J. Phys. D: Appl. Phys. 40 (2007) 5301-5305

Rocking curve FWHM maps of a chemically etched (001) oriented HPHT type Ib diamond crystal plate

Y Zhong, A T Macrander, S Krasnicki, Y S Chu, J Maj, L Assoufid and J Qian

Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439, USA

Received 20 February 2007, in final form 6 June 2007 Published 16 August 2007 Online at stacks.iop.org/JPhysD/40/5301

Abstract

Synchrotron radiation and a CCD detector were employed to map the full width at half maximum (FWHM) of rocking curves for a synthetic (001) oriented type Ib diamond plate. The plate was sawed from a diamond grown in the high-pressure–high-temperature (HPHT) process. Maps for broadening relative to a reference point on the diamond for the (224) reflection at 12 keV are reported before and after chemical etching. Significant rocking curve narrowing over most of the diamond was found, and we conclude that the diffraction performance of (001) oriented type Ib diamonds can be significantly improved over a large area by chemical etching. Stripes in the map before etching corresponded to grooves formed in the process of sawing the plate out of the as-grown stone. The FWHM map did not correlate with the surface height profile measured after ~10 μ m were removed from the surface by etching.

1. Introduction

Single crystal diamonds have been used on synchrotron beamlines as monochromators [1-4], beam splitters [5] and quarter-wave plates [6]. The excellent thermal properties of diamond relative to silicon make them very attractive for use under demanding heat loads from synchrotron radiation [7–10]. The crystalline quality of the diamonds is crucial for these x-ray optics applications.

Due to the inhomogeneous process of the growth, the defects and residual strain in high-pressure–high-temperature (HPHT) diamond crystal are not uniformly distributed. For many applications diffraction from only part of the full surface area is needed, and it is often important to have a map of the crystal perfection to delineate good parts of the sample. Furthermore, maps are useful in ascertaining the origin of the defects. Although maps with several millimetre spatial resolution have been applied to assess epitaxial growth [11], only recently has it become feasible to map out local diffraction peak broadening below 0.1 mm spatial resolution. This has become possible with the advent of CCD cameras which enables high resolution rocking curve mapping of diamonds [12–14].

In a preliminary study, projection topographs of the diamond studied presently were made with synchrotron radiation for the same diffraction conditions as used presently and were reported in a conference proceedings [15]. These topographs revealed changes after chemical etching. Also, shifts of the rocking curves of this same diamond made before etching for the (004) reflection at 8 keV have been studied on a rotating anode source [16]. Using a relationship between changes in the local Bragg spacing and the concentration of nitrogen due to Lang et al [17], the concentration of nitrogen impurities was deduced. To obtain the changes in d-spacings, the effect of variation in the local orientation had to be accounted for [15]. The resultant map of nitrogen impurity concentration is clearly correlated with growth sector boundary features. Growth sectors arising from faceted growth during the HPHT crystal growth process are known to incorporate nitrogen at different rates [17].

Surface etching can be performed to treat the surface of crystals in order to remove damage which can occur from sawing, polishing and lapping. Although we have reported that an overall reduction of rocking curve full width at half maximum (FWHM) after etching of a diamond crystal can be obtained [18], the spatial variation of the FWHM was not studied.

In this paper we report a study of the spatial variation of the FWHM of the (224) Bragg reflection at 12 keV. Since broadening is caused by crystal imperfections including point and line defects as well as mosaicity, the FWHM is a significant figure of merit for crystal quality [1]. We measured the variation in FWHM of a crystal before and after the surface etching. As also seen in the topography data reported previously [15], the FWHM map before etching shows linear features corresponding to grooves in the surfaces. After etching the FWHM values are reduced, but the growth sector related contrast is still identifiable. Subsequent to the x-ray measurements, we also measured the surface profile with a phase-shifting interferometer. We observed that FWHM data and the surface profile were not correlated after etching.

2. Diamond sample and etching procedure

The diamond was a type Ib plate cut from an ingot grown by the HPHT process [19–22] and was procured from Drukker (now renamed as Element 6). Type Ib diamonds have a yellowish tint due to nitrogen impurities [23]. High-quality type Ib crystals can have reasonably small FWHM. The diamond was procured in an 'as-sawn' condition and saw grooves along the (110) direction were visible to the eye.

The etching of the sample was performed in an oven. The etchant in the form of a solid mixture was prepared by mixing Na₂O₂ and KOH in a 5 : 1 weight ratio. The sample was covered with the mixture in a Ni beaker and was heated for 2 h up to 700 °C to melt the etchant. It was then kept at about 740 °C for 6 h and slowly cooled to the room temperature. The sample thickness was 521 μ m before etching and 500 μ m after. During the etching process sample material was removed from both sides of the crystal.

