evident that the diamond is largely comprised of essentially perfect regions of dimensions greater than the extinction length of a few microns. One should note that the three images as presented are distorted in that the length is shortened by a factor of three. This is due to the pictures being taken at an angle of 17.52° . This distortion can if desired be restored by software treatment. From these spatially resolved maps we can extract that the minimum width of the rocking curve was measured as 5.7 arcsec, while on average (excluding an outer 1 mm wide zone of the crystal) the rocking curve width was about 7.5 arcsec. These values may be compared with the equivalent measurements taken with the Si-PIN diode detector of 6.8 arcsec and 8.6 arcsec, respectively. We may note that the more precise minimum width value extracted from the spatially resolved data is close to the theoretically perfect value of 5.5 arcsec. This ideal value is obtained from the convolution of the silicon (220) with the diamond (111) Darwin curves. We can conclude in terms of the rocking curve width, that this diamond specimen is locally perfect over a substantial fraction of its volume. However, over the full dimensions of the specimen there may be a contribution of about 4 arcsec from additional mosaic spread due to both local defects and curvature. The effect of crystal curvature is indicated in the peak position images.

One can illustrate even more sensitively the degree of crystal perfection by extracting from the FReLoN data the rocking curve FWHM difference curves. By this we mean the difference as between the average total width variation and the average lattice tilt width. With an appropriate binning of camera pixels in the vertical 2θ scattering direction, double-crystal X-ray rocking curves corresponding to the integrated scattered intensity with microscopic spatial resolution can be obtained. The numerical procedure consists of integrating the diffracted intensity recorded in every column of each digital image of the angular scan. This permits spatially integrated double-crystal rocking curves across the crystal to be extracted. The FWHMs of these rocking curves provide a measure of the sum of the lattice strain, the local lattice parameter changes and the lattice tilts, as in traditional double-crystal rocking curve measurements, but with $10\text{ }\mu\text{m}$ spatial resolution. The spatial resolution is not the only advantage to be gained. When comparing these rocking-curve widths with the ones corresponding to the lattice tilt distribution from the ω -scan, the average variation of the lattice strain and the d -spacing can be deduced. To achieve this, the average value of the width related to the lattice tilt distribution within each column is calculated and then subtracted from the corresponding total double-crystal rocking-curve width. If the lattice parameter variation were predominant compared to other lattice deformations, the average $\Delta d/d$ could be evaluated and mapped along the crystal with these FWHM difference curves after deduction of an eventual peak shift effect. However, this was not the case for any of the HPHT synthetic diamonds which we have studied. Such difference curves thus reflect the overall lattice strain across the crystal which is also related to the crystal curvature. An example is given in Fig. 2 [5]. (Fig. 2a is for a type Ib in (111) orientation, Fig. 2b is for a type IIa in (100) orientation.)

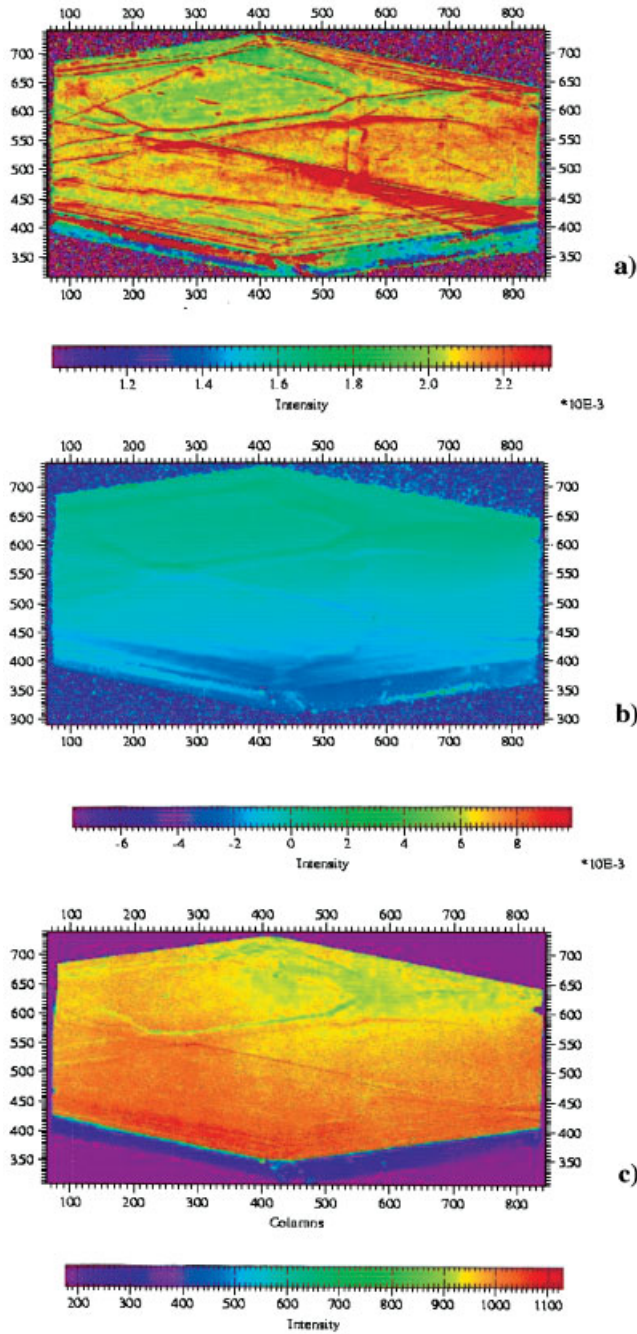


Fig. 1. a) Rocking curve width FWHM, b) peak reflectivity, and c) peak position contour maps of a (111) oriented thinned diamond recorded with the FReLoN camera. The colour codes for the FWHM and the peak position are given in degrees, the reflectivity scale is in arbitrary units