3. Diffraction geometry at Advanced Photon Source

All diffraction measurements were made at beamline 2-BM with a vertical diffraction plane and in reflection geometry. The sample was positioned 50 m from the bending magnet source. A schematic layout is shown in figure 1. The effective vertical source size was $61 \,\mu\text{m}$ FWHM, and the vertical divergence was $47 \,\mu\text{rad}$ FWHM. A double-crystal monochromator with



Figure 1. Schematic diffraction arrangement. X-rays from a bending magnetic source pass the double-crystal monochromator, and the sample is located 30 m downstream (50 m from the source). A CCD camera is located 5 cm away from the sample and at 90° to the incident beam. The angle between the incident x-rays and the sample surface is 9° for (2 2 4) reflection of a diamond crystal with (0 0 1) surface.

two symmetric Si $(1\ 1\ 1)$ reflections and a harmonic rejection mirror was used to tune the energy. The diffraction details are summarized in table 1.

We employed a (2 2 4) asymmetric reflection at an x-ray energy of 12.04 keV. The incident beam impinged the sample surface of (001) crystallographic orientation at 9°, and the diffraction angle was close to 90°. A CCD camera with 9 μ m sized pixels (Photometric Quantix 6303E) was positioned 5 cm above the sample. The measured point spread function (PSF) for the CCD was ~82 μ m FWHM. Upstream of the sample, an additional shutter and an ionization chamber to monitor the intensity of the beam illuminating the sample were also installed. The shutter was synchronized with the CCD camera. The resulting topographic image was only slightly foreshortened from a true image perspective.

Under this diffraction condition, the extinction depth in the case of a perfect diamond crystal is $2.8 \,\mu\text{m}$ and the Darwin width is $10 \,\mu\text{rad}$, which corresponds to $0.12 \,\text{eV}$ on the energy scale. In this study, we took advantage of the fact that the energy resolution of the Si(1 1 1) doublecrystal monochromator is a function of the detuning angle between the two parallel crystals [24, 25]. We increased the energy resolution (i.e. reduced the energy bandpass) of the monochromator by increasing the detuning angle for the investigation of the etched diamond crystals. We describe this method in detail in the following paragraph.

In figure 2 we show both the measured and the calculated diffraction profiles for two different detuning angles. The two diffraction profiles were taken at the most perfect region (i.e. the narrowest rocking width) of the as-sawn (figure 2(a)) and etched (figure 2(b)) diamond samples. These locations served as the reference points. The calculated diffraction profiles were obtained by assuming Darwin curves for a perfect diamond crystal with detuning angles of 1.4 arcsec and 3.2 arcsec, respectively. The calculations shown in figure 2 incorporated energy dispersion and were based on the following formula:

$$I(E_{\text{mono}} - E_0) = \int d(E - E_0)$$

$$\times \int d\alpha \left[R_{\text{Si}} \left(\alpha + \frac{E - E_0}{E} \tan \theta_{\text{B}}^{\text{Si}} \right) \right]$$

$$\times R_{\text{Si}} \left(\alpha - \beta + \frac{E - E_0}{E} \tan \theta_{\text{B}}^{\text{Si}} \right)$$

$$\times R_{\text{dia}} \left(\alpha - 2\beta + \frac{E_{\text{mono}} - E_0}{E} \tan \theta_{\text{B}}^{\text{dia}} + \frac{E - E_0}{E_0} \tan \theta_{\text{B}}^{\text{dia}} \right)$$
(1)

Here R_{Si} and R_{dia} denote dynamical reflectivity functions for ideal crystals.

This relation is written for the three sequential reflections and is analogous to the double-bounce dispersion relationship of Zachariasen equation (3.210) [26]. Here the angle away from parallelism between the Si(111) planes of the first and the second crystals of the monochromator is denoted

Table 1. Diamond diffraction summary.

Surface orientation	Bragg's reflection	X-ray energy	Bragg angle	Incident angle	Darwin width	Extinction depth
(001)	(224)	12.04 keV	45°	9 °	0.12 eV (10 µrad)	2.8 μm



Figure 2. Rocking curves at the reference points. (*a*) Before etching and (*b*) after etching. These are the minimum-width rocking curves in the two cases. The lines are calculated for an ideal diamond single crystal. The angle needed to obtain the fits shown was 1.4 arcsec for (*a*) and 3.2 arcsec for (*b*) for the angle between the two Si(111) monochromator crystals.

as β . The angles, $\theta_{\rm B}^{\rm Si}$ and $\theta_{\rm B}^{\rm dia}$, are the Bragg angles of Si(111) and diamond(224), respectively. $E_{\rm mono}$ is the energy of the monochromator and E_0 the Bragg energy for the diamond(224) reflection. The variables of integration are for the incident spectrum, $(E - E_0)$, and for the angular divergence, α . The divergence range is very small since a single pixel of the CCD corresponds to a vertical divergence of only 0.18 μ rad. Since we used bending magnet radiation, the incident spectrum is essentially infinite. The calculated diffraction profiles describe the measured diffraction profiles almost perfectly, providing experimental confidence that the detuning improved the energy resolution by about 30% without significantly affecting the overall lineshape of the rocking curve.

In producing the FWHM maps as shown in figure 3, we used the measured instrumental energy resolution function to extract the rocking curve width of the diamond.

In the deconvolution procedure a Gaussian diffraction profile was convolved with the instrumentation resolution



Figure 3. Relative FWHM maps. The resolution functions shown in figure 2 were used to deconvolve to obtain the FWHM maps. (*a*) Before etching. Although not clearly evident, pixels for zero relative broadening occur at lower left. (*b*) After etching. Pixels with zero relative broadening occur near the bottom. (*c*) Surface height profile taken using a phase shift interferometer. The arrows in (*b*) indicate the location and range of the height profile.

(This figure is in colour only in the electronic version)

function, and the resultant profile was fit to the measured rocking curve by a least square fitting procedure. The FWHM value was obtained from the fitting parameters. We used a Gaussian profile for the diffraction profile. This procedure may introduce some slight errors when the diffraction profile deviates from the Gaussian shape. We note that the FWHM values should be considered significant as a measure of broadening relative to the location on the diamond at which the resolution function was obtained, that is, relative to the reference point. Although this location was chosen to yield the narrowest resolution function, defect related broadening might still have occurred at that location. Our statement of overall narrowing after etching is based on the assumption that the broadening at the reference point was much less than the broadening at other locations.

4. FWHM maps: before and after etching

4.1. Before etching

The FWHM map of the sample before chemical etching is shown in figure 3(a). The mapped distribution of the FWHM has features that correspond to the growth sectors that we indexed previously [16]. The saw damage is also evident on the figure, in particular, as lines corresponding to saw grooves at the upper right. The average FWHM for the whole diamond was 0.58 eV before etching. The standard deviation of the FWHM values was 0.10 eV.

4.2. After etching

The FWHM map obtained after etching is shown in figure 3(b). The growth sector related contrast is identifiable. After the etching, the average FWHM value was reduced to 0.49 eV, a 15% improvement. The standard deviation of FWHM values was reduced to 0.08 eV after etching. That is, the uniformity was improved by 20%. However, we note that the average FWHM after etching is still considerably larger than the Darwin width of a perfect diamond (0.12 eV). We conclude that there are sources of broadening that cannot be removed by etching. The likely sources are crystal mosaic spread and strain locked in the bulk of the crystal associated with nitrogen impurities [17] as suggested by the growth sector related variations [27].

4.3. Surface height profile after etching

Surface height data were obtained to evaluate a possible correlation with the FWHM data. Atomic force microscope data revealed a scalloped surface morphology, with typical feature diameters of 65 μ m in the middle of the sample and 30 μ m near an edge. We note that both these sizes are smaller than the PSF of our CCD. Consequently, these features did not appear in our x-ray data. To look for correlations at larger length scales, we made surface height measurements with a phase-shifting interferometer that uses visible light [28, 29]. The resulting height scan across the middle of the diamond, indicated with arrows on figure 3(*b*), is shown in figure 3(*c*). Peaks and valleys of lateral sizes of roughly 2 mm and with roughly 4 μ m peak-to-valley height changes were observed. The surface height variation in figure 3(*c*) does not correlate with our x-ray data in figure 3(*b*).

5. Discussion of the diffraction geometry

In order to implement energy scanning, the wide energy spectrum available at the bending magnet beamline was very important for this study. If, instead of scanning the energy, we had physically rocked the diamond through the Bragg reflection, the projection of the sample on the CCD would have changed. Although the shift in the image that would have been incurred during angle scanning would have been smaller than the PSF of the CCD, it becomes a problem at higher spatial resolution studies. The shift is eliminated by scanning energy instead of angle to obtain rocking curves.

The method of varying the detuning angle in a doublecrystal monochromator to narrow the resolution function is also generally useful for the study of samples for which a highly perfect matching first crystal is not available. The simplest diffraction geometry for rocking curve measurements is to use a perfect diamond as the first crystal in a standard double-crystal arrangement. In that case, the sample is the second crystal. This wavelength-dispersion-free geometry is preferred by many workers because of its simplicity, but in our case it required a perfect diamond, which was not available. The present results imply that high angular resolution FWHM maps can be obtained for a variety of sample crystals at beamlines equipped with a Si(111) double-crystal monochromator, a somewhat standard arrangement at most synchrotron beamlines.