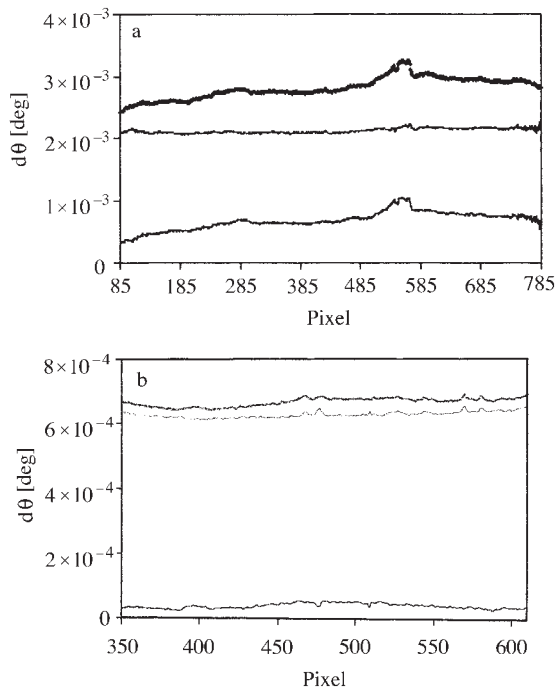


Fig. 2. a) Curves for the average total width variation, the average lattice tilt width, and the difference curve for a (111) type Ib synthetic diamond extracted from the rocking curve width contour map obtained with the FReLoN camera. b) As for part a) but for a (100) type IIa synthetic diamond. For further explanation, see text

The difference curve value is no different from the values obtained earlier but there is now the additional information on the spatial dependence in $10 \mu\text{m}$ resolution. The difference curves (the middle curve in Fig. 2a and the bottom curve in Fig. 2b) are both remarkably constant and the absolute values reflect the superior crystal quality of the type IIa (100) orientation sample over that of the type Ib (111) sample. From close inspection of these

data it may be concluded that growth sector boundaries are mainly responsible for the overall lattice strain gradients. Defect density may change in different growth sectors, as demarcated by the boundaries and may even be concentrated preferentially at the boundary itself.

5. Conclusions It is striking how excellent is the crystal quality of HPHT synthetic diamond on a local scale. It can match theoretical values for the perfect crystal. However, when considering larger areas of the typical HPHT synthetic diamond specimen there is a small but real deterioration in quality. This is often of no real consequence, but there are applications of diamond which are precluded. In particular, diffraction imaging and experiments based on coherence such as phase contrast tomography are presently not accessible due to the non-uniform intensity distribution. The defects responsible for limiting crystal quality include the boundaries to different growth sectors, in fact such growth boundaries may be preferentially decorated by defects. To the question that was posed as the title to this paper, the answer has to be that noting how the diamond target of ultimate perfection has come closer in recent years, it does now seem to be within our reach. But still further R & D will have to be invested before we will obtain contrast-free topographs from cm-sized synthetic diamond that will be capable of fully preserving the coherence of modern synchrotron X-rays or future free electron laser beams. At the present time, for a certain class of synchrotron based experiments, the current use of synthetic diamond on many beamlines worldwide bears testimony to the fact that the target has been partially reached.

Acknowledgement The authors acknowledge with appreciation the provision of materials by Messrs De Beers Industrial Diamonds (Pty) Ltd.

References

- [1] R. C. BURNS, J. O. HANSEN, R. A. SPITS, M. SIBANDA, C. M. WELBOURNE, and D. L. WELCH, *Diam. Relat. Mater.* **8**, 1433 (1999).
- [2] J. P. F. SELLSCHOP, S. H. CONNELL, R. W. N. NILEN, A. K. FREUND, J. HOSZOWSKA, C. DETLEFS, R. HUSTACHE, R. C. BURNS, M. REBAK, J. O. HANSEN, D. L. WELCH, and C. E. HALL, *New Diam. Front. Carbon Technol.* **10**, 253 (2000).
- [3] H. SUMIYA, N. TODA, and S. SATOH, *New Diam. Front. Carbon Technol.* **10**, 233 (2000).
- [4] M. MOORE, M. GOLSHAM, G. KOWALSKI, G. REID, J. S. COLLINS, and B. MURPHY, *J. Phys. D* **32**, 37(1999).
- [5] J. HOSZOWSKA, A. K. FREUND, T. ISHIKAWA, J. P. F. SELLSCHOP, M. REBAK, R. C. BURNS, J. O. HANSEN, D. L. WELCH, and C. R. HALL, *Proc. SPIE* **4501**, 106 (2001).