6. Conclusions

We compared maps of rocking curve broadening, relative to a reference point, for a single crystal diamond plate, a type Ib synthetic diamond, obtained before and after chemical etching. Under the assumption that the broadening at the reference point itself was small, these maps revealed significant narrowing after etching. We find a 15% average narrowing and a 20% improvement in uniformity. We infer that a remaining residual bulk strain arises from nitrogen impurities since the map after etching showed a variation reminiscent of growth sector variation and since it is known that different growth.

Acknowledgments

Use of the Advanced Photon Source is supported by the US Department of Energy, Office of Sciences, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

References

- Berman L E, Hastings J B, Siddons D P, Koike M, Stojanoff V and Hart M V 1993 Nucl. Instrum. Methods A 329 555
- [2] Fernandez P B, Graber T, Lee W K, Mills D M, Rogers C S and Assoufid L 1997 Nucl. Instrum. Methods A 400 476
- [3] Toda N, Sumiya H, Satoh S and Ishikawa T 1997 Proc. SPIE 3151 329
- [4] Fernandez P B, Lee W K, Mills D M, Tajiri G and Assoufid L 2001 Nucl. Instrum. Methods A 459 347
- [5] Als-Nielsen J, Freund A K, Grubel G, Linderholm J, Nielsen M, Sanchez del Rio M and Sellschop J P F 1994 *Nucl. Instrum. Methods* B 94 306
- [6] Giles C, Malgrange C, Goulon J, de Bergevin F, Vettier C, Fontaine A, Dartyge E, Pizzini S and Baudelet F 1995 *Rev. Sci. Instrum.* 66 1549
- [7] Khounsary A M, Smither R K and Davey S 1992 Proc. SPIE 1739 1
- [8] Sharma S, Berman L E, Hastings J B and Hart M 1992 Proc. SPIE 1739 604
- [9] Stephenson J D 1992 Phys. Status Solidi a 134 373
- [10] Blasdell R C, Assoufid L A and Mills D M 1995 Diamond monochromators for APS undulator-A beamlines Advanced Photon Source Technical Bulletin 24, ANL/APS/TB-24
- [11] Macrander A T and Lau S 1991 J. Electrochem. Soc. 138 1147

Rocking curve FWHM maps of type Ib diamond crystal plate

- [12] Hoszowska J, Freund A K, Boller E, Sellschop J F P, Level G, Hartwig J, Burns R C, Rebak M and Baruchel J 2001
 J. Phys. D: Appl. Phys. 34 A47
- [13] Lubbert D, Baumbach T, Hartwig J, Boller E and Pernot E 2000 Nucl. Instrum. Methods B 160 521
- [14] Lubbert D, Ferrari C, Mikulik P, Pernot P, Helfen L, Verdi N, Korytar D and Baumbach T 2005 J. Appl. Cryst. 38 91
- [15] Zhong Y, Krasnicki S, Macrander A T, Chu Y S and Maj J 2005 J. Phys. D: Appl. Phys. 38 A39
- [16] Macrander A T, Krasnicki S, Zhong Y, Maj J and Chu Y S 2005 Appl. Phys. Lett. 87 194113
- [17] Lang A R, Moore M, Makepeace A P W, Wierzchowski W and Welbourn C M 1991 Phil. Trans. R. Soc. Lond. 337 497
- [18] Maj J, Macrander A T, Krasnicki S F, Fernandez P B and Erck R A 2002 Rev. Sci. Instrum. 73 1546
- [19] Sato S, Sumiyah H, Tsuji K and Yazu S 1990 Science and Technology of New Diamond ed S Saito et al (Tokyo: KTK) p 351

- [20] Sumiya H and Satoh S 1996 Diamond Relat. Mater. 5 1359
- [21] Sumiya H, Toda N and Satoh S 2000 New Diamond and Frontier Carbon Technol. **10** 233
- [22] Hansen J O, Hall C E and Dodge C N 2004 Int. Workshop on Diamond Single Crystals for 3rd and 4th Generation X-Ray Sources (ESRF, Grenoble)
- [23] Sellschop J P F, Freund A K, Hoszowksa J, Connell S H, Rebak M and Burns R C 2002 Phys. Status Solidi a 193 415
- [24] Schulte-Schrepping H and Drube W 2001 Nucl. Instrum. Methods A 467 396
- [25] Hou Z 2005 Rev. Sci. Instrum. 76 013305
- [26] Zachariasen W H 1945 Theory of Diffraction in Crystals (New York: Dover)
- [27] Wierzchowski W, Moore M, Makepeace A P W and Yacoot Y 1991 J. Cryst. Growth 114 209
- [28] Malacara D 1992 Optical Shop Testing 2nd edn (New York: Wiley)
- [29] http://www.phase-shift.com/products/microxam-rts.shtml